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Abstract

The matching relationship between carbon material and Pd precursor was investigated by constructing Pd@C catalysts with four carbon materials (mesoporous carbon, activated carbon, N-doped carbon and O-doped carbon) and three Pd precursors (PdCl₂, Pd(C₂H₃O₂)₂ and Pd(NO₃)₂) and evaluating their catalytic performance in the phenol hydrogenation to cyclohexanone. The Pd precursor or the carbon material has no obvious influence on the cyclohexanone selectivity, but strongly affects the catalytic activity. The Pd@C prepared via PdCl₂ shows good performance among all tested catalysts due to higher Pd content and better Pd dispersion. Conversely, although Pd(NO₃)₂ is easily adsorbed by carbon carriers, the catalytic activity is poor due to the worse Pd dispersion. The Pd(C₂H₃O₂)₂ adsorption is very sensitive to the surface properties of carbon, and the N-doping can enhance the binding force between carbon and Pd²⁺, leading to higher Pd content and better Pd dispersion, thereby enhanced catalytic activity. This work would provide valuable references for the selection of Pd precursor for a given support.

Graphical Abstract



Keywords Carbon \cdot Pd precursor \cdot Matching relationship \cdot Phenol hydrogenation \cdot Cyclohexanone

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1 Introduction

Catalysts play a key role in the chemical industry by speeding up the reaction progress and improving the product selectivity. The homogeneous catalysts have limited industrial applications owing to the difficult and costly catalysts



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separation and recovery [1, 2]. Many attentions have been focused on the heterogeneous catalysts (such as supported catalysts), due to easy removal of the catalysts from the reaction mixture and permission of a continuous operation mode [3, 4]. For heterogeneous catalysts, the interaction between active metal and support affects significantly the catalytic properties. Simultaneously, the support plays an important role in product distribution [5]. Therefore, it is significantly important to select suitable supports for heterogeneous catalysts.

Carbon materials, such as mesoporous carbon (MC) and activated carbon (AC), have been considered as good supports for heterogeneous catalysts due to large specific surface area, superior chemical and thermal stability [6]. In addition, it is easy to modify the carbon materials to change the catalytic performance, such as introducing nitrogen-containing or oxygen-containing groups [5, 7–18]. The introduction of nitrogen-containing groups not only enhances the binding of the metal with the support and improves the metal dispersion [9–11], but also forms a basic position in the carbon support, conducive to the adsorption of acidic molecules, like phenolic compounds [19, 20]. Introducing oxygen-containing groups can adjust the hydrophilicity or hydrophobicity of the carbon materials, and remove the impurities and increase the number of defects for anchoring the metal particles [16, 17].

Pd nanoparticles (NPs) are widely used in hydrogenation reactions due to the significant ability to activate H_2 [19, 21]. Notably, the precursors of Pd are various, such as PdCl₂, $Pd(C_2H_3O_2)_2$ and $Pd(NO_3)_2$ [7, 8, 22–34], and the catalytic performance of Pd based catalysts using different Pd precursors is often quite different [23–34]. For example, Shen et al. [25] studied the preparation of Pd/CeO₂ catalysts from three Pd sources (PdCl₂, Pd(C₂H₃O₂)₂ and Pd(NO₃)₂) and applied them to the methanol synthesis through CO hydrogenation. They pointed out that the interaction between Pd NPs and CeO_2 of Pd–Cl and Pd–Ac (using PdCl₂ and Pd(C₂H₃O₂)₂ as Pd precursor, respectively) catalysts was stronger than that of Pd-NO catalyst (using Pd(NO₃)₂ as Pd precursor), making the Pd NPs disperse better and smaller in size, thereby higher catalytic activities. And the Pd-Cl exhibited higher activity than Pd-Ac at higher temperature. Borkowski et al. [26] prepared two Pd catalysts by loading PdCl₂ and Pd(OAc)₂ on cyclohexyldiamine-modified glycidyl methacrylate polymer (GMA-CHDA) and applied in the Suzuki-Miyaura reaction. They found that Pd(OAc)₂ was reduced completely after reaction, forming Pd(0) NPs with a diameter of 3-5 nm. In contrast, PdCl₂ was reduced only in ca. 50%, producing the big Pd aggregates with lower catalytic activity. Ali et al. [24] used three supports (SiO₂, SiO₂-Al₂O₃ and Al₂O₃) and two Pd precursors (PdCl₂ and Pd(NO₃)₂) to prepared catalysts applied in CO hydrogenation. The results suggested that the support and the Pd precursor did not affect the Pd dispersion. However, the catalysts synthesized by PdCl₂ exhibited higher catalytic activities as compared to $Pd(NO_3)_2$, because the presence of Cl ions led to an obvious increase in the number of intermediates/sites of CO hydrogenation. The literature showed that the selection of Pd precursor had a significant effect on the structure and catalytic performance of immobilized Pd NPs. However, no knowledge on how to select a suitable Pd precursor for a given support was achieved. Therefore, it is necessary to investigate the matching relationship between Pd precursors and supports.

In this work, Pd@C catalysts were designed and constructed using two kinds of carbon materials (MC and AC) and three Pd precursors (PdCl₂, Pd(C₂H₃O₂)₂ and Pd(NO₃)₂). XRD, ICP, BET, X-ray photoelectron spectrometry (XPS), TEM, TG and other technologies were used to characterize the microstructure of the supports and the Pd@C catalysts. The phenol hydrogenation to cyclohexanone was used as a model system to test the catalytic performance of Pd@C catalysts, and the matching relationship between carbon materials and Pd precursors was evaluated. Furthermore, nitrogen-containing groups and oxygen-containing groups were introduced into carbon materials, respectively, and the influence of the groups in carbon materials on the selection of Pd precursor was investigated.

2 Experimental

2.1 Chemicals

All the chemicals were used as received: AC (Jiangsu Zhuxi AC Co., Ltd., China), MC (Nanjing JCNANO Technology Co., Ltd., China), palladium acetate $(Pd(OAc)_2)$ and palladium chloride $(PdCl_2)$ (Sin-Platinum Metals Co., Ltd, China), Palladium nitrate $(Pd(NO_3)_2 \cdot 2H_2O)$ (Shanghai Macklin Biochemical Co., Ltd., China), chlorhydric acid (HCl), dicyandiamide $(C_2H_4N_4)$ and anhydrous sodium carbonate (Na_2CO_3) (Shanghai Linfeng Chemical Reagent Co., Ltd., China), nitric acid (HNO₃), glacial acetic acid (CH₃COOH), phenol (C₆H₅OH), ethyl alcohol absolute (C₂H₅OH), methanol (CH₃OH) and citric acid monohydrate (C₆H₈O₇·H₂O) (Sinopharm Chemical Reagent Co., Ltd, China).

2.2 Catalyst Preparation

2.2.1 Preparation of N-Doped Carbon

The N-doped carbon was synthesized according to the literature [35]. Firstly, 0.132 g of citric acid monohydrate and 0.067 g of dicyandiamide were dispersed in 30 mL of methanol with agitating. 0.4 g of MC was introduced into the above solution and the mixture was continuously agitated for 12 h. The black powders were achieved after removing the

methanol with rotation evaporation, and dried at 60 °C overnight followed by calcined under Ar atmosphere at 550 °C for 4 h, and then naturally cooled to room temperature. The produced solid is named MC–N; similarly, the name of AC after N-doping is AC–N.

2.2.2 Preparation of O-Doped Carbon

0.4 g MC was dispersed into aqueous solution of nitric acid (30 wt%), and the mixture was refluxed at 60 °C for 4 h. After cooling, the black solid was obtained by centrifugation, repeatedly washed with deionized water and ethanol to neutral, then dried at 60 °C for 12 h. The resulting material is denoted as MC–O; similarly, the name of AC after O-doping is AC–O.

2.3 Loading of Pd NPs

The Pd@MC catalysts were prepared by a wet impregnation route. Briefly, the MC was dispersed into aqueous solution of PdCl₂, Pd(OAc)₂ or Pd(NO₃)₂ containing 2 wt% Pd with respect to MC. Na₂CO₃ was slowly added to the above solution at room temperature with stirring until the pH value of the mixture reached neutral, then continued stirring for 12 h. Centrifugation was used to remove the filtrate and the obtained black solid was repeatedly washed by deionized water and ethanol to neutral, then dried at 60 °C for 12 h. These obtained catalysts are designed as Pd@MC–Cl, Pd@ MC–Ac and Pd@MC–NO, respectively. Similarly, for AC supports, the corresponding catalysts are marked as Pd@ AC–Cl, Pd@AC–Ac and Pd@AC–NO, respectively.

2.4 Characterization of Catalysts

A Rigaku Miniflex 600 diffractometer was used to analyze the crystal structure. Morphology and microstructure were investigated by transmission electron microscopy (TEM, JEOL JEM 2100). The samples used for XRD and TEM characterization were the recovered catalysts after the hydrogenation of phenol. Textural properties were characterized by using an ASAP 2020 analyzer. The pore volume and surface area were achieved by the BJH and BET formulas, respectively. The element composition and chemical state were investigated by XPS operating at the Thermo ESCALAB 250 instrument. The Pd content was measured by ICP-AES (Optima 2000DV). Thermal gravity analysis was carried out on a NETZSCH STA449F3 under nitrogen atmosphere.

2.5 Catalytic Tests

The phenol hydrogenation to cyclohexanone (Scheme 1) was performed in a 50 mL Schlenk flask. Typically, 0.1 g



Scheme 1 Reaction pathways for phenol hydrogenation

of phenol, 20 mL of water and 0.2 g of Pd@C catalyst were loaded into the reactor in order. The reactor was evacuated and filled by a hydrogen-filled balloon (1 bar), and then placed in an oil bath (80 °C). After 75 min, the catalyst was separated from the reaction mixture by centrifugation, and the products were analyzed by GC [7].

3 Results and Discussion

3.1 Matching Relationship Between MC and Pd Precursor

From Fig. 1a, the selectivity of cyclohexanone is basically the same, indicating that the Pd precursors have no significant influence on the cyclohexanone selectivity, in line with the literature [28]. However, the conversions of three Pd@ MC catalysts are quite different. The catalytic activity of Pd@MC–Cl (conversion: 73.63%) is obviously higher than Pd@MC–NO (conversion: 15.6%) and Pd@MC–Ac (conversion: 3.33%), indicating PdCl₂ is the most suitable Pd precursor for MC. ICP, XRD and TEM were performed to investigate the role of Pd precursor.

The Pd loadings of Pd@MC–Cl and Pd@MC–NO are higher, about 1.8 wt% closed to the theoretical Pd content of 2 wt% (Table 1). However, the Pd loading of Pd@ MC–Ac is lower, only 0.37 wt%, suggesting that MC has a strong adsorption capacity for PdCl₂ and Pd(NO₃)₂, but poor adsorption capacity for Pd(C₂H₃O₂)₂. To intuitively observe the difference in adsorption performance of Pd precursors by MC materials, a set of adsorption experiments was designed (Fig. 2). The solution color of three Pd precursors is yellow before wet impregnation, and the filtrate of PdCl₂ or Pd(NO₃)₂ solution turns colorless after wet impregnation. But the filtrate of Pd(C₂H₃O₂)₂ solution still keeps yellow, further illustrating the poor adsorption performance of Pd(C₂H₃O₂)₂ by MC. The phenomena may be caused



Fig. 1 Phenol hydrogenation performance of a Pd@MC, b Pd@MC–N, c Pd@MC–O

 Table 1
 Pd contents of Pd@MC catalysts

Samples	Pd (wt%)
Pd@MCCl	1.77
Pd@MC–Ac	0.37
Pd@MC–NO	1.81
Pd@MC-N-Cl	1.46
Pd@MC-N-Ac	1.01
Pd@MC-N-NO	1.66
Pd@MC-O-Cl	1.65
Pd@MC-O-Ac	0.56
Pd@MC-O-NO	1.34

by the bigger and more complicated structure (trinuclear molecular complex $[Pd_3(CH_3COO)_6]$ [36, 37] or polymeric complex catena- $[Pd(CH_3COO)_2]n$ composed of linear chains [38, 39]) of $Pd(C_2H_3O_2)_2$. The minimal Pd content in Pd@ MC–Ac catalyst is consistent with the lowest catalytic activity (Fig. 1a). But the lower catalytic activity of Pd@MC–NO catalyst cannot match with the higher Pd content (Table 1), which may be caused by the difference in Pd dispersion.

In Fig. 3a, for Pd@MC–Cl and Pd@MC–NO, besides the C peak at 23.8° [9], other three peaks can be observed at 2 θ of ~40.1°, 46.6° and 68.0°, corresponding to the (111), (200) and (220) planes of crystalline Pd, respectively [9,



Fig. 2 Pictures of the solutions before and after wet impregnation: **a**, **a'** PdCl₂, **b**, **b'** Pd(C₂H₃O₂)₂, **c**, **c'** Pd(NO₃)₂



Fig. 3 XRD patterns of a Pd@MC, b Pd@MC-N, c Pd@MC-O

40]. But there is obvious difference in the peak intensity. The intensity of Pd peaks for Pd@MC-Cl is obviously lower than Pd@MC-NO irrespective of the similar Pd loading (Table 1), which suggests that the Pd dispersion in Pd@MC-Cl is better than Pd@MC-NO. It also has been reported that PdCl₂ tends to have good dispersibility on the carrier, while Pd(NO₃)₂ has poor dispersibility due to strong intermolecular forces [23, 25, 28]. The Pd peaks for Pd@ MC-Ac cannot be observed because of the less content of Pd (Table 1). The TEM images show that the Pd dispersion in Pd@MC-Cl is better than Pd@MC-NO (Fig. 4), in consistent with the XRD patterns (Fig. 3a) and the catalytic activity (Fig. 1a). Notably, the Pd dispersion in Pd@MC-Ac is very worse, indicating that the MC not only has weak adsorption ability for $Pd(C_2H_3O_2)_2$, but also has weak binding force with $Pd(C_2H_3O_2)_2$, thereby worse Pd dispersion and poor catalytic activity (Fig. 1a). This phenomenon is different from the literature, and $Pd(C_2H_3O_2)_2$ often exhibits good dispersibility on other carriers like Al₂O₃, MgO, GMA-CHDA, etc. [26, 28].

In order to further investigate the effect of groups (such as N-containing and O-containing groups) on the selection of Pd precursor for MC, MC materials were modified by N-doping and O-doping (Fig. S2 and Table S2).

Compared to Pd@MC catalysts (Fig. 1a), the catalytic activities of Pd@MC-N catalysts are all significantly increased (Fig. 1b). That's because the introduction of nitrogen-containing groups can increase the binding force between the Pd NPs and the support [9, 11], thereby increasing the Pd dispersion. In addition, the introduction of nitrogen-containing groups can also form strong basic sites in the carbon support [19, 41], which can significantly increase the adsorption of phenol [19, 20], leading to the increase in catalytic activity. The catalytic activities of three Pd@MC-N catalysts follow the order: Pd@ MC-N-Cl > Pd@MC-N-Ac > Pd@MC-N-NO, indicating PdCl₂ is still the most suitable Pd precursor for MC after N-doping. However, compared to Pd@MC-Ac, the catalytic activity of Pd@MC-N-Ac is significantly improved from 3.33 to 82.78%, larger than Pd@MC-N-NO, unlike the Pd@MC catalysts (Fig. 1a). ICP and XRD were performed to explain the mechanism.

The Pd contents in Pd@MC-N-Cl and Pd@ MC-N-NO catalysts are slightly decreased compared to Pd@MC-Cl and Pd@MC-NO catalysts (Table 1), which should be caused by the decrease in specific surface area after N-doping (Fig. S1 and Table S1) [5]. In addition, there is no obvious difference in the Pd dispersion by comparing Fig. 3a, b. However, the N-containing groups can improve the phenol adsorption [19, 20], which can offset the negative effect of the decrease in Pd content and make the catalytic activity increase (Fig. 1a, b). The Pd content in Pd@MC-N-Ac is significantly increased from 0.37 to 1.01 wt% after N-doping, possibly due to the enhanced binding force between MC-N with Pd²⁺ [5, 9, 11, 42]. The increase in Pd content combined with the improvement in phenol adsorption should be the major reasons for the significant enhancement in catalytic activity of Pd@ MC-N-Ac (Fig. 1b). The results confirm that the N-containing groups in MC have great effect on the adsorption ability for $Pd(C_2H_3O_2)_2$, and $Pd(C_2H_3O_2)_2$ may be a good Pd precursor for N-doped MC materials.

There are no changes in the selection of Pd precursor for MC–O in comparison with MC (Fig. 1a, c), and PdCl₂ is still the optimal Pd precursor. However, the catalytic activities of Pd@MC–O catalysts are all significantly decreased compared to Pd@MC catalysts (Fig. 1a). ICP and XRD were used to confirm the reasons.

With respect to Pd@MC–O–Cl or Pd@MC–O–NO, the Pd loading is reduced (Table 1), owing to the reduction in the specific surface area of MC–O (Fig. S1 and Table S1). No obvious difference in the Pd dispersion after O-doping is observed (Fig. 3a, c). Additionally, the introduction of O-containing groups increases the hydrophilicity of MC (Fig. S4), leading to the preferential adsorption of water by MC–O, thereby inhibited adsorption of phenol [14]. These aspects make the catalytic activity of Pd@MC–O–Cl or Pd@MC–O–NO decrease (Fig. 1c). For Pd@MC–O–Ac, the Pd loading is increased, possibly because of the formed defects on the carbon surface by HNO₃ treatment [16, 17].



Fig. 4 TEM images of a Pd@MC-Cl, b Pd@MC-Ac, c Pd@MC-NO

But the O-doping inhibits the phenol adsorption, resulting in the reduced catalytic activity (Fig. 1c).

The above results indicate that $PdCl_2$ is the most suitable Pd precursor for MC materials, regardless of the introduction of the groups (N-containing or O-containing). The choice of $Pd(NO_3)_2$ as a palladium precursor for MC is not suitable. Similar phenomena were observed on other supports including Al_2O_3 , CeO_2 , SiO_2 , MgO, etc. [23-25, 28]. $Pd(C_2H_3O_2)_2$ is an optional precursor for N-doped MC because the N-doping can improve the adsorption of $Pd(C_2H_3O_2)_2$ on the MC.

3.2 Matching Relationship Between AC and Pd Precursor

In order to verify whether $PdCl_2$ is the most suitable Pd precursor for other carbon materials, the matching relationship between AC and Pd precursor was also investigated.

Like Pd@MC catalysts (Fig. 1a), the three Pd@AC catalysts exhibit significantly different catalytic activities (Fig. 5a). The Pd@AC–Cl has the highest catalytic activity (conversion: 74%), indicating PdCl₂ is also the most suitable precursor for AC. However, the catalytic activity of Pd@ AC–Ac (conversion: 62.11%) is higher than Pd@AC–NO (conversion: 35.89%), which is not coincided with Pd@MC catalysts (Fig. 1a). The reasons for the difference in catalytic activities of Pd@AC catalysts were investigated as follows.

Like MC (Table 1), AC has a strong adsorption capacity for PdCl₂ and Pd(NO₃)₂ (Table 2). The adsorption capacity for Pd(C₂H₃O₂)₂ by AC (1.09 wt%) is common but stronger than the slight adsorption by MC (0.37 wt%), indicating that the Pd(C₂H₃O₂)₂ adsorption is very sensitive to the support properties and the AC surface is beneficial for the Pd(C₂H₃O₂)₂ adsorption. The literature shows that surface oxygen containing functionality of carbonaceous support favors the Pd loading [16, 17]. Analogously, the nitrogen-containing groups on the carbon surface also contribute to the Pd loading by strengthening the dispersion [9, 11]. According to the XPS results (Table S2 and Figs. S2, S3), there is only one oxygen-containing group (C–O) on the MC surface, while there are not only a plurality of

Table 2 Pd contents of Pd@AC catalysts	Samples	Pd (wt%)
	Pd@AC-Cl	1.53
	Pd@AC-Ac	1.09
	Pd@AC-NO	1.56
	Pd@AC-N-Cl	1.62
	Pd@AC-N-Ac	1.17
	Pd@AC-N-NO	1.99
	Pd@AC-O-Cl	1.31
	Pd@AC-O-Ac	0.79
	Pd@AC-O-NO	1.63

oxygen-containing groups (C–O, C=O and COOH) but also nitrogen-containing groups (Pyridine N and Graphite N) on the AC surface. Thus, the abundant groups on the AC surface may enhance its binding force with Pd^{2+} , leading to the increased adsorption capacity for $Pd(C_2H_3O_2)_2$, thereby higher Pd content (Table 2). But the ICP results cannot be coincided with the catalytic activity (Fig. 5a). For example, Pd@AC–NO has higher Pd content, but exhibits the worst catalytic activity. In contrast, Pd@AC–Ac with lower Pd content has a good catalytic performance, indicating the Pd content is not a key factor in determining the catalytic activity of Pd@AC. According to the characterization results of Pd@MC catalysts, the Pd dispersion may be a dominant factor.

From Fig. 6a, the intensity of Pd peaks follows the order: Pd@AC-NO > Pd@AC-Cl > Pd@AC-Ac, which indicates the Pd dispersion in Pd@AC-NO is worse than Pd@AC-Cl. The Pd peaks for Pd@AC-Ac cannot be observed, which can be explained by the less Pd content or good Pd dispersion. The Pd NPs in Pd@AC-Cl disperses well (Fig. 7a), and combined with higher Pd content can lead to the highest catalytic activity (Fig. 5a). Very interestingly, compared to Pd@MC-Ac (Fig. 4b), the Pd dispersion in Pd@AC-Ac can be significantly improved (Fig. 7b), possibly because of the enhanced binding force between AC and Pd²⁺ [9, 11, 16, 17]. Thus, despite of the lowest Pd content in Pd@AC-Ac, the best Pd dispersion guarantees the higher catalytic activity.



Fig. 5 Phenol hydrogenation performance of a Pd@AC, b Pd@AC-N, c Pd@AC-O



Fig. 6 XRD patterns of a Pd@AC, b Pd@AC-N, c Pd@AC-O



Fig. 7 TEM images of a Pd@AC-Cl, b Pd@AC-Ac, c Pd@AC-NO

Like Pd@MC–NO (Fig. 4c), the worst Pd dispersion in Pd@AC–NO (Fig. 7c) results in the lowest catalytic activity (Fig. 5a). These results confirm that the Pd dispersion is a key factor in determining the catalytic activity of Pd@AC.

Similarly, AC materials were also modified by N-doping and O-doping (Fig. S3 and Table S2) to investigate the effect of groups on the selection of Pd precursor.

Like Pd@MC–N catalysts (Fig. 1b), the catalytic activities of Pd@AC–N catalysts are improved by N-doping (Fig. 5b). However, the selection of suitable Pd precursor for AC is changed after N-doping. The catalytic activity of Pd@ AC–N–Ac is significantly increased from 62.11 to 93.48%and becomes the highest, indicating Pd(C₂H₃O₂)₂ is the most suitable Pd precursor for AC after N-doping. ICP and XRD were used to investigate the mechanism.

The Pd contents are all improved (Table 2), which is different from Pd@MC–N catalysts (Table 1). The increase in Pd contents for Pd@AC–N catalysts can be explained as follows. On one hand, the introduction of N can increase the interaction between AC–N and Pd²⁺ [5, 9, 11, 42], leading to higher adsorption of Pd precursor, thereby increased Pd content. On the other hand, the N-doping makes the specific surface area of AC reduce, but its specific surface area is significantly larger than MC (Fig. S1 and Table S1), providing enough loading sites to support the Pd NPs and inhibiting the negative effect of the decrease in specific surface area. The increase in Pd content can make the catalytic activity of Pd@AC–N enhance (Fig. 5b). However, there is no line relation between the increase in Pd content and catalytic activity. For Pd@AC–N–Ac, the increase in Pd content is not high, but the better Pd dispersion (Fig. 6b) results in the extraordinary catalytic performance. In contrast, with respect to Pd@AC–N–NO, although the increase in Pd content is the highest, the poor Pd dispersion (Fig. 6b) offsets the positive effect due to the increase in Pd content, thereby lower increased degree of catalytic activity.

Like Pd@MC–O catalysts (Fig. 1c), the catalytic activities of Pd@AC–O catalysts are significantly decreased after O-doping (Fig. 5c). However, the selection of Pd precursor for AC–O in comparison with AC (Fig. 5a) is changed. The catalytic activity of Pd@AC–O–Ac is lower than Pd@ AC–O–NO. To evaluate the reasons, the three Pd@AC–O catalysts were characterized by ICP and XRD.

The Pd contents in Pd@AC–O–Cl and Pd@AC–O–Ac are decreased after O-doping (Table 2), which may be caused by the following reasons. On one hand, the O-doping makes the specific surface area of AC–O reduce (Fig. S1 and Table S1). On the other hand, the treatment with HNO₃ decreases the basic N-containing groups (pyridine nitrogen and graphite nitrogen) in AC (Fig. S3), leading to the decreased adsorption of PdCl₂ and Pd(C₂H₃O₂)₂ [5], especially for Pd(C₂H₃O₂)₂. The Pd dispersion in Pd@AC–O–Cl

or Pd@AC-O-Ac after O-doping does not significantly changes (Fig. 6c). The reduction in Pd content, combined with decreased phenol adsorption due to the change in the hydrophilicity of AC (Fig. S4), will make the catalytic activity of Pd@AC-O-Cl or Pd@AC-O-Ac decrease (Fig. 5c). Interestingly, the Pd content in Pd@AC-O-NO is slightly increased, and the Pd dispersion is significantly improved (Fig. 6c), which may be related with the change in surface groups of AC after O-doping. A new O-containing group, namely nitrogen oxide [43], is formed on the carbon surface by the treatment with HNO₃ (Fig. S3). The nitrogen oxide on the AC–O surface is similar with the anion of $Pd(NO_3)_2$, which may be conducive to the adsorption of $Pd(NO_3)_2$ and improving the binding force between AC–O and Pd^{2+} . Thus, improved Pd content and dispersion can be obtained. However, the hydrophilicity of the O-doped AC is increased (Fig. S4), inhibiting the phenol adsorption. Compared to the improvement in Pd content and dispersion, the influence of the decrease in phenol adsorption may be more obvious, leading to the reduction in catalytic activity of Pd@ AC-O-NO (Fig. 5c). At the same time, the improvement in Pd content and dispersion can make lower reduced degree of catalytic activity as compared to Pd@AC-O-Cl and Pd@ AC-O-Ac.

The above results suggest that $PdCl_2$ is a suitable Pd precursor for AC materials, while $Pd(NO_3)_2$ is not suitable. The $Pd(C_2H_3O_2)_2$ adsorption is very sensitive to the surface properties of support, and the surface modification by N-doping can improve the $Pd(C_2H_3O_2)_2$ adsorption on the AC, making the $Pd(C_2H_3O_2)_2$ be as the suitable Pd precursor for AC materials to synthesize Pd@C catalysts.

4 Conclusions

In this contribution, PdCl₂, Pd(C₂H₃O₂)₂ and Pd(NO₃)₂ were supported on carbons to synthesize Pd@C catalysts, and their catalytic properties were tested in the phenol hydrogenation to investigate the matching relationship between carbon material and Pd precursor. The cyclohexanone selectivity is neither affected by either the Pd precursor nor the carbon material. However, the catalytic activity strongly depends on the Pd precursor and carbon material. PdCl₂ is a suitable Pd precursor for these adopted carbon materials. $Pd(C_2H_3O_2)_2$ is very sensitive to the surface properties of carbon, and the proper surface modification such as N-doping can make the $Pd(C_2H_3O_2)_2$ be the suitable Pd precursor to prepare Pd@C catalysts. Furthermore, the introduction of N-containing groups can significantly increase the catalytic activity by improving the Pd dispersion and the phenol adsorption, while the introduction of O-containing groups significantly decreases the catalytic activity by inhibiting the

phenol adsorption. The work can aid the development of the Pd@C catalysts with high catalytic performance.

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Compliance with Ethical Standards

Conflict of interest All authors declare no conflicts of interest.

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