

# Constructing SiO<sub>2</sub>-Supported Atomically Dispersed Platinum Catalysts with Single-Atom and Atomic Cluster Dual Sites to Tame Hydrogenation Performance

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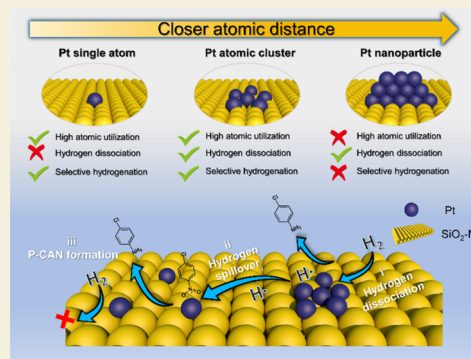
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**ABSTRACT:** Construction and optimization of stable atomically dispersed metal sites on SiO<sub>2</sub> surfaces are important yet challenging topics. In this work, we developed the amino group-assisted atomic layer deposition strategy to deposit the atomically dispersed Pt on SiO<sub>2</sub> support for the first time, in which the particle size and ratio of Pt entities from single atom (Pt<sub>1</sub>) to atomic cluster (Pt<sub>n</sub>) and nanoparticle (Pt<sub>n</sub>) on the SiO<sub>2</sub> surface were well modulated. We demonstrated the importance of dual-site synergy for optimizing the activity of single-atom catalysts. The Pt<sub>1+n</sub>/SiO<sub>2</sub>-N catalysts with the coexistence of Pt<sub>1</sub> and Pt<sub>n</sub> showed excellent activity and optimized selectivity (99% for haloanilines) in halonitrobenzenes hydrogenation, while Pt<sub>1</sub>/SiO<sub>2</sub>-N catalysts were almost inactive in the reaction. Mechanism investigation indicates that the Pt<sub>n</sub> site is beneficial for H<sub>2</sub> dissociation, and the Pt<sub>1</sub> site is energetically favorable for adsorption of the nitro group to complete the selective hydrogenation, which synergistically contributes to the optimized catalytic performances. This study provides a new strategy for constructing atomically dispersed metal species over the SiO<sub>2</sub> support and demonstrates the significance of the synergy of dual active sites for enhancing the catalytic efficiency.

**KEYWORDS:** atomic layer deposition, Pt single atoms and clusters, dual active sites, synergy, selective hydrogenation



## INTRODUCTION

Heterogeneous catalysts with maximized metal dispersion, optimal intrinsic activity per metal atom, and well-defined coordination structure are the long-term pursuit in catalysis.<sup>1–3</sup> Single-atom catalysts (SACs), as an emerging catalytic material system, have drawn extensive attention in many applications due to their ultimate atomic utilization, uniform active sites, and unsaturated coordination configurations.<sup>4–12</sup> Although numerous studies on SACs have been reported over the past decades,<sup>13–18</sup> they generally present unsatisfactory apparent activity in many reactions. For instance, it is difficult for SACs to break the linear scaling relationship for the reactions involving multiple steps/intermediates due to the lack of synergistic effects between the neighboring metal atoms.<sup>19–27</sup> Therefore, it is significant to systematically optimize the activity of SACs by rationally modulating the structure of active sites such as constructing SA-cluster dual sites catalysts, which is also beneficial for an in-depth understanding of the structure–activity relationship at the atomic scale.<sup>28–40</sup>

Numerous atomically dispersed catalysts (ADSs) including SACs have been achieved on various supports such as carbon materials, CeO<sub>2</sub>, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>; however, controllably synthesizing silica (SiO<sub>2</sub>)-supported ADSs with high activity and stability is still challenging due to its “inert” surface.

SiO<sub>2</sub>, a typical nonreducible oxide, is widely used as support in both scientific and industrial fields due to its high stability, low cost, nontoxicity, and large specific surface area, which also can afford a clean platform for regulating and understanding the real active sites from the complex catalyst structure.<sup>42</sup> Nevertheless, to the best of our knowledge, systematically constructing and optimizing atomically dispersed active sites through atom-by-atom fabrication on SiO<sub>2</sub> surfaces has been rarely reported.<sup>43–47</sup> Therefore, developing a facile and general approach to preparing stable atomically dispersed metal-SiO<sub>2</sub> catalysts is of great necessity.

Herein, we report the controllable construction of SiO<sub>2</sub>-supported atomically dispersed Pt<sub>1</sub>/SiO<sub>2</sub>-N and Pt<sub>1+n</sub>/SiO<sub>2</sub>-N catalysts for the first time by the amino group-assisted atomic layer deposition (ALD) strategy. The key feature of the approach is controlling the uniform and isolated adsorption of Pt precursors (MeCpPtMe<sub>3</sub>) on the SiO<sub>2</sub> surface during the

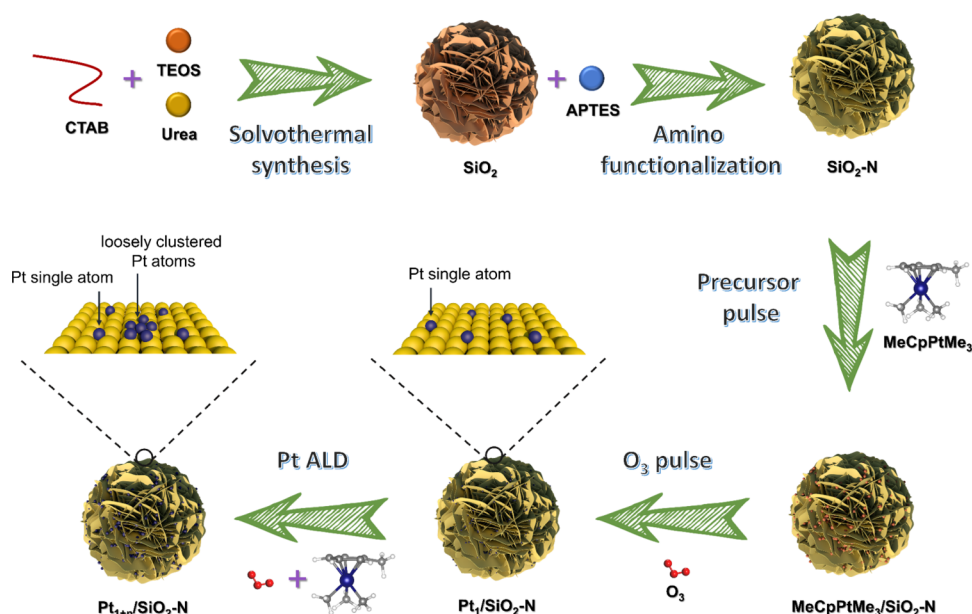
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**Figure 1.** Schematic illustration of the catalyst synthesis (CTAB, TEOS, and APTES represent cetyltrimethylammonium bromide, tetraethyl orthosilicate, and 3-aminopropyltriethoxysilane, respectively).

ALD process to achieve the precise synthesis of atomically dispersed Pt species through atom-by-atom fabrication starting from SACs. Experimental results and density functional theory (DFT) calculations revealed a strong dependence of the catalytic activity and selectivity on the geometric and electronic structures of Pt species. The  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  catalysts with SA atomic cluster coexisted dual sites exhibit excellent catalytic activity, stability, and optimized selectivity toward desired haloanilines products (99%). Note that the  $\text{Pt}_1/\text{SiO}_2\text{-N}$  catalysts, with the highest atomic utilization efficiency, are almost inactive for the hydrogenation reaction, while the  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  catalysts present poor selectivity toward haloanilines. Our present strategy presented here is general and can be potentially extended to synthesizing other  $\text{SiO}_2$ -supported metal catalysts with atomic dispersion.

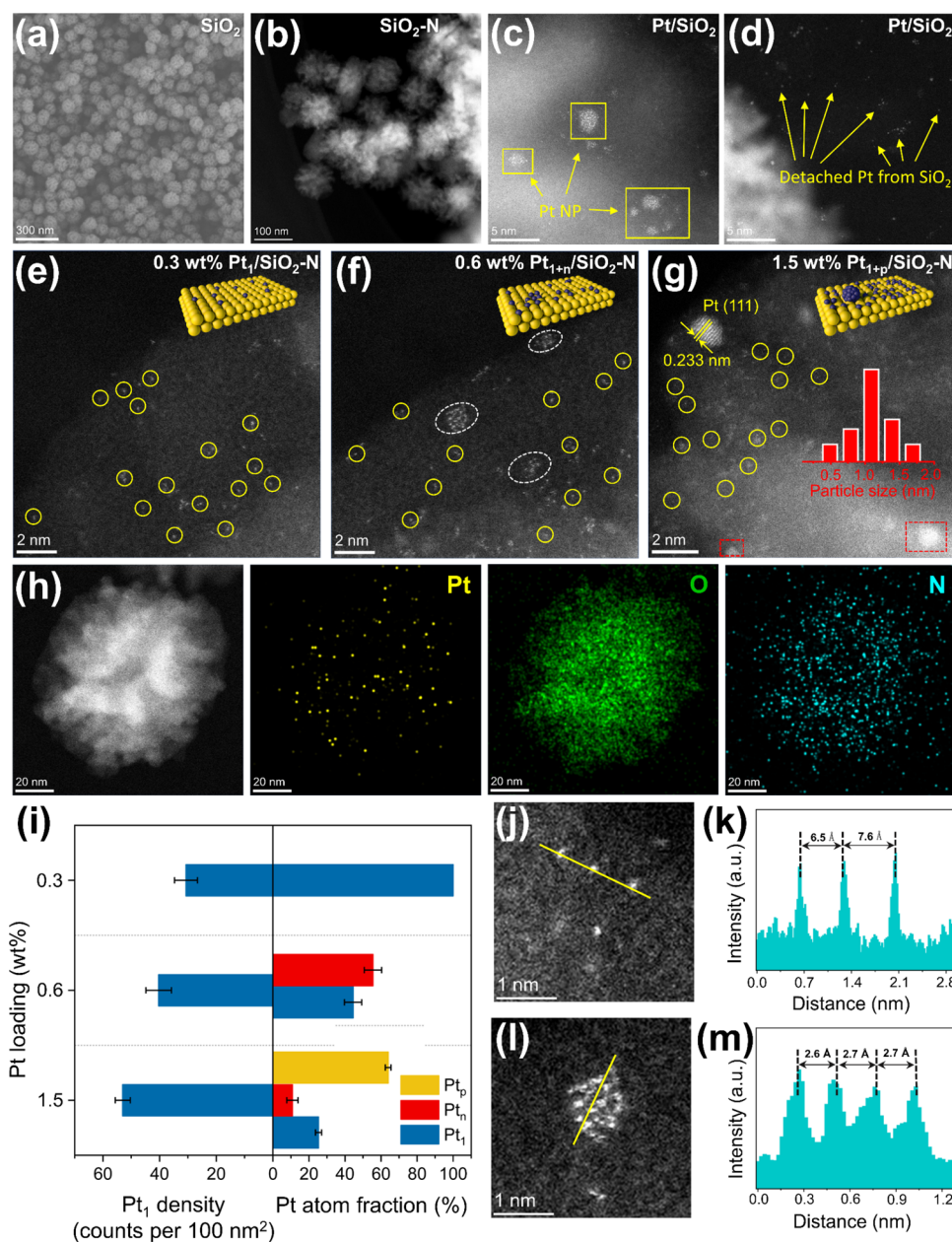
## RESULTS AND DISCUSSION

### Preparation and Characterization of $\text{Pt}_1/\text{SiO}_2\text{-N}$ , $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$ , and $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$ Catalysts

The dendritic  $\text{SiO}_2$  nanoflower sphere was first synthesized by the typical solvothermal method (Figure 1), which possesses a high specific surface area and developed a hierarchical porous structure (Figures 2a, S1, and S2, Supporting Information). The unique structure can not only well confine the Pt species to improve the stability of the catalysts but also enhance the accessibility of reactant molecules to/away from the internal metal. The obtained  $\text{SiO}_2$  was then functionalized with 3-aminopropyltriethoxysilane (APTES) named as  $\text{SiO}_2\text{-N}$  to provide the adsorption sites for  $\text{MeCpPtMe}_3$  precursor molecules. The structure and morphology of nanoflower spheres were well maintained after the amino functionalization process (Figures 2b, S1, and S3, Supporting Information). A series of atomically dispersed catalysts including 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$ , 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$ , and 1.5 wt %  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  were successfully synthesized through the atom-by-atom fabrication method starting from SACs by ALD, and the Pt content was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Table S1, Supporting

information). The key step to construct Pt SAs is that the  $\text{MeCpPtMe}_3$  molecules are uniformly adsorbed and bonded with amino groups, and then the second reactant  $\text{O}_3$  reacts with  $\text{MeCpPtMe}_3$  on the precursor-saturated surface. The Pt species were well controlled by varying the Pt ALD cycles (Figure S4, Supporting information).

The amino functionalization process has a significant influence on the particle size, distribution, and stability of Pt. As revealed by the HAADF-STEM images of  $\text{Pt}/\text{SiO}_2$  catalysts with as-prepared  $\text{SiO}_2$  as supports (Figure 2c,d), the main species are the Pt nanoparticles ( $\text{Pt}_p$ ) coexisted with some SAs, and the many  $\text{Pt}_p$  are detached from the  $\text{SiO}_2$  support even during the sample preparation process (just shaking ca. 5 s in ethanol solution) for transmission electron microscopy (TEM) measurement, indicating the poor stability of the catalysts due to the weak interaction between Pt and  $\text{SiO}_2$ . Therefore, the amino functionalization toward  $\text{SiO}_2$  is an indispensable step to achieve the high-stability and high-dispersion  $\text{SiO}_2$ -based catalyst. Figure 2e shows the typical HAADF-STEM image of 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$  catalysts, and the Pt species mainly exist in the form of isolated Pt single atom ( $\text{Pt}_1$ ) with an atomic distance of ca. 0.7 nm and a surface density of about 31  $\text{Pt}_1$  per  $100 \text{ nm}^2$  (Figures 2i, S5a–c, and S6a, Supporting information). With the further increase of Pt loading, the 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  catalysts with  $\text{Pt}_1$  and atomic cluster ( $\text{Pt}_n$ ) dual sites are achieved (Figures 2f and S5d–f, Supporting information). As expected, the catalysts show a higher Pt atom density (40  $\text{Pt}_1$  per  $100 \text{ nm}^2$ , Figure 2i). Note that the  $\text{Pt}_n$  is composed of a few loosely assembled atoms still exhibiting atomically dispersed property and that the Pt single atoms of  $\text{Pt}_n$  are different from that of isolated  $\text{Pt}_1$ . The distance of adjacent Pt atoms in  $\text{Pt}_n$  sites is much shorter than the adjacent distance of Pt atom in  $\text{Pt}_1/\text{SiO}_2\text{-N}$ , and the corresponding distance of Pt atom in  $\text{Pt}_n$  is ca. 0.3 nm (Figures 2j–m, S6b, and S7, Supporting Information). Moreover, when the Pt loading is further increased to 1.5 wt %,  $\text{Pt}_p$  with an average size of 1.1 nm (inset in Figure 2g) is found in the 1.5 wt %  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  catalysts (Figures 2g and S5g–i, Supporting Information), and

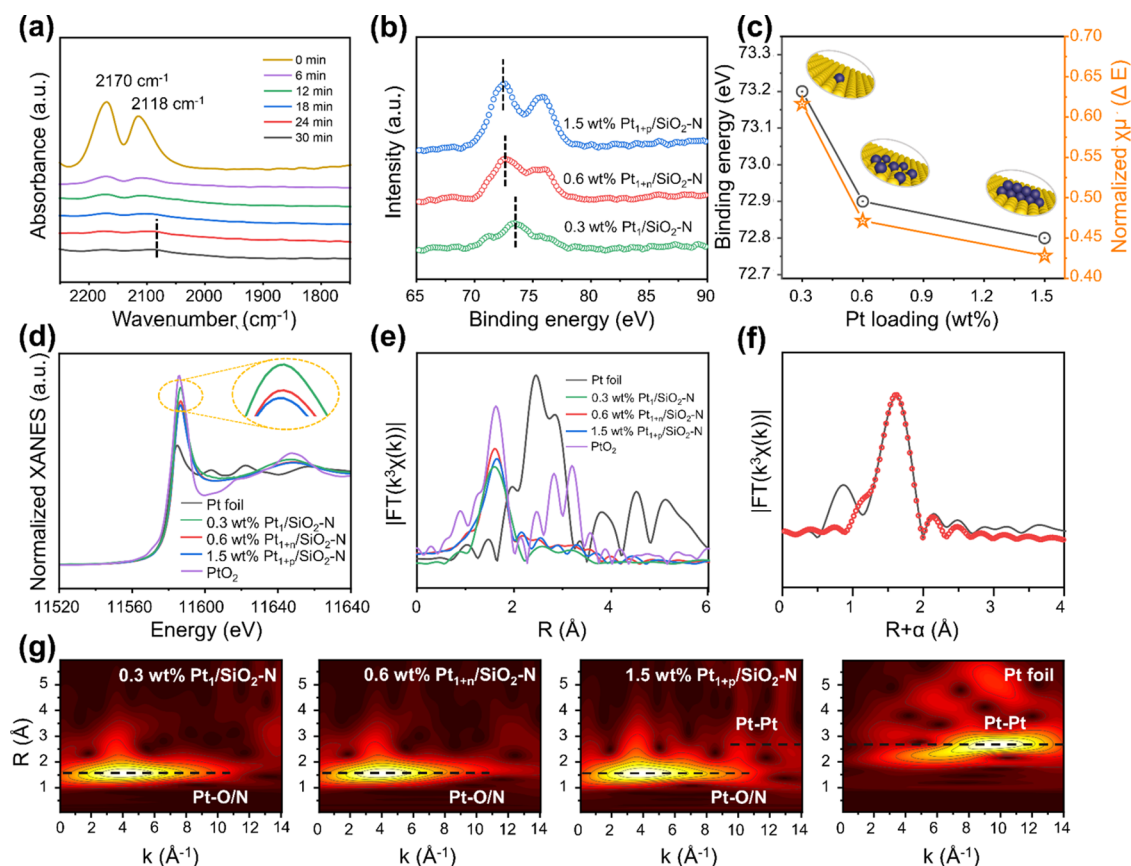


**Figure 2.** (a) Scanning electron microscopy (SEM) image of  $\text{SiO}_2$ . (b) HAADF-STEM image of amino-functionalized  $\text{SiO}_2\text{-N}$ . High-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM) images of (c, d)  $\text{Pt}/\text{SiO}_2$ , (e) 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$ , (f) 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$ , and (g) 1.5 wt %  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  catalysts (inset is the corresponding histogram of particle size distribution and SA is not included). (h) HAADF-STEM and the corresponding elemental mapping images of 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  catalysts. (i) Statistics of Pt atomic species in 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$ , 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$ , and 1.5 wt %  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  catalysts.  $\text{Pt}_1$ ,  $\text{Pt}_n$ , and  $\text{Pt}_p$  stand for Pt single atom, Pt atomic cluster, and Pt nanoparticle, respectively. (j) HAADF-STEM image of 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$  and (k) the corresponding line intensity profiles along the yellow lines. (l) HAADF-STEM image of 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  catalysts and (m) the corresponding line intensity profiles along the yellow lines.

the measured lattice fringe distance of the Pt NPs is approximately 0.223 nm (Figure 2g), which matches well with the Pt(111) plane. Additionally, the Pt NPs can be observed from the low-magnification HAADF-STEM images of 1.5 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$ , while it is not observed from the HAADF-STEM images of 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$  and 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  catalysts (Figure S8, Supporting Information). It is noteworthy that there are still a large amount of  $\text{Pt}_1$  (about 53  $\text{Pt}_1$  per  $100 \text{ nm}^2$ ) and  $\text{Pt}_n$  sites (Figure 2i). Impressively, no detached Pt is observed for the  $\text{SiO}_2\text{-N}$ -supported three catalysts, strongly demonstrating the stabilization effect of amino groups toward Pt species. Moreover, there is no

diffraction peak ascribed to Pt species from the X-ray diffraction (XRD) patterns, which again indicates the high dispersion of Pt species in the catalysts (Figure S9, Supporting Information).

To further unravel the physicochemical properties of the catalysts, thorough characterizations were conducted by multiple techniques. The CO absorption-diffuse reflectance infrared Fourier transform (CO-DRIFT) spectroscopy was first adopted to investigate the local structure of catalysts. On the 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$  catalysts, no peak can be observed (Figure S10a, Supporting Information). While there is only one very weak peak located at  $2093 \text{ cm}^{-1}$  for 0.6 wt %  $\text{Pt}_{1+n}/$



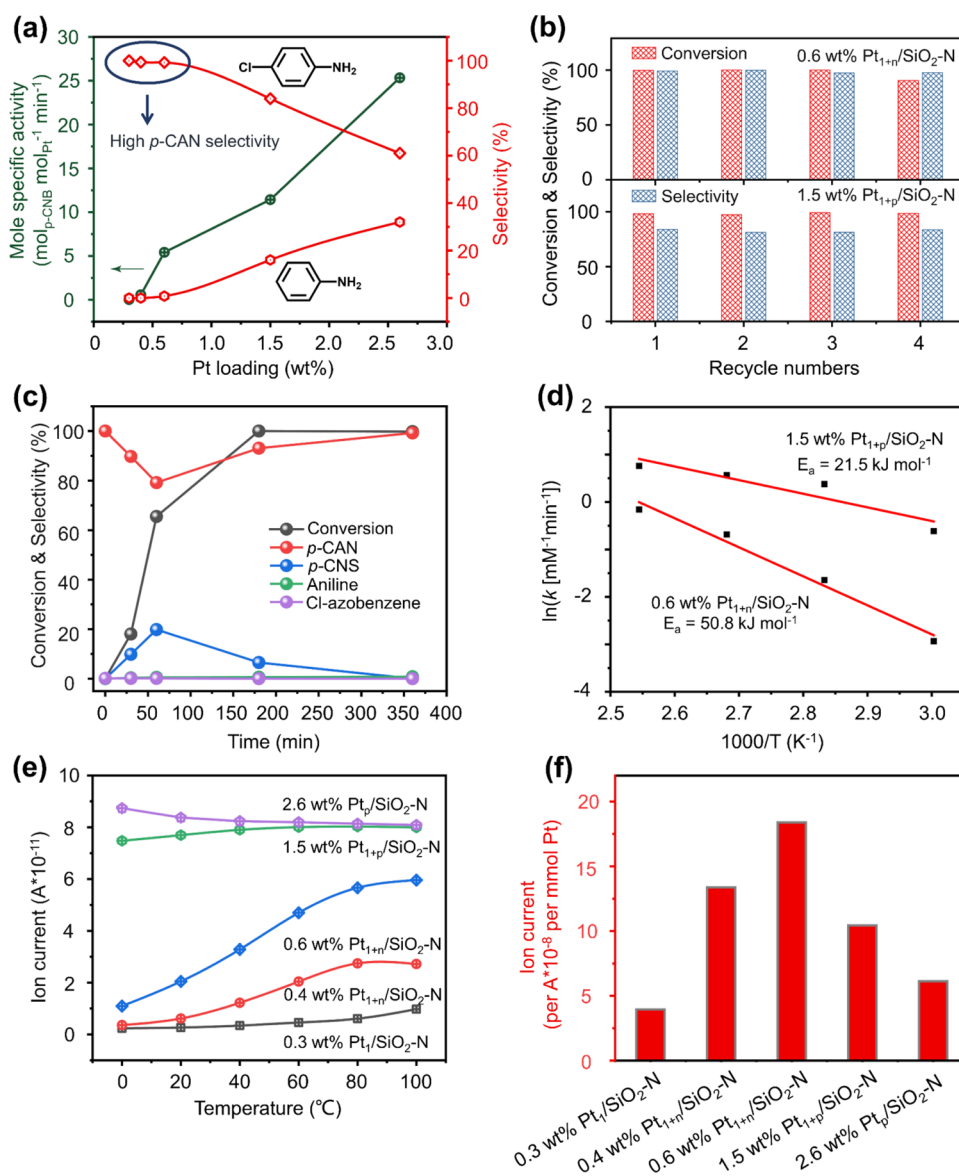
**Figure 3.** (a) CO–DRIFT spectra of 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  catalysts. (b) XPS Pt 4f spectra and (c) the corresponding statistics of electronic state Pt over the catalysts. (d) Pt  $L_3$ -edge XANES and (e) EXAFS spectra of the catalysts, Pt foil, and  $\text{PtO}_2$ . (f) EXAFS fitting curve of the representative 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  catalyst. (g) WT-EXAFS spectra of Pt  $L_3$ -edge of the catalysts and Pt foil.

$\text{SiO}_2\text{-N}$  catalysts, assigned to linearly bonded CO on Pt SAs (Figure 3a), again indicating the atomically dispersed property. In contrast, the CO peaks at  $2073\text{ cm}^{-1}$  are observed from the spectra of 1.5 wt %  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  catalysts, which can be attributed to the linear CO adsorption on metallic Pt nanoparticles/nanocluster,<sup>48,49</sup> again indicating the existence of  $\text{Pt}_p$  over the 1.5 wt %  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  catalysts, which complies well with the above HAADF-STEM results (Figure S10b, Supporting Information). The spatial intimacy of the Pt atom is expected to have an important influence on the local electronic structure of Pt species ( $\text{Pt}_1$ ,  $\text{Pt}_n$ , and  $\text{Pt}_p$ ). To this end, X-ray photoelectron spectroscopy (XPS) spectra of the three catalysts are given (Figures 3b and S11, Supporting Information). For the 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$  catalysts with longer atomic distances, the Pt  $4f_{7/2}$  possesses the higher binding energy, while the Pt  $4f_{7/2}$  of 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  and 1.5 wt %  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  catalysts present apparently lowered binding energies. Moreover, the N 1s peaks at 399.5 eV were also detected from the spectra of the catalysts, again indicating the successful functionalization toward  $\text{SiO}_2$  supports, which should play a significant role in stabilizing the Pt species through the potential Pt–N bond.

Similar results are observed in the Pt  $L_3$ -edge X-ray absorption near-edge structure (XANES) spectra. The white-line intensity, reflecting the average oxidation state of Pt, decreases with the increased Pt loading (Figure 3d), indicating that the  $\text{Pt}_1$  species are located in cationic states.<sup>50,51</sup> The white-line intensity of 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  catalysts is clearly lower than that of 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$  catalysts and

close to that of 1.5 wt %  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  catalysts due to the synergistic effect of neighboring Pt atoms. The coordination environments of the catalysts were further investigated by the extended X-ray absorption fine structure (EXAFS) spectra, as shown in Figure 3e. For the 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$  catalysts, the most noticeable scattering at around  $1.5\text{ \AA}$  can be ascribed to the first coordination shell of Pt–O/N (Table S2, Supporting Information), confirming the existence of  $\text{Pt}_1$ . Meanwhile, the main peak is still the peak at  $1.5\text{ \AA}$  for the 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  catalysts, indicating that the Pt atoms in the  $\text{Pt}_n$  existed in the form of few loosely assembled Pt SAs,<sup>52,53</sup> which is in line with CO–DRIFTS spectra and HAADF-STEM, and it also demonstrated by the EXAFS fitting curve (Figures 3f and S12, Supporting Information). Meanwhile, for the 1.5 wt %  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  catalysts, the Pt–Pt scattering path at around  $2.5\text{ \AA}$  is quite weak, and the Pt–O/N scattering path can still be observed, which should be due to the partially oxidized property and relatively low crystallinity of ALD-prepared Pt NPs with small size (ca. 1.1 nm); a large number of Pt SAs on 1.5 wt %  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  catalysts and detection limit of XAFS still existed.<sup>54</sup> Similar results can also be seen from the wavelet transforms (WT) of EXAFS (Figure 3g).

Based on the structural analysis results, the 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$ , 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$ , and 1.5 wt %  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  catalysts with the corresponding isolated  $\text{Pt}_1$ ,  $\text{Pt}_1 + \text{Pt}_n$ , and  $\text{Pt}_1 + \text{Pt}_p$  sites were successfully prepared. Note that the obtained  $\text{Pt}_n$  sites composed of randomly assembled Pt atoms still present atomically dispersed features, which is significantly



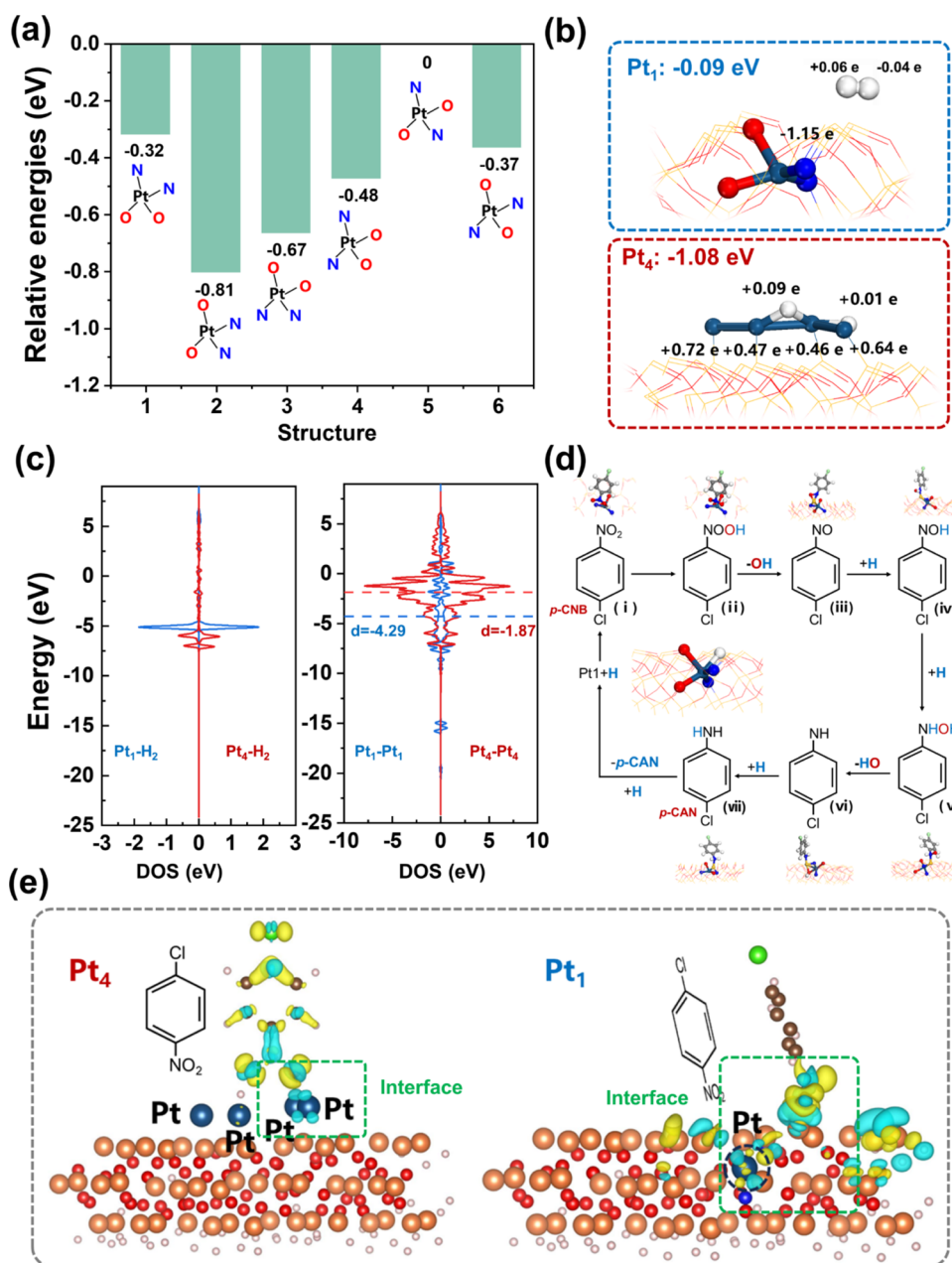
**Figure 4.** (a) Selective hydrogenation of *p*-CNB over different catalysts. (b) Stability tests of 0.6 wt % Pt<sub>1+n</sub>/SiO<sub>2</sub>-N and 1.5 wt % Pt<sub>1+p</sub>/SiO<sub>2</sub>-N catalysts. (c) Catalytic activity of 0.6 wt % Pt<sub>1+n</sub>/SiO<sub>2</sub>-N catalysts as a function of time. (d) Arrhenius plots of 0.6 wt % Pt<sub>1+n</sub>/SiO<sub>2</sub>-N and 1.5 wt % Pt<sub>1+p</sub>/SiO<sub>2</sub>-N catalyst for hydrogenation of *p*-CNB. (e) TPSRs of H<sub>2</sub> and D<sub>2</sub> over the catalysts at different temperatures (0–100 °C). (f) Formation rate of HD of different catalysts at 80 °C.

different from Pt<sub>1</sub> and Pt<sub>p</sub> sites (Figures S5 and S8, Supporting Information). Therefore, the 0.6 wt % Pt<sub>1+n</sub>/SiO<sub>2</sub>-N catalysts with Pt<sub>n</sub> sites present a unique electronic and geometric configuration compared with the other two catalysts; i.e., the catalysts not only have the advantages of high atom utilization efficiency and unsaturated coordination structure but also show the property of metallic Pt species, which may lead to unique catalytic properties due to the synergistic effect of spatially intimate Pt atom.

#### Catalytic Performances of Pt/SiO<sub>2</sub> Catalysts in Selective Hydrogenation

The selective hydrogenation of nitroarenes to produce unsaturated anilines is an important route in the fine chemicals industry. Moreover, it serves as a classic model reaction, benefiting the exploration of structure–activity relationships, an in-depth understanding of catalytic mechanisms, and the identification of active sites. The selective hydrogenation of *p*-

CNB was performed to quantify the catalytic property of the catalysts with different structures (Figure 4a; Tables S3 and S4 Supporting Information). Although the 0.3 wt % Pt<sub>1</sub>/SiO<sub>2</sub>-N catalyst possesses the highest atomic utilization efficiency, it is almost inactive for the hydrogenation reaction. In contrast, the 0.6 wt % Pt<sub>1+n</sub>/SiO<sub>2</sub>-N catalysts show a much higher mole specific activity (5.4 mol<sub>p-CNB</sub> mol<sub>Pt</sub><sup>-1</sup> min<sup>-1</sup>) with the selectivity of 99% toward the desired product of *p*-chloroaniline (*p*-CAN) at 99% conversion. The turnover frequency results show a similar tendency with the mole specific activity (Figure S14, Supporting Information). However, for the 1.5 wt % Pt<sub>1+p</sub>/SiO<sub>2</sub>-N catalysts with Pt<sub>p</sub> sites, the selectivity to *p*-CAN rapidly decreases to 83%. To further demonstrate the negative impact of Pt<sub>p</sub> sites on the selectivity of *p*-CAN, the 2.6 wt % Pt<sub>p</sub>/SiO<sub>2</sub>-N catalysts with only Pt<sub>p</sub> sites were prepared (Figure S15, Supporting Information). The selectivity to *p*-CAN over the catalysts decreased dramatically to 61%, further indicating that Pt<sub>p</sub> sites have a detrimental influence on the selectivity of



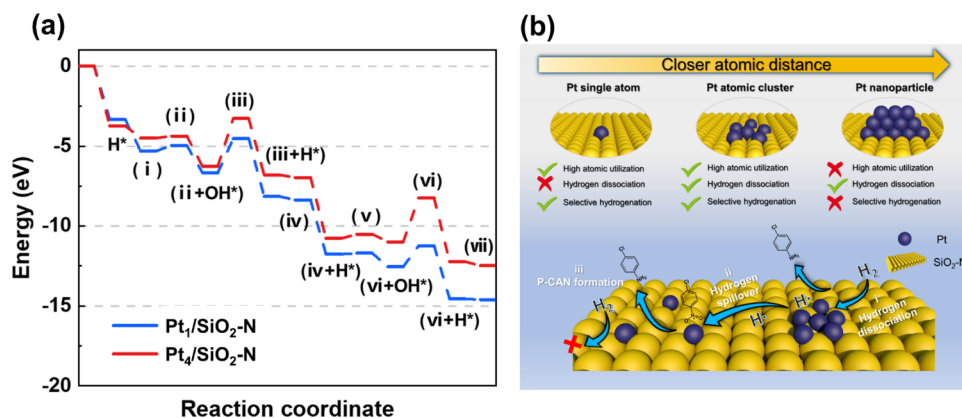
**Figure 5.** (a) Relative energies of six different single Pt atoms coordinated with two O atoms and two N atoms incorporated into the SiO<sub>2</sub> framework. (b) Electron distribution of H<sub>2</sub> adsorbed on Pt<sub>4</sub> and Pt<sub>1</sub> sites. Blue ball: nitrogen atom; red ball: oxygen atom; dark blue ball: platinum atom; white ball: hydrogen atom. Red and yellow line: SiO<sub>2</sub> support. (c) Total density of states (DOS) of H<sub>2</sub> adsorbed on Pt<sub>4</sub> and Pt<sub>1</sub> sites. (d) Schematic diagram of reaction process of *p*-CNB hydrogenation over Pt<sub>1</sub> sites. (e) Differential charge density plots of *p*-CNB over Pt<sub>4</sub> and Pt<sub>1</sub> sites. The light blue and light yellow isosurfaces represent the decrease and increase of 0.01 eV Å<sup>-3</sup> charge density, respectively.

the desired products. Moreover, the stability tests of the 0.6 wt % Pt<sub>1+n</sub>/SiO<sub>2</sub>-N and 1.5 wt % Pt<sub>1+p</sub>/SiO<sub>2</sub>-N catalysts were also carried out. The results indicate that the catalysts are quite stable after multiple cyclic tests, without presenting the obvious decrease in view of the activity and structural change (Figures 4b and S16, Supporting Information), while the Pt/SiO<sub>2</sub> catalysts without grafting amino groups exhibit poor stability (Figures S17 and S18, Supporting Information).

#### Catalytic Mechanism Investigation

In general, the *p*-CNB hydrogenation reaction is divided into dissociation of hydrogen, active hydrogen spillover, and hydrogenation of nitro groups, which is also accompanied by a dechlorination process. The processes could occur on

different active sites or the same one. We further studied the catalytic behavior of different catalysts. For the optimized 0.6 wt % Pt<sub>1+n</sub>/SiO<sub>2</sub>-N catalysts, excellent performance was obtained with 99% selectivity to *p*-CAN at 99% *p*-CNB conversion, and the sequential hydrogenation for *p*-CNB to *p*-CNS, and then to *p*-CAN was observed (Figure 4c). In contrast, for the 1.5 wt % Pt<sub>1+p</sub>/SiO<sub>2</sub>-N catalysts with Pt nanoparticles, the hydrogenation and dechlorination processes occur simultaneously (Figure S19, Supporting Information). Subsequently, the values of apparent activation energy ( $E_a$ ) are determined to be approximately 50.8 and 21.5 kJ mol<sup>-1</sup>, respectively, for 0.6 wt % Pt<sub>1+n</sub>/SiO<sub>2</sub>-N and 1.5 wt % Pt<sub>1+p</sub>/SiO<sub>2</sub>-N catalysts (Figure 4d). The attenuated total reflectance



**Figure 6.** (a) Adsorption energies of different reaction coordinates over  $\text{Pt}_4$  and  $\text{Pt}_1$  sites. (b) Proposed synergistic catalytic mechanism of dual-site catalyst for nitroarenes selective hydrogenation.

infrared (ATR-IR) spectroscopy was conducted to probe the adsorption of the *p*-CNB substrate (Figure S20, Supporting Information). For the pure *p*-CNB, two bands at 1510 and 1337  $\text{cm}^{-1}$  are the asymmetric stretching and symmetric stretching vibrations of the nitro group, respectively, which shift to 1525 and 1345  $\text{cm}^{-1}$  when *p*-CNB is adsorbed on 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$  catalysts. Similar cases can be found when *p*-CNB is adsorbed on 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  and 1.5 wt %  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  catalysts. The results indicate that the adsorption/activation of *p*-CNB on  $\text{Pt}_1$  sites is feasible. Also, control experiments were conducted using ammonia borane as the hydrogen source, and the 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$  catalysts could achieve the hydrogenation reaction of *p*-CNB, i.e., a 100% selectivity to *p*-CAN at complete conversion was obtained, again indicating that the  $\text{Pt}_1$  should be the potential activation and hydrogenation site of the nitro group (Table S5, Supporting Information). These results indicate that  $\text{H}_2$  can be easily dissociated on  $\text{Pt}_n$  and  $\text{Pt}_p$  sites generating active hydrogen, while the  $\text{Pt}_n$  and  $\text{Pt}_1$  sites provide the preferential adsorption sites for nitro groups. Note that the hydrogenation and dechlorination processes occur simultaneously on the  $\text{Pt}_p$  sites due to the existence of multiple sites such as edge, corner, and step,<sup>55</sup> resulting in the decreased selectivity of *p*-CAN, which can be further demonstrated by control experiments using *p*-CNB and *p*-CAN as the reaction substrates (Figure S21, Supporting Information). The optimized activity and high selectivity of 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  catalysts can also be verified in the hydrogenation of other nitrobenzene derivatives (Figure S22, Supporting information).

The dissociation of  $\text{H}_2$  and the subsequent spillover have important influences on hydrogenation reactions. The temperature-programmed surface reactions (TPSRs) of the mixture of  $\text{H}_2$  and  $\text{D}_2$  were performed to reveal the nature of hydrogen dissociation ability on Pt species with different structures (Figures 4e and S23–S27, Supporting Information), in which the appearance of HD in the TPSRs suggested the dissociation of  $\text{H}_2$ . For the 0.3 wt %  $\text{Pt}_1/\text{SiO}_2\text{-N}$  catalysts, the formation rate of HD is only observed at 80 °C with limited activity, which should account for the poor activity of  $\text{Pt}_1$  species for hydrogenation of *p*-CNB. In contrast, the formation rates of HD on 0.4 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  and 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  catalysts containing  $\text{Pt}_n$  sites are enhanced obviously with the increase of temperatures. Moreover, the 1.5 wt %  $\text{Pt}_{1+p}/\text{SiO}_2\text{-N}$  and 2.6 wt %  $\text{Pt}_p/\text{SiO}_2\text{-N}$  catalysts exhibit further enhanced apparent hydrogen dissociation ability. For the quantification

of intrinsic activity, the metal normalized activity for hydrogen dissociation at 80 °C was calculated, as shown in Figure 4f. The 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  catalysts show the highest reaction activity (Table S6, Supporting Information).

### Theoretical Perspectives of the Difference in Catalytic Performances

Based on the aforementioned experimental results, we have delineated the distinct roles played by various Pt species in the hydrogenation reactions and obtained the optimized 0.6 wt %  $\text{Pt}_{1+n}/\text{SiO}_2\text{-N}$  catalysts with synergistic  $\text{Pt}_1$  and  $\text{Pt}_n$  dual sites. Specifically, atomically dispersed  $\text{Pt}_1$  and  $\text{Pt}_n$  sites exhibit remarkably high selectivity for the hydrogenation of nitro groups, while  $\text{Pt}_p$  sites demonstrate poor selectivity. Moreover,  $\text{Pt}_n$  sites display a superior dissociation hydrogenation capability. To gain further deep insights into the synergy between  $\text{Pt}_1$  and  $\text{Pt}_n$  sites in *p*-CNB hydrogenation, we conducted first-principles theoretical calculations utilizing periodic DFT, as depicted in Figure 5. According to the EXAFS results (Figure 2e), six different single Pt atoms coordinated with two O atoms and two N atoms incorporated into the  $\text{SiO}_2$  framework were constructed (Figure S28, Supporting Information). It is found that the second single Pt atom exhibits the highest stability, as evidenced by the lowest relative energy (−0.81 eV) in Figure 5a. As a contrast, the  $\text{Pt}_4$  sites supported on  $\text{SiO}_2\text{-N}$  were also constructed to model  $\text{Pt}_n$  sites.

The hydrogen adsorption characteristics on  $\text{Pt}_1$  and  $\text{Pt}_4$  sites supported on  $\text{SiO}_2\text{-N}$  were initially investigated (Figure 5b). Notably,  $\text{Pt}_4$  sites exhibited a significantly lower adsorption energy of gaseous  $\text{H}_2$  than  $\text{Pt}_1$  sites (−1.08 < −0.09 eV). This disparity underscores the stronger interaction between  $\text{Pt}_4$  sites and  $\text{H}_2$  molecules, as evidenced by the dissociative adsorption of gaseous hydrogen on  $\text{Pt}_4$  sites and the weak interaction of gaseous hydrogen on  $\text{Pt}_1$  sites. After  $\text{H}_2$  adsorption on  $\text{Pt}_4$  sites, the two H atoms adsorbed on  $\text{Pt}_4$  sites gained more electrons (+0.09e and +0.01e) from Pt compared to those adsorbed on  $\text{Pt}_1$  sites (+0.06e and −0.04e). For deeper insight into the electronic structure, we computed the density of states (DOS) of  $\text{H}_2$  adsorbed on different  $\text{Pt}_4$  and  $\text{Pt}_1$  sites (Figure 5c). The broader peaks in the DOSs of  $\text{H}_2$  on the  $\text{Pt}_4$  sites emphasize the stronger electronic interaction between the  $\text{Pt}_4$  sites and  $\text{H}_2$ . Additionally, the average d-band center of  $\text{Pt}_4$  sites, closer to the Fermi level than that of  $\text{Pt}_1$  sites (−1.87 > −4.29), underscores the higher activation activity of  $\text{H}_2$  on  $\text{Pt}_4$  sites. These results demonstrate that  $\text{Pt}_4$  sites are more favorable for

the dissociative adsorption of hydrogen, which is in accordance with the experimental results (Figure 4f).

The entire reaction process of *p*-CNB hydrogenation over Pt<sub>1</sub> and Pt<sub>4</sub> to form *p*-CAN is illustrated in Figures 5d and S29, Supporting Information. Initially, H<sub>2</sub> dissociates from Pt<sub>4</sub> sites to form two H atoms which are then further adsorbed by Pt<sub>4</sub> and adjacent Pt<sub>1</sub> sites.<sup>56</sup> In comparison to Pt<sub>1</sub> sites, Pt<sub>4</sub> sites exhibit a higher adsorption energy for H proton (−3.7 < −3.3 eV). Subsequently, reactants *p*-CNB adsorb on both the Pt<sub>4</sub> and Pt<sub>1</sub> sites. Notably, the adsorption energy of *p*-CNB on Pt<sub>1</sub> sites is lower than that on Pt<sub>4</sub> sites (−1.99 < 0.76 eV). Differential charge density plots (Figure 5e) illustrate stronger electrical interactions at the interfaces of Pt<sub>1</sub> sites and *p*-CNB, indicating the enhanced activation of *p*-CNB on Pt<sub>1</sub> sites. The adsorption energy profiles in different reaction coordinates (Figure 6a) reveal that Pt<sub>1</sub> sites follow a lower-energy reaction path than Pt<sub>4</sub> sites during *p*-CNB hydrogenation. Consequently, the aforementioned experimental and DFT calculations suggest that Pt<sub>n</sub> sites are advantageous for H<sub>2</sub> adsorption and dissociation to form H proton, while Pt<sub>1</sub> sites are favorable for *p*-CNB hydrogenation with H proton (Figure 6b). The synergistic interplay between Pt<sub>1</sub> and Pt<sub>n</sub> sites should elucidate the exceptional overall activity of 0.6 wt % Pt<sub>1+n</sub>/SiO<sub>2</sub>–N catalysts. Meanwhile, the dynamic stability of Pt<sub>1</sub> and Pt<sub>n</sub> sites was investigated through systematic AIMD simulations at 353 K. From the results, the structure of the Pt<sub>1</sub> and Pt<sub>4</sub> sites remain stable throughout the simulation process (Figure S30).

## CONCLUSIONS

In summary, we achieve the controllable synthesis of atomically dispersed Pt species over SiO<sub>2</sub> by the amino group-assisted ALD strategy and unravel the strong dependence of *p*-CNB hydrogenation activity and selectivity on the size of Pt species. Especially, the Pt<sub>1+n</sub>/SiO<sub>2</sub>–N catalysts with stable Pt<sub>1</sub> and Pt<sub>n</sub> dual sites exhibit optimized selectivity toward *p*-CAN due to the remarkable synergy of dual sites, which can dissociate hydrogen via the Pt<sub>n</sub> species and preferentially activate nitro groups with the help of nearby Pt<sub>1</sub> species to generate *p*-CAN. In contrast, the isolated Pt<sub>1</sub> site is almost inactive for hydrogen dissociation. Nitro and chlorine groups can be simultaneously activated on the Pt<sub>p</sub> sites due to the existence of multiple sites, which results in poor selectivity toward *p*-CAN. The present strategy can be potentially applied to other SiO<sub>2</sub>-supported metal catalysts with atomic dispersion, and the unique design of dual sites will afford new guidance for the atomically dispersed catalysts with high efficiency.

## METHODS

### Preparation of Dendritic Mesoporous SiO<sub>2</sub>

Typically, cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and triethanolamine (TEAH<sub>3</sub>) were dissolved in H<sub>2</sub>O and stirred for an hour at 80 °C. After that, the tetraethyl orthosilicate (TEOS) was added to the mixture and continued stirring for 2 h at 80 °C. The molar ratio is 1.0 TEOS:0.06 CTAB:0.02 SDS:0.026 TEAH<sub>3</sub>:80 H<sub>2</sub>O. Afterward, a whitish solid was collected by centrifugation, washed with water and ethanol three times, respectively, and dried at 60 °C for 12 h. The products were calcined at 750 °C in air for 6 h to obtain dendritic mesoporous SiO<sub>2</sub>.

### Preparation of SiO<sub>2</sub>–N

1 g of dendritic mesoporous SiO<sub>2</sub> was dispersed in 100 mL of toluene with stirring in a three-neck flask at 80 °C, and then 5 mL of 3-aminopropyltriethoxysilane (APTES) was added into the solution,

which was continuously stirred at 80 °C for 48 h. After that, the suspension was centrifuged with ethanol and water three times, respectively. Finally, the samples were dried by a vacuum freeze-dryer to obtain the SiO<sub>2</sub>–N.

### Preparation of Pt/SiO<sub>2</sub>–N Catalysts

First, the functionalized SiO<sub>2</sub>–N was dispersed on a quartz wafer and dried at room temperature in air. Pt species were then deposited onto SiO<sub>2</sub>–N by using a homemade hot-wall, closed-chamber ALD reactor. Pt ALD was performed by sequentially exposing the SiO<sub>2</sub>–N to MeCpPtMe<sub>3</sub> and ozone (O<sub>3</sub>), which served as the Pt precursor and oxidant, respectively. The deposition temperature was set at 250 °C, and MeCpPtMe<sub>3</sub> was maintained at 60 °C. Ultrahigh-purity N<sub>2</sub> (99.999%) was used as the carrier and purge gas. The Pt structure and loading were controlled by adjusting the Pt ALD cycles, obtaining 0.3 wt % Pt<sub>1</sub>/SiO<sub>2</sub>–N (10 cycles), 0.6 wt % Pt<sub>1+n</sub>/SiO<sub>2</sub>–N (30 cycles), and 1.5 wt % Pt<sub>1+p</sub>/SiO<sub>2</sub>–N (50 cycles) catalysts. For comparison, Pt/SiO<sub>2</sub> catalysts with original SiO<sub>2</sub> as the support were also prepared using the same method.

## ASSOCIATED CONTENT

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacsau.4c00924>.

Detailed experimental section; characterization methods; and additional material characterization (DOCX)

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◆ H.X., D.L., J.S., and Z.L. authors contributed equally. H.X.: data curation, formal analysis, investigation, writing—original draft, writing—review and editing; D.L.: data curation, formal analysis, investigation; J.S.: data curation, formal analysis, investigation; Z.L.: data curation, formal analysis, investigation; X.Z.: data curation, investigation; L.N.: data curation, investigation; J.X.: data curation, investigation; L.C.: data curation, investigation; J.Z.: review and editing; J.Y.: data curation, investigation; X.F.: review and editing; Y.Q.: review and editing; J.Z.: conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, writing—original draft, writing—review and editing.

### Notes

The authors declare no competing financial interest.

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