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# Insight into Single-Atom-Induced Unconventional Size Dependence over CeO<sub>2</sub>-Supported Pt Catalysts



Atomically precise catalysis specially concentrates on the interaction between the central active atom and the coordinating environment nearby, as well as the resulting catalytic performance. The neighboring atoms can have a great impact on the frontier orbitals of the metal active site and further its catalytic performance. Here, we provide a thorough example discussing the origin of unexpected selectivity variation for a structural sensitive reaction on supported catalysts with various steric hindrances of Pt sites.

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### HIGHLIGHTS

An unexpected volcano curve was first reported in the hydrogenation of p-CNB

Relationship between selectivity and the quantified steric hindrance of Pt was built

The steric-hindrance effect was clearly disclosed from the electronic level



Wang et al., Chem 6, 1–14 March 12, 2020 © 2019 Elsevier Inc. https://doi.org/10.1016/j.chempr.2019.12.029

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# Insight into Single-Atom-Induced Unconventional Size Dependence over CeO<sub>2</sub>-Supported Pt Catalysts

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### SUMMARY

Identification of the structure-performance relationship at the atomic level is vital for getting a deep understanding of the size-dependence behavior of metal catalysts. Here, an unconventional size dependence of Pt toward selective hydrogenation of p-chloronitrobenzene has been extensively investigated over  $CeO_2$  support. An upturned volcanic curve toward the selectivity of p-chloroniline was found by decreasing the size of Pt from nanoparticles to single atoms. Differences on predominant orbitals among diverse coordination-environment Pt sites were identified to be the key factors influencing the modes of interaction with the C-Cl bond of p-chloroniline. Specifically, electrostatic repulsion between nonbonding orbitals of Cl and predominant orbitals of Pt sites with high steric hindrance were speculated to be responsible for the suppression of dehalogenation and the high selectivity. This strategy to build correlation between the valence orbitals of active sites and their catalytic behavior could well be expanded to other structure-sensitive reactions and atomically dispersed catalysts.

### INTRODUCTION

Selective hydrogenation reactions have attracted much attention for many decades in view of their widespread use in the chemical industry.<sup>1,2</sup> These processes have been intensively studied from both fundamental and practical points of view, and much has been learned from them.<sup>3-5</sup> However, some key fundamental issues associated with catalytic hydrogenation remain unsolved. For example, although noble metal catalysts are active under mild conditions for a variety of heterogeneous hydrogenations, they are not always selective toward the preferred products and are expensive. Especially, the realization of high chemoselectivity is increasingly challenging as the reducibility of the competing functional groups increases.<sup>6,7</sup> Haloanilines (HANs), for instance, as the vital organic intermediate widely used in the production of polymers, pharmaceuticals, herbicides, dyes, etc., are usually obtained through the selective reduction of the corresponding halonitrobenzenes (HNBs).<sup>8</sup> A range of noble-metal-based heterogeneous catalysts such as Pt,<sup>9,10</sup> Pd,<sup>11,12</sup> Ru,<sup>13,14</sup> and Au<sup>15,16</sup> have been studied for HNBs hydrogenation. However, hydrogenolysis of the carbon-halogen bonds always occurs,<sup>17,18</sup> especially at high conversions, resulting in loss of the HANs yield and the extra cost for the product purification. Hence, to achieve high selectivity of HANs, it is necessary to maximally limit or, if possible, totally suppress hydrogenolysis of the carbon-halogen bonds.

Generally, two approaches are used to control the selectivity in hydrogenation of HNBs: adding a second substance or engineering the catalytic surface structure of

### **The Bigger Picture**

The 100% exposed atomic sites have made the single-atom catalyst (SAC) very different from the nanoparticle ones with unique selectivity and reactivity. However, the deep reasons for this have not been well documented in most cases. Lacking the knowledge for the specific structure-activity relationship of the SACs suppressed their extensive application in industry. Here, an unexpected upturned volcano curve of selectivity to p-chloroaniline (p-CAN) in the hydrogenation of p-chloronitrobenzene (p-CNB) was firstly disclosed at atomic level on the Pt1/CeO2-SAC and the Pt/CeO<sub>2</sub> catalysts with Pt nanoparticles on CeO<sub>2</sub> support. The electrostatic repulsion between the non-bonding orbitals of Cl and the predominant orbitals of Pt sites with high steric hindrance, including Pt<sub>1</sub>/CeO<sub>2</sub>-SAC and Pt (111), was speculated to be the profound reason behind the size-dependence behavior. The strategy to build correlation between valence bands of metal atoms and catalytic performance could be expanded to other heterogeneous reactions as well.

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the catalyst, which can be addressed by using metal nanoparticles (NPs) with specific sizes and shapes. One effective method of the first-mentioned approach to prevent the selectivity decrease is adding substances such as amines, sulfur-containing compounds, phosphoric acid derivatives, etc.<sup>19</sup> to the reaction medium. However, it generated new problems associated with isolation and purification of the final product. Additionally, much efforts were also made at alloying common noble metals with a transition metal, but a simple bimetallic composite usually provides a limited number of active sites, and the high selectivity is achieved at the expense of activity.<sup>20,21</sup> Moreover, catalytic reactions are traditionally characterized as structure sensitive or structure insensitive.<sup>22</sup> Dechlorination of HNBs (or HANs) compounds, which accounts for the undesirable selectivity of HANs, has typically been considered to belong to the former category. Hence, attempts at inhibiting hydrogenolysis of the weak carbon-halogen bond were also made in controlling the metal particle dispersion.<sup>23,24</sup> For instance, it was reported that the selectivity of p-chloroaniline (p-CAN) depended closely on metal particle size, and the higher selectivity to p-CAN was achieved on large metal particles.<sup>25,26</sup> Note that facile adsorption of reactants and weak binding of products (intermediates) are key requirements for efficient and selective catalysis. However, these two variables are intimately linked in some ways that do not allow the optimization of both properties simultaneously. In this way, high p-CAN selectivity was achieved only under relative low p-chloronitrobenzene conversion because of the competitive adsorption between p-chloronitrobenzene (p-CNB) and p-CAN or at the expense of the low atom utilization of a noble metal (large metal particles).

Many studies have shown that individual atoms of Pt,<sup>27–29</sup> Pd,<sup>30,31</sup> or Ru<sup>32,33</sup> supported on oxides or carbons can efficiently catalyze numerous important reactions with high selectivity. However, the in-depth reasons for the extraordinary performance of these single-atom catalysts have not been well documented in most cases. In this work, through a series of controlling experiments and density functional theory (DFT) studies, the unconventional size dependence toward selectivity in the hydrogenation of p-CNB over CeO<sub>2</sub>-supported Pt catalysts was investigated in detail. It was found that the selectivity toward p-CAN changed drastically with Pt loading and showed an upturned volcanic curve. DFT calculations suggested that the differences on predominant orbitals among Pt sites of diverse, coordinated environments had a great influence on the modes of interaction with the C-Cl bond and was a key factor to determine the selectivity of p-CAN in p-CNB hydrogenation. The monodispersed Pt active site, Pt<sub>1</sub>/CeO<sub>2</sub>, which was formed by filling a single Pt atom into the vacancies on CeO<sub>2</sub>, could be regarded as an alternative of high-steric-hindrance terrace sites to achieve both high selectivity and atomic economy in the hydrogenation of p-CNB.

#### **RESULTS AND DISCUSSION**

#### Characterizations of Pt/CeO<sub>2</sub>

A series of Pt catalysts over CeO<sub>2</sub> support were synthesized with a conventional wet impregnation method, followed by various characterizations to figure out the dispersion and configuration of Pt on the catalysts (Tables S1 and S2), especially for the samples with Pt loadings below 3 wt %. As shown in the representative high-resolution HAADF-STEM images of the Pt/CeO<sub>2</sub> catalysts with different Pt loadings (Figures 1A–1C, S1, and S2), the Pt atoms or nanoclusters were exhibited as the bright dots with higher contrast than the CeO<sub>2</sub> lattice. The images of the 0.6 wt % Pt/CeO<sub>2</sub> (denoted as 0.6% Pt/CeO<sub>2</sub>-SAC) indicated that Pt was atomically dispersed over the CeO<sub>2</sub> (110) plane (Figures 1A and S1). These insets in Figures 1A and S1 showed the intensity profile taken along the lines indicated by the yellow rectangle, highlighting the positions of Pt<sub>1</sub> atoms in the sample. And both single-atom and nanoclusters

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were simultaneously present on the support when the ratio of Pt increased from 0.6 to 2 wt % (Figure 1B). When further increasing the loading to 3 wt %, most of Pt would aggregate to small nanoclusters (~1.7 nm, Figures 1C and S2). Furthermore, the magnitude Pt L<sub>3</sub>-edge X-ray near-edge structure (XANES) spectra and extended X-ray absorption fine structure (EXAFS) analyses were performed to elucidate detailed structures of these catalysts. The white-line intensity, reflecting the oxidation state of Pt, decreased steadily with the rising of Pt loadings (Figure 1D). The white-line intensity in 0.6% Pt/CeO2-SAC was similar with that of the PtO2 foil, demonstrating the Pt single atoms in this sample were in oxidized state. Whereas, the white-line in the 2% Pt/CeO<sub>2</sub> sample is between the intensities of Pt foil and PtO<sub>2</sub> and clearly lower than that of 0.6% Pt/CeO<sub>2</sub>-SAC, suggesting Pt was partially reduced in this sample. In other words, lower Pt loading results in higher percentages of single-atom structures in the catalysts. Correspondingly, in the Fourier transform (R space, Figures 1E and S3; Table S2) of the EXAFS data of the 0.6% Pt/CeO<sub>2</sub>-SAC sample, Pt is coordinated with O and Ce with coordination numbers CN = 3.8  $\pm$  0.50 and 1.1  $\pm$  0.6, respectively. The absence of a Pt-Pt bond confirmed that Pt was singly dispersed. While in the 2% Pt/CeO<sub>2</sub> sample, except for the Pt-O peak at 1.7 Å, a Pt-Pt contribution also occurred at a distance of 2.72 Å with an average CN of 6.2. The much lower CN and Pt-Pt bonding distance in the 2% Pt/CeO<sub>2</sub> sample than those in bulk platinum of 12 at a distance of 2.78 Å, suggested that the 2% Pt/CeO<sub>2</sub> contained Pt<sub>x</sub> subnanoclusters,<sup>34</sup> which is consistent with Figure 1B mentioned above.

The X-ray photoelectron spectroscopy (XPS) provided further information about the oxidation state of Pt (Figure S4). The characteristic Pt 4f peaks of the samples can be clearly identified. Notably, only partially oxidized  $Pt^{\delta+}$  species were found in 0.6% Pt/CeO<sub>2</sub>-SAC. The absence of Pt<sup>0</sup> species provided further evidence for the single-atom structure in this sample. Additionally, it can be easily seen that the content of Pt<sup>0</sup> increased with size, in good agreement with the EXAFS results discussed above. Further, in-situ infrared spectroscopy of adsorbed CO (Figure 1F) were carried out to provide more information about the dispersion and oxidation state of Pt. It can be found that two major regions were detected in the three samples, a main peak above  $2,000 \text{ cm}^{-1}$  usually corresponding to linearly adsorbed CO on Pt atop sites and less intense and broader section below  $1,900 \text{ cm}^{-1}$  typically belonging to the bridge adsorption mode.<sup>35</sup> Only one peak was observed at 2,088  $\text{cm}^{-1}$  for 0.6% Pt/CeO<sub>2</sub>-SAC, which can be assigned to the linearly bonded CO on the partially oxidized Pt in the single-atom catalyst.<sup>25</sup> The spectra of 2% Pt/CeO<sub>2</sub> not only displayed the features of the 0.6% Pt/CeO<sub>2</sub>-SAC (Figure 1F inset) but also showed other peaks around  $1,850 \text{ cm}^{-1}$  for the bridge adsorption of CO, demonstrating that the Pt clusters coexisted with individual Pt atoms on this sample. The peak belonging to bridge-bonded CO increased in a drastic fashion on the 3% Pt/CeO<sub>2</sub> sample, which could be because of the increased Pt particle size and the vanishing of the single Pt atoms. The dispersion of Pt on 0.6% Pt/CeO2 derived from CO titration experiments was 95%, confirming the atomically dispersed state of Pt in this catalyst. As is expected, the dispersion of Pt decreased when raising the Pt loadings and the calculated average particle size increased from 1.1 to 11.1 nm (Table S3), consistent with the HRTEM results. The XRD patterns also confirmed this (Figure S5). When the loading of Pt was less than 3 wt %, no significant diffraction peaks of metallic Pt particles were visible, suggesting the high dispersion of Pt. The peak intensity attributed to metal Pt appeared when further increasing the Pt loading. The average particle size of Pt NPs calculated according to Scherrer formula were all close to the values derived from CO titration experiments (Table S3). Based on the above discussion, it can be concluded that Pt had

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#### Figure 1. Structural Properties of Pt/CeO<sub>2</sub>

(A–C) Representative high-resolution HAADF-STEM images of 0.6% (A), 2% (B), and 3% Pt/CeO<sub>2</sub> (C), respectively. Scale bars represent 2 nm. (D and E) The magnitude Pt L<sub>3</sub>-edge XANES (D) and FT-EXAFS (E) spectra of 0.6% and 2% Pt/CeO<sub>2</sub>, respectively. (F) Infrared spectroscopy of CO adsorption of 0.6%, 2%, and 3% Pt/CeO<sub>2</sub>, respectively.

successfully been transformed from single-atom to NPs with the rising of Pt loading on these samples.

#### Catalytic Performances of Pt/CeO<sub>2</sub> for p-CNB Hydrogenation

The hydrogenation of p-CNB was then conducted to evaluate the catalytic performance of the Pt/CeO<sub>2</sub> catalysts with different Pt particle sizes (Table S4). Surprisingly, an upturned volcanic curve of the selectivity toward p-CAN was observed (Figure 2A), which has not been reported before. When Pt loading was beyond 3 wt %, the selectivity to p-CAN decreased in a dramatic fashion along with the decrease of the Pt particle sizes, which is consistent with previous results. However, the p-CAN selectivity increased reversely when further decreasing the Pt loading, and it was surprising that both 0.3% Pt/CeO2-SAC and 0.6% Pt/CeO2-SAC with atomically dispersed Pt showed nearly 100% selectivity to p-CAN under this condition. Furthermore, 0.6% Pt/CeO2-SAC was much more active than other catalysts (Table S5). This means that high activity, high selectivity, and theoretical 100% atom utilization could be achieved by using this single-atom catalyst. In addition, in order to eliminate the influence of Cl in the precursor, the catalysts, which were prepared with [Pt(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> were also tested in the hydrogenation of p-CNB (Figures S6–S9; Tables S6 and S7). The same results were obtained as that of H<sub>2</sub>PtCl<sub>6</sub>, further confirming that it was the inherent structure of Pt rather than other factors that controlled the selectivity.

The extraordinarily high selectivity of the 0.6%  $Pt/CeO_2$ -SAC catalyst was further evidenced by the evolution of the reactant and products distribution with the reaction time in Figure 2B. Since the complete conversion of p-CNB was achieved

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#### Figure 2. Catalytic Performance of Pt/CeO<sub>2</sub>

(A) Selectivity change in p-CNB hydrogenation on serial  $\mbox{Pt/CeO}_2$  catalysts with different Pt loadings.

(B) Distribution of products during the hydrogenation of p-CNB over 0.6% Pt/CeO<sub>2</sub>-SAC. Reaction conditions: 15 mL ethanol, 1 MPa H<sub>2</sub>, 40°C, 0.8 mmol p-CNB, Pt/p-CNB: (A) 31.7 wt  $_{\infty}$  and (B) 0.48 wt  $_{\infty}$ ; AN, aniline; p-CAN, p-chloroaniline; p-CNB, p-chloronitrobenzene; Cl-AZOXY, Cl-azoxybenzene; Cl-AZO, Cl-azobenzene.

in several minutes when the ratio of Pt and p-CNB was 31.7 wt ‰, only 0.48 weights of Pt per thousand of p-CNB was then elaborately added to probe the product distribution versus the reaction time. As shown in Figure 2B, p-CNB can be transformed into p-CAN in 32 min and almost no dechlorination product (AN) was detected. At the same time, no nitrobenzene (NB) was detected during the reaction, indicating that the nitro group was preferentially hydrogenated and subsequently dehalogenation proceeded. It needs to be emphasized that the selectivity still remained as high as 99.5%, even prolonging the reaction time to 70 min (Figure S10), revealing the superior performance of 0.6% Pt/CeO<sub>2</sub>-SAC in the selective hydrogenation of p-CNB compared with the catalysts with higher Pt loadings. Additionally, Figure S11 can confirm that there was no dissolved part contributing to the overall performance via a homogeneous mechanism, indicating that it is a heterogeneously catalytic process.

### **DFT Calculations**

Hydrogenation of p-CNB was a pseudo-consecutive reaction, where hydrogenation of nitro proceeded priorly and was not structure sensitive.<sup>26</sup> As a result, selectivity of p-CAN would depend strongly on the level of the C-Cl hydrogenolysis. Previous reports<sup>26,36</sup> showed that the hydrogenolysis of p-CAN to AN was size dependent, and the performance of 3% Pt/CeO<sub>2</sub> also confirmed that Pt NPs of 1.7 nm had a higher tendency to break the C-Cl bond than those with bigger particle sizes. The controlled experiments in Figure 2A, however, indicated that both atomic-dispersed Pt and large Pt NPs contributed to a superior selectivity for hydrogenation of p-CNB. Such a unique catalytic behavior intrigued us to discover the key factors at atomic level inducing dechlorination on diverse sites. It is clear that p-CAN must adsorb on the surface of the catalyst before it can be dechlorinated,<sup>25</sup> but there has been little discussion in the literature about the nature of the C-Cl bond in the adsorbed p-CAN. Additionally, it is well-known that the distribution of various sites (terrace, edge, corner, etc.) would vary with the size of the nanocrystal according to the Wulff construction.<sup>37</sup> The fraction of atoms located at the edge and corner sites increases with particle size and decreases at the expense of terrace sites, and the low-coordinated sites would be predominant when the particle size is less than 2 nm.<sup>38</sup> In this work, diverse models with different CNs of Pt were built to simulate the catalysts used in the reaction, and the capability of these models to activate

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Figure 3. DFT Calculation Studies on the Adsorption and Dissociation of p-CAN

(A) Adsorption energies (E<sub>ads</sub>) of Cl on Pt-based catalyst models.

(B) Summary of the optimized structures for the adsorption (3B-a series) and dissociation (3B-d series) of p-CAN on Pt-based catalysts.

(C and D)  $E_{ads}$  (C) and dissociation energies ( $E_{dis}$ ) (D) of p-CAN versus energy barriers ( $E_a$ ) of p-CAN dehalogenation on Pt-based catalysts.

The configurations in B: Pt (111) (a-1, d-1), Pt<sub>1</sub>/CeO<sub>2</sub> (a-2, d-2), Pt<sub>4</sub>/CeO<sub>2</sub> (a-3, d-3), Pt<sub>19</sub>/CeO<sub>2</sub> (a-4, d-4), Pt<sub>e</sub> (a-5, d-5), Pt<sub>c</sub> (a-6, d-6), Pt<sub>4</sub>/C (a-7, d-7); Ce, , O, , Pt, O; Cl, O; C, O; N, O; H, O.

the C-Cl bond was then evaluated in detail by first-principles calculations to explore the key factors influencing the C-Cl bond cleavage (Figures S12–S14; Notes S1 and S2).

First of all, the adsorption of a single chlorine atom on these models was calculated to probe their abilities to stabilize Cl since the reception of Cl would affect the thermodynamics of the dehalogenation of p-CAN (Figure S15). As indicated by the results (Figure 3A), the adsorption energies ( $E_{ads}$ ) clearly displayed that a single chlorine atom was preferentially adsorbed on the edge and corner sites rather than on the Pt<sub>1</sub>/CeO<sub>2</sub>-SAC and Pt (111). Further, the adsorption and dissociation of the C-Cl bond in p-CAN on these model catalysts revealed similar trends to single chlorine atom adsorption (Figure 3B–3D). On the catalysts of low-coordinated sort, the

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C-Cl bond of p-CAN preferentially adsorbed at edge or corner sites with high  $E_{ads}$  (>-0.78 eV). However, the interaction between the C-Cl bond and Pt sites became very weak or even repulsive on Pt<sub>1</sub>/CeO<sub>2</sub>-SAC and Pt (111), respectively. To be specific, p-CAN was only physically adsorbed on Pt<sub>1</sub>/CeO<sub>2</sub> with an  $E_{ads}$  of just -0.23 eV (Figures 3B and 3C), and the C-Cl bond even tilted away from the Pt (111) surface (Figure 3B). Note that the  $E_{ads}$  of p-CAN on Pt (111) was actually contributed via the aromatic ring, rather than via the C-Cl bond. Compared with the  $E_{ads}$  of p-CAN, the dissociation energy ( $E_{dis}$ ) is more straightforward to value the trends for the dechlorination of p-CAN. Clearly, the dechlorination was more thermodynamically favorable on these Pt sites, which typically have less coordinated atoms as seen in Figure 3D.

However, the Brønsted-Evans-Polanyi or scaling relationship for the dechlorination of C-Cl was not found on these catalysts, which indicated a different type of transition state of p-CAN on the catalysts with multiple Pt coordination environments.<sup>39–42</sup> Then the process of C-Cl cleavage on the three kinds of catalysts was carefully analyzed. For clarity, the Cl atom in the C-Cl bond would adjust to a stable state as with the single Cl atom alone before the p-CAN reached the transition state on Pt<sub>e</sub> (Figure S16). The stabilization of Cl in the C-Cl bond on the Pt<sub>e</sub> site would greatly stabilize the transition state so that the energy barrier (E<sub>a</sub>) for C-Cl cleavage was reduced (0.37 eV). In contrast, a nucleophilic attack occurred to the C atom of the C-Cl bond on Pt<sub>1</sub>/CeO<sub>2</sub> and the Cl atom was radicalized before reaching the transition state (Figure S17) due to the weak interaction between Cl and Pt. The radicalization of CI would greatly increase the energy of the transition state. As a result, the  $E_a$  for C-Cl cleavage on Pt<sub>1</sub>/CeO<sub>2</sub> was rather high (1.78 eV). The analysis of C-Cl cleavage on Pt (111) told the same story as Pt1/CeO2 (Figure S18). Actually, the main energy contribution of the E<sub>a</sub> for C-Cl cleavage on Pt (111) was derived from the E<sub>dis</sub> of the C-Cl bond.

Based on the above analysis, it was clear that the dechlorination of p-CAN strongly depended on the coordination environment of Pt. It can be found that the Pt sites of Pt<sub>1</sub>/CeO<sub>2</sub> and Pt (111), which had high energy barriers for the C-Cl cleavage, were both confined in a 2D matrix. As for edge and corner sites, the former ones could be considered as being localized in 1D Pt wires and the corner ones were just like adatoms on the Pt (111) surface. From a geometric view, these sites had different steric hindrance, which would be a key factor influencing the catalytic performance. The cone angle, as shown in Figure 4A, was defined to quantify this steric hindrance, since it was easy to understand that small cone angles of Pt sites meant a broader outer space for reactants to attack. Combined with the E<sub>a</sub> of p-CAN (Figure 4B), it can be seen clearly that the C-Cl cleavage would proceed more smoothly on the Pt sites with less steric hindrance. This was consistent with the experimental data (Figure 4C). 3% Pt/CeO<sub>2</sub> with an average particle size of 1.7 nm, mostly exposing edge and corner sites<sup>38</sup> (cone angle =  $88.5^{\circ}$ ), showed a relatively low selectivity to p-CAN. Whereas, 16% Pt/CeO<sub>2</sub>, mostly exposed terrace Pt sites (cone angle = 180.0°), and 0.6% Pt/CeO<sub>2</sub>-SAC (cone angle =  $147.4^{\circ}$ ) produced negligible hydrogenolysis products. In addition, considering the complex deposited surface sites of the CeO<sub>2</sub>, there may be other coordinated Pt single sites. In order to draw a more accurate conclusion, other Pt1/CeO2 catalysts with different coordination environments of Pt were also simulated by DFT calculations and all these sites with a high steric hindrance showed weak affinity (physical adsorption) for p-CAN and low dissociation energies of the C-Cl bond as illustrated in Figure S19 and Table S8. This further confirmed the conclusions we have drawn above (Note S3).

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#### Figure 4. The Steric Hindrance of Pt on the Models

(A) The cone angle of Pt on Pt-based catalyst models.

(B) The energy barriers (E<sub>a</sub>) of dehalogenation for p-CAN versus the cone angle of Pt on Pt-based catalyst models.

(C) The selectivity of p-CAN from experiment, the absolute value of dissociation energy ( $E_{dis}$ ), and  $E_a$  of dehalogenation for p-CAN versus the cone angle of Pt on 3% Pt/CeO<sub>2</sub>, 0.6% Pt/CeO<sub>2</sub>-SAC, and 16% Pt/CeO<sub>2</sub>, respectively. Ce,  $\bigcirc$ ; O,  $\bigcirc$ ; Pt,  $\bigcirc$ .

#### **DFT Calculation Studies on the Orbital Analysis**

In order to unveil how the steric hindrance of Pt influences the C-Cl cleavage, the orbitals interactions between p-CAN and Pt active sites of various coordination environments were then analyzed systematically. For molecular p-CAN alone, the occupied non-bonding and highest unoccupied C-Cl  $\pi^*$  orbitals of Cl are shown in Figure 5A. The non-bonding p orbitals of Cl, which extend along the xy plane (denoted as  $p_{xy}$  orbitals of CI) and occupied by lone electron pairs, give rise to a large space expansion (Figure S20). In contrast, the non-bonding  $p_z$  orbitals and C-Cl  $\pi^*$ orbitals are relatively more shrank and in turn wrapped in  $p_{xy}$  orbitals, forming a "core-shell" structure with  $p_z$  and C-Cl  $\pi^*$  orbitals as cores and  $p_{xy}$  orbitals as shells (Figure 5A). Since it is necessary to fill electrons into the C-Cl  $\pi^*$  orbitals to activate and dissociate the C-Cl bond,<sup>18</sup> the d orbitals of Pt had to interact with the lone electron pairs on the non-bonding  $p_{xy}$  orbitals of CI before reaching the C-CI  $\pi^*$ orbitals according to the core-shell electronic structure. Considering the requirement of orbital symmetry, 43-45 the orbitals of the representative catalysts, i.e., Pt (111), Pt<sub>1</sub>/CeO<sub>2</sub>, and Pt<sub>e</sub> were then calculated, respectively. As expected, great distinctions could be visualized among different coordinated Pt sites (Figures S21-S23). As for Pt (111) terrace, influenced by the adjacent Pt atoms, the shape of the Pt d orbitals has changed a lot. The most intensive peak shown in projected density of states (DOS) was attributed to the orbitals of  $d_z^2$  character. However, the  $d_z^2$ orbitals cannot interact effectively with the non-bonding orbitals of Cl due to the

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#### Figure 5. The Orbital Analysis between P-CAN and Different Coordinated Pt Sites

(A) The 0.005 e<sup>-</sup>/Å<sup>3</sup> isosurfaces of C-Cl  $\pi^*$  orbitals (unoccupied) and non-bonding orbitals of Cl in p-Journal of Cancer Molecules.

(B –D) The 0.0005 e<sup>-/</sup>Å<sup>3</sup> isosurfaces orbital interaction between Cl in p-CAN and Pt (111) (B), Pt<sub>1</sub>/CeO<sub>2</sub> (C), and Pte (D) with the energy E<sub>0</sub> in the correspondingly projected density of states, respectively. Projected density of states of Pt<sub>1</sub>/CeO<sub>2</sub> was shown in Figure S24.

(E and F) Projected density of states of d orbitals of Pt, p orbitals of Cl and C in p-CAN adsorbed on Pt (111) (E) and Pt<sub>e</sub> (F), respectively.  $\blacklozenge$ , Non-bonding orbitals of Cl.

unmatched orbital symmetry between them. Furthermore, under the influence of the adjacent coordinated atoms, two other major orbitals extending along the z axis of Pt had lost the d<sub>xz</sub> and d<sub>yz</sub> characters and thereby could not interact with the non-bonding p<sub>xy</sub> orbitals (Figure S21). Thus, C-Cl bond would be repelled from the surface due to electrostatic repulsion as shown in Figure 5B. This could also be confirmed by the fact that the peak attributed to the non-bonding orbitals of Cl were broadened (Figure 5E) when p-CAN adsorbed on Pt (111). In the case of Pt<sub>1</sub>/CeO<sub>2</sub>, the occupation of O vacancy made the Pt single atom partially embedded in CeO<sub>2</sub> (110), which resulted in a relatively high cone angle of Pt in the model (147.4°) (Figure 4A). The highest occupied orbitals E<sub>1</sub> could be assigned to be the d-p  $\pi^*$  orbitals of the Pt-O bonds (Figure S22). As shown in Figure 5C, E<sub>1</sub> could not interact effectively with the non-bonding p<sub>xy</sub> orbitals of Cl either because of the incompatible orbital symmetry. This would again lead to the electrostatic

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repulsion between the non-bonding  $p_{xy}$  orbitals of Cl and the predominant orbitals on Pt<sub>1</sub>/CeO<sub>2</sub>, which is similar to the situation on Pt (111) (Figure 5B). Detailed phase distributions of other chosen orbitals were shown in Figure S22 in the Supplemental Information, in which they all encountered the same situation. However, the main orbitals on the low-coordinated Pt sites with less steric hindrance were quite different from those mentioned above. Due to the absence of adjacent Pt atoms in the xy plane, the d<sub>xz</sub> orbitals of Pt<sub>e</sub> maintained their original characters and became the most intensive orbitals (Figure S23). The phase of these orbitals matched very well with that of the non-bonding  $p_{xy}$  orbitals of Cl, which turned the electrostatic repulsion items on the high-coordinated catalysts into attractive ones and then promoted the cleavage of C-Cl on Pt via the adsorption of Cl (Figures 5D, 5F, and S25).

#### Self-Induced Enhancement of Selectivity

Based on the discussion above, it is clear that the selectivity of p-CAN would be poor on the small particles, which contain more low-coordinated Pt sites with less steric hindrance responsible for dehalogenation. In principle, the selectivity of p-CAN should be constant if the ratio of low-coordinated and terrace Pt sites remained unchanged under certain reaction conditions. However, the selectivity of p-CAN for 3% Pt/CeO2 rose from 76.4% to 98.8% as the ratio of Pt/p-CNB decreased from 31.7 to 2.3 wt ‰ (Figure 6A; Table S9). A similar phenomenon was also observed on 2% Pt/C (Figure 6B; Table S10). Furthermore, the selectivity continued to rise before the complete conversion of p-CNB at the ratio of 2.3 wt ‰, whereas it decreased monotonously as reported in many other reactions when raising the ratio to 31.7 wt ‰ (Figures 6C, 6D, and S26). According to a previous report,<sup>46</sup> the *in-situ* generated CI species by dehalogenation could poison the low-coordinated Pt sites preferentially. It might well be speculated that this Cl-induced poisoning would actually increase the steric hindrance of surface Pt, inhibit the dehalogenation, and finally, lead to a rise of the selectivity toward p-CAN during the conversion of p-CNB.

To gain a deeper understanding of the in-situ passivation by CI species, the infrared spectroscopy of adsorbed CO was performed on the fresh and used 3% Pt/CeO<sub>2</sub> samples. This method has previously been demonstrated to be effective in identifying the metal sites. For the fresh 3% Pt/CeO<sub>2</sub> sample, the signals of both linear-bond and bridged-bond CO stretching were observed (Figure 7A). In the region above 2,000  $\text{cm}^{-1}$ , there were three peaks linked to the linear adsorption of CO molecule on the surface of the catalyst. The peaks at 2,102 and 2,064  $\text{cm}^{-1}$  were attributed to CO linearly bonded on  $Pt^{\delta+}$  and metallic Pt (111) facets, respectively, whereas the shoulder at 2,034 cm<sup>-1</sup> was associated to CO molecules adsorbed on the lowcoordinated Pt atoms of the small particles.<sup>47–49</sup> Additionally, the adsorption of CO also produced a strong vibration band at 1,936, and 1,849 cm<sup>-1</sup>. According to Bazin et al.,<sup>47</sup> the band at 1,936 cm<sup>-1</sup> was attributed to bridge-adsorbed CO species bound to both low-coordinated Pt and Ce at the support surface. As for the peaks at 1,849 cm<sup>-1</sup>, it should be attributed to the bridge-adsorbed CO molecules on the Pt (111).<sup>49,50</sup> However, the spectra of the used catalysts showed many differences from the fresh ones. As for the used 3% Pt/CeO2 sample, it was collected after the reaction at the conversion of approximately 70% p-CNB with a 2.3 wt ‰ ratio of Pt/p-CNB (Figure 7B). The linear-bonded CO stretching at 2,108 and 2,082 cm<sup>-1</sup> for  $Pt^{\delta+}$  and metallic Pt (111) facets still existed. While the peaks at 2,034 and 1,936 cm<sup>-1</sup> almost disappeared, this suggested that these sites were blocked by Cl produced in the reaction,<sup>51</sup> which can explain the high selectivity under this reaction condition. As for another used 3% Pt/CeO2 sample with the ratio of Pt/p-CNB increasing to 31.7 wt  $\frac{1}{200}$  (Figure 7C), the peak at 2,034 cm<sup>-1</sup> for CO adsorbed on

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**Figure 6.** Catalytic Performance of 3% Pt/CeO<sub>2</sub> and 2% Pt/C with Different Ratios of Pt/p-CNB (A and B) Selectivity change in p-CNB hydrogenation on 3% Pt/CeO<sub>2</sub> (A) and 2% Pt/C (B) with different Pt loadings.

(C and D) Conversion and selectivity versus reaction time over 3% Pt/CeO<sub>2</sub> catalyst with different ratio of Pt/p-CNB. Reaction conditions: 15 mL ethanol, 1 MPa H<sub>2</sub>, 40°C, 1.2 mmol p-CNB; Pt/p-CNB: (C) 2.3 wt  $_{\infty}$  (D) 31.7 wt  $_{\infty}$ .

the low-coordinated Pt sites also disappeared, whereas bands at 1,936 cm<sup>-1</sup> survived, suggesting that there still existed a part of low-coordinated Pt sites responsible for poor selectivity toward p-CAN. All the *in-situ* poisoning led to increase of the steric hindrance of the exposed Pt site, which should account for the enhancement of selectivity toward p-CAN when increasing the ratio of Pt/p-CNB in the reaction. And this was further confirmed by catalytic performance with Cl-containing additives (Table S11; Note S4).

### DISCUSSION

In summary, the unconventional size dependence toward selectivity in the hydrogenation of p-CNB over CeO<sub>2</sub>-supported Pt catalysts have been extensively investigated at the atomic level combining both experimental and theoretical analyses. An inverse volcano curve of the selectivity to p-CAN against the size of Pt active sites was obtained, in which both atomic-dispersed Pt<sub>1</sub>/CeO<sub>2</sub> and catalysts with large Pt NPs exhibited desirable selectivity to p-CAN. This means that high activity, high selectivity, and theoretical 100% atom utilization could be achieved at the same time by using this single-atom catalyst. Further analysis illustrated that the Pt coordination environment affected the dehalogenation of p-CAN and determined the final yield. High-coordinated Pt sites with a high steric hindrance were quite inert to dehalogenation, whereas the low-coordinated ones with less steric hindrance showed notable activity to the C-Cl bond cleavage. The electrostatic repulsion between the non-bonding pxv orbitals of Cl and the predominant orbitals on highcoordinated Pt sites was speculated to be the main electronic-structure factor derived from the Pt coordination environment for the suppression of the dehalogenation of p-CAN.

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Figure 7. Infrared Spectroscopy of CO Adsorption with Prolonging Purging Time on Different Catalysts

(A) The fresh 3% Pt/CeO<sub>2</sub> samples.

(B and C) The used 3% Pt/CeO\_2 samples with Pt/p-CNB ratio of 2.3 wt  $_{\infty}$  (B) and 31.7 wt  $_{\infty}$  (C) in the reaction.

#### **EXPERIMENTAL PROCEDURES**

The  $Pt/CeO_2$  catalysts were prepared by impregnation method and the percentage of Pt in this paper is quality score. In a typical synthesis process of 0.6 wt % Pt/CeO2 (denoted as 0.6% Pt/CeO<sub>2</sub>-SAC), 240 μL of H<sub>2</sub>PtCl<sub>6</sub> solution (37.5%, 20 mg/mL) as the precursor was added into a 20 mL crucible containing 10 mL deionized water under magnetic stirring for 10 min. Then 300 mg of the porous nanorods CeO<sub>2</sub> was added into the mixture. The suspension was allowed to be heated to 50°C and kept under vigorous stirring. After the water was evaporated overnight, the catalyst was collected and treated under H<sub>2</sub> at 200°C for 2 h and then cooled to room temperature to obtain the final product. The synthesis of other Pt/CeO<sub>2</sub> catalysts with various Pt loading was similar to that of 0.6% Pt/CeO2-SAC but with different dosages of the Pt precursor (denoted as n% Pt/CeO<sub>2</sub>, n was the Pt loading). These catalysts, which denoted as Pt/CeO2-N were prepared in the same way mentioned above with the precursor of  $[Pt(NH_3)_4](NO_3)_2$ . The hydrogenation of p-CNB was carried out in a 50 mL stainless steel high-pressure batch reactor. Typically, p-CNB (0.8 mmol), the catalyst Pt/CeO<sub>2</sub>, and C<sub>2</sub>H<sub>5</sub>OH (15 mL) were loaded into the autoclave. First, the reactor was purged three times with pure  $H_2$  to remove air. After that, the reactor was charged with 1 MPa  $H_2$  and the reaction mixture was stirred at 40°C. After the reaction, the reactor was placed into a water bath and cooled to room temperature. The remaining H<sub>2</sub> was carefully vented and the reaction mixture was centrifuged to obtain the supernatant and the supernatant was followed to be analyzed by GC.

#### SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.chempr. 2019.12.029.

#### ACKNOWLEDGMENTS

Financial support from the National Key R&D Program of China (2016YFA0202900), the National Natural Science Foundation of China (21622308, 21908189, and 21872121), and the Key Program supported by the Natural Science Foundation of Zhejiang Province, China (LZ18B060002) is greatly appreciated. The XAS experiments were conducted in the Shanghai Synchrotron Radiation Facility (SSRF).

### **AUTHOR CONTRIBUTIONS**

C.P.W., S.J.M., and Y.W. designed the research. C.P.W. synthesized the catalysts and conducted the experimental work. C.P.W. and Y.Z.C. performed the DFT calculations. Z.W. assisted the experimental work. H.Z., B.B.M., and Z.J. helped with the

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X-ray absorption fine-structure measurements. W.T.Y, Y.O., and Y.W helped collect HAADF-STEM images. C.P.W., S.J.M., and Y.W. co-wrote the paper. All authors discussed the results and commented on the manuscript.

### **DECLARATION OF INTERESTS**

The authors declare no competing interests.

Received: August 2, 2019 Revised: September 18, 2019 Accepted: December 26, 2019 Published: January 23, 2020

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