

# Tandem synthesis strategy for atomically precise Pt<sub>1</sub>/Pt<sub>2</sub>/Pt<sub>3</sub> catalysts: Enhanced nitrobenzene selective hydrogenation via atomic number regulation

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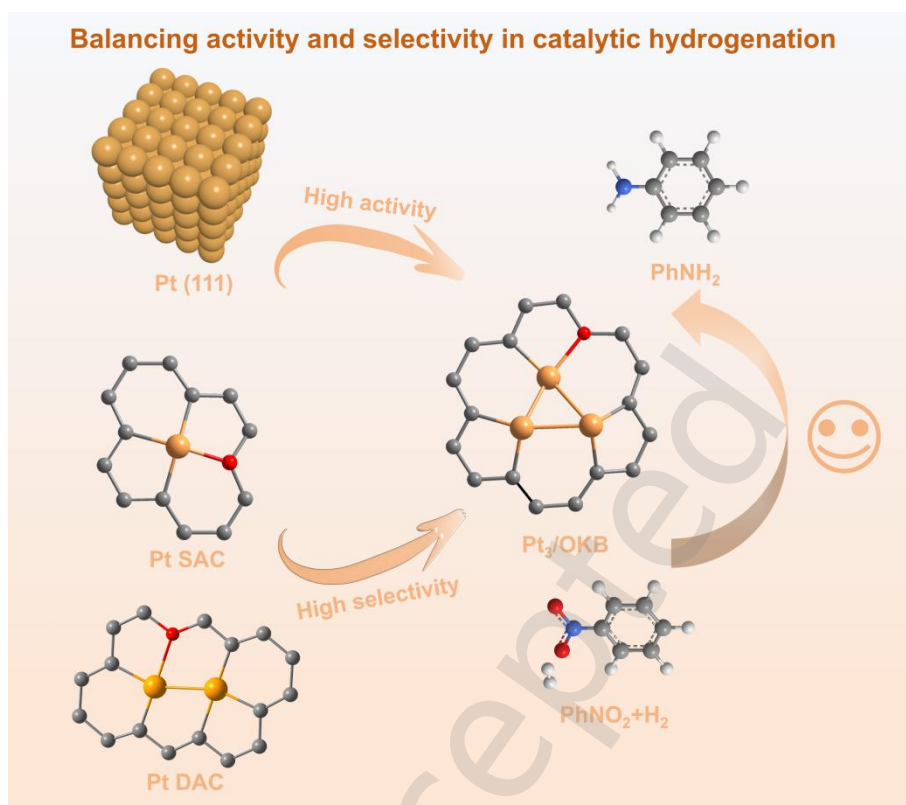
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### Balancing activity and selectivity in catalytic hydrogenation



This study develops Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB, and Pt<sub>3</sub>/OKB catalysts through a tandem strategy that integrating ligand protection and precursor engineering. The Pt<sub>3</sub>/OKB catalyst demonstrates superior performance in nitrobenzene hydrogenation to aniline under mild conditions, outperforming single-atom, dual-atom, and nanoparticle catalysts. DFT calculations reveals that optimized adsorption strength synergistically enhances activity and selectivity while suppressing excessive hydrogenation of the benzene ring.

# Tandem synthesis strategy for atomically precise Pt<sub>1</sub>/Pt<sub>2</sub>/Pt<sub>3</sub> catalysts: Enhanced nitrobenzene selective hydrogenation via atomic number regulation

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**ABSTRACT:** Atomically precise heterogeneous catalysts offer unprecedented opportunities for establishing clear structure-activity relationships in catalysis. However, the precise control over the number of metal atoms in such systems remains a significant challenge, primarily due to difficulties in maintaining atomic-level dispersion, preventing metal migration and aggregation. This study develops a tandem synthesis strategy combining ligand protection and precursor engineering. First, atomic-level precision precursors Pt<sub>1</sub>(C<sub>44</sub>H<sub>32</sub>P<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>, Pt<sub>2</sub>(C<sub>18</sub>H<sub>12</sub>Cl<sub>3</sub>P)<sub>3</sub>Br<sub>2</sub>(CO)<sub>1</sub> and Pt<sub>3</sub>(C<sub>18</sub>H<sub>21</sub>P)<sub>5</sub>(CO)<sub>2</sub> are synthesized using mixed ligands. Subsequently, by integrating Joule induction rapid thermal annealing technology, structurally well-defined Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB, and Pt<sub>3</sub>/OKB catalysts are successfully constructed on oxidized Ketjenblack (OKB) support. In mild conditions (60 °C, 0.5 MPa H<sub>2</sub>) for nitrobenzene selective hydrogenation, the Pt<sub>3</sub>/OKB catalyst achieves >99% conversion and >99% aniline selectivity, significantly outperforming Pt single-atom, Pt dual-atom, and Pt nanoparticle catalysts. Density functional theory (DFT) calculations demonstrate that the unique coordination environment in the triatomic structure optimizes adsorption strength, suppressing excessive benzene ring hydrogenation while facilitating H<sub>2</sub> activation and intermediate stabilization, thereby achieving synergistic regulation of activity and selectivity at the atomic scale. This study provides an atomically precise synthetic method for heterogeneous catalysts and elucidates the dependence of catalytic hydrogenation performance on the number of metal atoms.

**KEYWORDS:** tri-atoms, dual-atoms, single-atoms, nanoparticles, selective hydrogenation

## 1 Introduction

Atomically precise heterogeneous catalysts represent a paradigm shift in modern catalysis, enabling precise control over the structure-performance relationship through atomic-scale engineering of the geometric and electronic configurations of active sites [1-9]—a longstanding challenge limited by structural disorder in conventional catalysts. Unlike traditional systems with complex and unevenly distributed active centers, these catalysts demonstrate highly uniform site distributions, tunable electronic properties, and well-defined coordination configurations, offering a promising solution to the activity-

selectivity trade-off bottleneck that plagues catalytic processes [10-14]. Among transition metals, platinum stands out as the “star” metal for hydrogenation reactions due to its unique electronic configuration, which efficiently H<sub>2</sub> activates and enables moderate adsorption with organic substrates [15-18]. A representative example is the selective hydrogenation of nitrobenzene to aniline—a critical intermediate in the synthesis of pharmaceuticals, agrochemicals, and high-performance polymers [19-22]. However, the heterogeneous size distribution of platinum nanoparticles (Pt NPs) gives rise to multiple active sites with diverse coordination geometries and electronic states, promoting non-selective pathways such as over-

hydrogenation of aromatic rings to form cyclohexylamine. This side reaction significantly compromises the yield of desired aromatic amine products [23-25]. Therefore, achieving high activity without sacrificing selectivity remains a central challenge in catalyst design.

To address the aforementioned challenges, researchers have developed atomically precise heterogeneous catalysts, such as single-atom catalysts (SACs) and dual-atom catalysts (DACs), by engineering uniform and well-defined coordination environments [23,26-28]. However, the isolated nature of SACs introduces new limitations: restricted electronic delocalization and mononuclear coordination geometries lead to a linear scaling relationships between the adsorption energies of reaction intermediates [29-32]. This thermodynamic constraint leads to two major drawbacks: high barriers for hydrogen dissociation and kinetic imbalance between the reactant adsorptions and product desorption, leading to extremely low activity and poor catalytic efficiency at mild reaction conditions [32]. Although DACs improve adsorption behavior through electronic coupling and geometric synergy between dual metal atoms, thereby enhancing substrate activation and improving hydrogen dissociation and intermediate stability[33], the limited number of atoms and weak synergistic effects still hinder the simultaneous optimization of energy barriers across multiple reaction steps. Consequently, significant challenges remain in achieving efficient catalysis under mild conditions [23]. In contrast, tri-atom catalysts (TACs) preserve atomic-level dispersion while exploiting enhanced metal-metal interactions within a triangular configuration to create multifunctional active sites with moderate adsorption strength and high H<sub>2</sub> activation capacity [12-14,34-36] enabling precise control over reaction pathway [37-44]. However, the propensity of sub-nanometer precursors to aggregate during synthesis[45-47], combined with insufficient regulation of metal-support interface interactions, leads to inadequate dispersion and compromised structural stability[48-50]. These issues underscore the urgent need for controllable synthetic strategies for atomic-scale heterogeneous catalysts and a systematic understanding of how catalytic hydrogenation performance depends on the number of platinum active sites.

Herein, we proposed a tandem strategy that integrates ligand protection with precursor engineering to achieve atomic-level control over precursor formation, dispersion, and stabilization. Firstly, atomically precise precursors of Pt<sub>1</sub>(C<sub>44</sub>H<sub>32</sub>P<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>, Pt<sub>2</sub>(C<sub>18</sub>H<sub>12</sub>Cl<sub>3</sub>P)<sub>3</sub>Br<sub>2</sub>(CO)<sub>1</sub> and Pt<sub>3</sub>(C<sub>18</sub>H<sub>21</sub>P)<sub>5</sub>(CO)<sub>2</sub> were synthesized via mixed-ligands design. Subsequently, those three precursors were immobilized onto oxidized Ketjenblack (OKB) support. Finally, rapid Joule thermal annealing enabled efficient removal of surface ligands, while strong metal-support interactions suppressed cluster migration and aggregation, yielding structurally stable Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB catalysts. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) and X-ray absorption spectroscopy (XAS) confirmed the well-defined atomic dispersion and local

coordination structures of the supported Pt species. In the selective hydrogenation of nitrobenzene, the Pt<sub>3</sub>/OKB catalyst achieved >99% conversion and >99% aniline selectivity under mild reaction conditions (60 °C, 0.5 MPa H<sub>2</sub>), significantly outperforming Pt NPs/OKB (>99% conversion, 39% selectivity), Pt<sub>1</sub>/OKB (9% conversion, >99% selectivity) and Pt<sub>2</sub>/OKB (21% conversion, >99% selectivity). Density functional theory (DFT) calculations revealed that the moderate adsorption strength in tri-atom Pt, modulated by Pt-Pt coordination, not only facilitates H<sub>2</sub> activation and intermediate stabilization but also effectively suppresses excessive hydrogenation of the benzene ring, thereby synergistically optimizing catalytic activity and selectivity at the atomic scale.

## 2 Experimental

### 2.1 Chemicals and Materials

The chemicals and materials used in this study included chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, Aladdin, AR), cyclohexyldiphenylphosphine (C<sub>18</sub>H<sub>21</sub>P, Alfa Aesar, 98%), tris(4-chlorophenyl)phosphine (C<sub>18</sub>H<sub>12</sub>Cl<sub>3</sub>P, Alfa Aesar, 98%), (S)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (Boide Pharma, 99.9%), dichloromethane (Fuyu Fine Chemical, 99.9%), n-pentane (Fuchen Chemical, AR), petroleum ether (Fuyu Fine Chemical Industry, 99.9%), sodium borohydride (NaBH<sub>4</sub>, Aldrich, 98%), tetraoctylammonium bromide (Aladine, 98%), quaternary octylammonium iodide (Aladine, 99%), nitrobenzene (McLean, GR), ethanol (Fuyu Fine Chemical, 99.9%), Ketjenblack (KB, Adamas, 98%), and HNO<sub>3</sub> (Beijing Chemical Plant, 65%). Deionized water with a resistivity of 18.25 MΩ cm was used.

### 2.2 Catalyst Synthesis

**Synthesis of Pt<sub>1</sub>(C<sub>44</sub>H<sub>32</sub>P<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub> (abbreviated as Pt<sub>1</sub>).** First, 1 g H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was dissolved in 19.3 mL of deionized water in a 20 mL reagent flask to prepare a 0.1 M solution. All subsequent reactions were performed under ice-bath conditions. Next, 1 mL of the H<sub>2</sub>PtCl<sub>6</sub> solution (0.1 mmol) and tetra-n-octylammonium iodide (156 mg, 0.263 mmol) were added to a 50 mL round-bottom flask, followed by the addition of 14 mL of dichloromethane (DCM) to facilitate phase transfer of the H<sub>2</sub>PtCl<sub>6</sub> into the organic layer. Carbon monoxide (CO) was then bubbled through the mixture for 1.5 min, after which the reaction proceeded for 1 h under stirring. Subsequently, (S)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (62.3 mg, 0.1 mmol) was dissolved in 5 mL of DCM and rapidly injected into the reaction vessel. After 3 h of reaction, the orange-yellow solution became noticeably lighter in color. A solution of sodium borohydride (37.8 mg, 1 mmol) in 0.1 M sodium hydroxide was prepared on ice and added to the reaction mixture, which was then stirred for an additional 6 h until the solution turned orange-yellow. The entire reaction was carried out at 800 rpm to ensure efficient mixing, while temperature was maintained near 0 °C using an ice bath to ensure mild reaction conditions. Upon completion, Pt<sub>1</sub> were isolated from the crude product by preparative thin layer chromatography (PTLC) using DCM/PE (1:1, v/v) as eluent. Finally, the purified products were collected and lyophilized under vacuum for 12 hours to yield the Pt<sub>1</sub>(C<sub>44</sub>H<sub>32</sub>P<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>.

**Synthesis of Pt<sub>2</sub>(C<sub>18</sub>H<sub>12</sub>Cl<sub>3</sub>P)<sub>3</sub>Br<sub>2</sub>(CO)<sub>1</sub> (abbreviated as Pt<sub>2</sub>).** H<sub>2</sub>PtCl<sub>6</sub> solution (1 mL, 0.1 mmol) and

tetraoctylammonium bromide (156 mg, 0.285 mmol) were added to a 50 ml round-bottom flask. 14 ml of dichloromethane was then added to transfer the  $\text{H}_2\text{PtCl}_6$  solution to the organic phase. Carbon monoxide was introduced for 1.5 minutes, followed by an additional hour of reaction. Next, 110 mg of  $\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P}$  (0.3 mmol) was dissolved in 5 ml of dichloromethane and quickly added to the flask. After 2 hours of reaction, the orange-yellow solution color significantly lightened. Then, 20 mg of sodium borohydride was dissolved in a 0.1 M sodium hydroxide solution on ice, and the reaction continued for another 6 hours, during which the solution turned yellow-green. The whole reaction was carried out at a speed of 800 rpm. In order to control the mild reaction conditions, the reaction process was carried out in an ice bath. After the reaction was complete, preparative thin layer chromatography (PTLC) was used with DCM/PE as the developing solvent in a ratio of 3:1 to isolate  $\text{Pt}_2$  precursors from the crude product. Finally, the purified clusters were dried in a vacuum freeze-dryer for 12 hours, resulting in  $\text{Pt}_2(\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P})_3\text{Br}_2(\text{CO})_1$ .

**Synthesis of  $\text{Pt}_3(\text{C}_{18}\text{H}_{21}\text{P})_5(\text{CO})_2$  (abbreviated as  $\text{Pt}_3$ ).** First, 1 mL of the  $\text{H}_2\text{PtCl}_6$  solution (0.1 mmol) and tetraoctylammonium bromide (156 mg, 0.285 mmol) were added to a 50 mL round-bottom flask, followed by the addition of 14 mL of dichloromethane (DCM) to facilitate phase transfer of the  $\text{H}_2\text{PtCl}_6$  into the organic layer. Carbon monoxide (CO) was then bubbled through the mixture for 1.5 min, after which the reaction proceeded for 1 h under stirring. Subsequently,  $\text{C}_{18}\text{H}_{21}\text{P}$  (80.5 mg, 0.3 mmol) was dissolved in 5 mL of DCM and rapidly injected into the reaction vessel. After 2 h of reaction, the orange-yellow solution became noticeably lighter in color. A solution of sodium borohydride (60 mg, 1.6 mmol) in 0.1 M sodium hydroxide was prepared on ice and added to the reaction mixture, which was then stirred for an additional 24 h until the solution turned orange-red. The entire reaction was carried out at 800 rpm to ensure efficient mixing, while temperature was maintained near 0 °C using an ice bath to ensure mild reaction conditions. Upon completion,  $\text{Pt}_3$  precursors were isolated from the crude product by preparative thin layer chromatography (PTLC) using DCM/PE (1:1, v/v) as eluent, affording an orange-red solid in 44.2% yield. Finally, the purified clusters were collected and lyophilized under vacuum for 12 hours to yield the  $\text{Pt}_3(\text{C}_{18}\text{H}_{21}\text{P})_5(\text{CO})_2$ .

**The pre-treatment process of oxidized Ketjenblack.** Add 200 mg of ketjenblack to 30 mL of 6 mol/L  $\text{HNO}_3$ . Ultrasonicate the mixture for 5 minutes to ensure complete dispersion, followed by stirring at 70 °C for 24 hours. After completing these steps, cool the mixture, centrifuge to collect the solid, and wash thoroughly with deionized water until the solution becomes neutral. Finally, dry the product in an oven at 80 °C to obtain OKB.

**Synthesis of  $\text{Pt}_1(\text{C}_{44}\text{H}_{32}\text{P}_2)_2(\text{CO})_4/\text{OKB}$ .** 5 mg of  $\text{Pt}_1(\text{C}_{44}\text{H}_{32}\text{P}_2)_2(\text{CO})_4$  (used as the platinum precursor) was dissolved in 10 mL dichloromethane by sonicate. Slowly add the solution dropwise to 100 mL of dichloromethane containing 100 mg of uniformly dispersed OKB support. After 12 hours of magnetic stirring, the mixture is centrifuged and washed twice with dichloromethane at

10,000 rpm. The resulting black product is designated as  $\text{Pt}_1(\text{C}_{44}\text{H}_{32}\text{P}_2)_2(\text{CO})_4/\text{OKB}$ . The final product must be dried in a vacuum drying oven prior to use.

**Synthesis of  $\text{Pt}_1/\text{OKB}$  catalyst.** A portion of the obtained  $\text{Pt}_1(\text{C}_{44}\text{H}_{32}\text{P}_2)_2(\text{CO})_4/\text{OKB}$  was transferred onto carbon cloth and calcined at 400 °C for 10 seconds in a  $\text{N}_2$  atmosphere using a Joule heating furnace with rapid heating and cooling capabilities. The sample was then rapidly cooled to remove the ligands, yielding  $\text{Pt}_1/\text{OKB}$ .

**Synthesis of  $\text{Pt}_2(\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P})_3\text{Br}_2(\text{CO})_1/\text{OKB}$ .** 5 mg of  $\text{Pt}_2(\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P})_3\text{Br}_2(\text{CO})_1$  (used as the platinum precursor) was dissolved in 10 mL dichloromethane by sonicate. Slowly add the solution dropwise to 100 mL of dichloromethane containing 100 mg of uniformly dispersed OKB support. After 12 hours of magnetic stirring, the mixture is centrifuged and washed twice with dichloromethane at 10,000 rpm. The resulting black product is designated as  $\text{Pt}_2(\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P})_3\text{Br}_2(\text{CO})_1/\text{OKB}$ . The final product must be dried in a vacuum drying oven prior to use.

**Synthesis of  $\text{Pt}_2/\text{OKB}$  catalyst.** A portion of the obtained  $\text{Pt}_2(\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P})_3\text{Br}_2(\text{CO})_1/\text{OKB}$  was transferred onto carbon cloth and calcined at 400 °C for 20 seconds in a  $\text{N}_2$  atmosphere using a Joule heating furnace with rapid heating and cooling capabilities. The sample was then rapidly cooled to remove the ligands, yielding  $\text{Pt}_2/\text{OKB}$ .

**Synthesis of  $\text{Pt}_3(\text{C}_{18}\text{H}_{21}\text{P})_5(\text{CO})_2/\text{OKB}$ .** 5 mg of  $\text{Pt}_3(\text{C}_{18}\text{H}_{21}\text{P})_5(\text{CO})_2$  (used as the platinum precursor) was dissolved in 10 mL dichloromethane by sonicate. Slowly add the solution dropwise to 100 mL of dichloromethane containing 100 mg of uniformly dispersed OKB support. After 12 hours of magnetic stirring, the mixture is centrifuged and washed twice with dichloromethane at 10,000 rpm. The resulting black product is designated as  $\text{Pt}_3(\text{C}_{18}\text{H}_{21}\text{P})_5(\text{CO})_2/\text{OKB}$ . The final product must be dried in a vacuum drying oven prior to use.

**Synthesis of  $\text{Pt}_3/\text{OKB}$  catalyst.** A portion of the obtained  $\text{Pt}_3(\text{C}_{18}\text{H}_{21}\text{P})_5(\text{CO})_2/\text{OKB}$  was transferred onto carbon cloth and calcined at 400 °C for 30 seconds in a  $\text{N}_2$  atmosphere using a Joule heating furnace with rapid heating and cooling capabilities. The sample was then rapidly cooled to remove the ligands, yielding  $\text{Pt}_3/\text{OKB}$ .

**Synthesis of Pt NPs/OKB catalyst.** Dissolve 5 mg of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (as a platinum precursor) in 10 mL of ethanol and process with ultrasonic treatment. Gradually add the solution to 100 mL of ethanol containing 100 mg of uniformly dispersed OKB carrier. After 12 hours of magnetic stirring, centrifuge the mixture and wash twice with ethanol at 10,000 rpm, followed by drying in a vacuum drying oven. Transfer the dried product to a high-temperature resistant porcelain boat and heat it to 800 °C at a rate of 5 °C/min in a tubular heating furnace with rapid heating and cooling capability, then, calcination was performed for 2 hours under an Ar atmosphere. Finally, cool the sample to room temperature to obtain Pt NPs/OKB.

## 2.3 Material Characterizations

The morphology and structure of the samples were examined using a transmission electron microscope (TEM, FEI Tecnai G2 20 STwin, operating at 200 kV). High-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) with aberration correction

and elemental mapping images were recorded on a JEOL JEM-ARM200F TEM/STEM, utilizing a spherical aberration corrector (200 kV). Powder X-ray diffraction (XRD) patterns were recorded on an X-ray powder diffractometer (MeasSrv F9XDZ42) with Cu K $\alpha$  ( $\lambda = 0.154$  nm) radiation at a scan rate of  $10^\circ \text{ min}^{-1}$  in the  $2\theta$  range from  $10$  to  $90^\circ$ . Ultraviolet-visible (UV-vis) spectra were acquired using a Shimadzu UV-vis spectrometer (Shimadzu 2600). Electrospray ionization mass spectrometry (ESI-MS) analysis was performed using an ultra-high-performance liquid chromatography-tandem mass spectrometer (SYNAPT G2-Si, Waters). Platinum concentration was determined via inductively coupled plasma emission spectroscopy (ICP-OES) on a Shimadzu ICPE-9800. X-ray photoelectron spectroscopy (XPS) measurements were conducted using an ESCALAB 250 thermal electron analyzer. Binding energies were calibrated by setting the binding energy of C1s to  $284.8$  eV. The L<sub>3</sub>-edge X-ray absorption spectrum of platinum was measured at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility and the 1W1B beamline of the Beijing Synchrotron Radiation Facility. The sample was prepared as a disc-shaped particle with a diameter of  $10$  mm and a thickness of approximately  $1$  mm. A silicon (111) monochromator was used to tune the photon energy. Data were extracted using the Athena and Artemis software programs, followed by systematic data fitting.

#### 2.4 Catalytic Performance Test

The catalytic hydrogenation reactions were conducted in a stainless steel autoclave with a pressure gauge, a mechanical stirrer and automatic temperature control apparatus (Anhui Kemi Machinery Technology Co., Ltd). In a typical experiment, a Teflon vessel loaded with  $2$  mL ethanol containing  $0.5$  mmol reactants and  $10$  mg catalyst was placed into the autoclave, purged three times with  $\text{N}_2$  to remove the air, pressurised with  $\text{H}_2$  to a pre-decided level, and heated to a pre-decided temperature under a stirring speed of  $500$  rpm for a pre-decided time period. After reaction, the catalyst was separated from the reaction mixture by centrifugation and the reaction products were obtained for quantitative analysis. For the reusability test, after each test cycle, the catalyst was collected by centrifugation, washed with ethanol several times, and dried under vacuum oven at  $60^\circ\text{C}$ .

The obtained liquid products were identified by GC-MS (Thermo Fisher Scientific-TXQ Quantum XLS, column-TG-WAXMS) and quantitatively analysed by GC (Shimadzu, GC-2010 Plus), equipped with a flame ionization detector and a KB-WAX capillary column ( $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ , Kromat Corporation, USA). The carbon balance was checked after every run and it was found to be  $>98\%$ .

The conversion, the selectivity and yield of the targeted product were calculated by the following equations:

$$\text{Conversion (\%)} = \left(1 - \frac{n_a}{n_b}\right) \times 100 \quad (1)$$

$$\text{Selectivity (\%)} = \frac{n_i}{n_p} \times 100 \quad (2)$$

$$\text{TOF (h}^{-1}\text{)} = \frac{n_b - n_a}{n_{\text{metal}}} \times \frac{1}{t} \quad (3)$$

Here,  $n_b$  and  $n_a$  are the moles of the reactants before and after the reaction,  $n_p$  is the moles of all products,  $n_i$  is the moles of the target product, while  $n_{\text{metal}}$  is the total moles of Pt in the sample, and  $t$  is the reaction time (hour).

#### 2.5 In Situ DRIFTS Measurements

Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) measurements were performed using the Bruker IFS66v Fourier transform spectrometer equipped with the Harrick diffuse reflection accessory at the Infrared and Microspectroscopy Terminal Station (BL01B) of the NSRL. Each spectrum was obtained by stacking  $256$  scans at a resolution of  $4 \text{ cm}^{-1}$ . The experiments employed a custom-made infrared reaction cell containing samples, which featured a zinc selenide (ZnSe) transparent window specifically designed for diffuse reflection detection of highly scattering powder samples. After loading the samples, the reaction cell was purged with  $99.999\%$  pure argon for  $30$  minutes to establish the background spectrum. Prior to in situ characterization, high-purity argon was continuously flowed for  $30$  minutes to allow the solvent and nitrobenzene (NB) to pass through the sample chamber. Subsequently, the system switched to a  $\text{H}_2/\text{Ar}$  mixture containing  $5\%$   $\text{H}_2$  and initiated the heating program, with spectral data automatically acquired every  $6$  minutes.

#### 2.6 Computational Methods

Density functional theory (DFT) computations were carried out employing the Vienna Ab initio Simulation Package (VASP) [63,64]. The electron-ion interactions were represented via the projector-augmented wave (PAW) method.<sup>65</sup> For the exchange–correlation energy, the Perdew–Burke–Ernzerhof (PBE) functional under the generalized gradient approximation (GGA) scheme was adopted.<sup>66</sup> Structural optimizations were executed until the total energy converged to  $10^{-5}$  eV and the residual atomic forces fell below  $0.05 \text{ eV } \text{\AA}^{-1}$ . A  $3 \times 3 \times 1$  Monkhorst–Pack k-point grid was utilized for Brillouin zone sampling throughout the geometry relaxation process. For the DOS calculations, a denser  $6 \times 6 \times 1$  k-point mesh was employed, with the smearing width reduced to  $0.2$  eV to improve the energy resolution. A  $15 \text{ \AA}$  vacuum layer along the z-axis was introduced to eliminate artificial interferences between neighboring periodic supercells.

The optimized C–C bond length in graphene was determined to be  $1.42 \text{ \AA}$ , with an in-plane lattice parameter of  $2.64 \times 2.64 \text{ \AA}^2$ . Meanwhile, the lattice constant of bulk Pt was relaxed to  $3.98 \text{ \AA}$ , both of which are in good agreement with reported experimental data [67,68]. For the Pt (111) surface in the Pt NPs/OKB system, a four-layer  $p(4 \times 4)$  supercell was constructed, in which the bottom two atomic layers were fixed and the top two layers were fully relaxed. To construct Pt single-atom ( $\text{Pt}_1/\text{OKB}$ ), diatomic ( $\text{Pt}_2/\text{OKB}$ ), and triatomic ( $\text{Pt}_3/\text{OKB}$ ) catalysts, a single-layer  $p(6 \times 6)$  graphene model was employed.

The adsorption energy  $E_{\text{ads}}$  is calculated as follow, which is used to calculate the adsorption ability:

$$E_{\text{ads}} = E_{\text{slab}} + E_{\text{adsorbate}} - E_{\text{adsorbate/slab}} \quad (4)$$

where  $E_{\text{adsorbate/slab}}$ ,  $E_{\text{slab}}$ ,  $E_{\text{adsorbate}}$  are the total energies of surface with molecules, clean metal surface and free molecules, respectively.

The Gibbs free energy ( $G$ ) was calculated according to the equation:

$$G = E + E_{\text{zpe}} + PV - TS \quad (5)$$

here,  $G$  denotes the Gibbs free energy, where  $E$  and  $E_{\text{zpe}}$  correspond to the DFT-derived electronic energy and zero-point energy, respectively. The pressure-volume term ( $PV$ ) is regarded as negligible in the present calculations [69]. All calculations were performed at a temperature ( $T$ ) of 298 K, with  $S$  representing the entropy term.

The definition of selectivity is given as follows:

$$\text{Selectivity} = G_{\text{hydro}} - G_{\text{des}} \quad (6)$$

where  $G_{\text{hydro}}$  is the free energy change associated with the further hydrogenation of the benzene ring in aniline, while  $G_{\text{des}}$  denotes the free energy required for the desorption of aniline from the catalyst surface. A positive value of this energy difference indicates that the catalyst tends to selectively produce aniline, whereas a negative value implies that aniline is more likely to undergo further reduction to form cyclohexylamine.

### 3 Results and discussion

#### 3.1 The Preparation and Characterization of Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB Catalysts

The detailed synthetic procedure for synthesizing mixed-ligands-protected single-atom, dual-atom, and tri-atom precursors are presented in **Figure 1a** and **Experimental section**. Specifically, phase transfer was initially performed by adding an aqueous solution of hexachloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) to a dichloromethane (DCM) solution containing phase-transfer reagent under ice-bath conditions. Subsequently, carbon monoxide (CO) and (S)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl ( $\text{C}_{44}\text{H}_{32}\text{P}_2$ )/tris(4-chlorophenyl)phosphine ( $\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P}$ )/cyclohexyldiphenylphosphine ( $\text{C}_{18}\text{H}_{21}\text{P}$ ) were introduced sequentially into the system. Subsequently, sodium borohydride was added as a reducing agent to chemically reduce the mixture. The resulting product was separated to obtain  $\text{Pt}_1(\text{C}_{44}\text{H}_{32}\text{P}_2)_2(\text{CO})_4$ ,  $\text{Pt}_2(\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P})_3\text{Br}_2(\text{CO})_1$  and  $\text{Pt}_3(\text{C}_{18}\text{H}_{21}\text{P})_5(\text{CO})_2$  precursors stabilized by mixed ligands (**Figure S4 in the electronic supplementary material**).

The UV-Vis spectra analysis showed that  $\text{Pt}_1(\text{C}_{44}\text{H}_{32}\text{P}_2)_2(\text{CO})_4$  had three distinct absorption peaks at 320 nm, 355 nm and 405 nm,  $\text{Pt}_2(\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P})_3\text{Br}_2(\text{CO})_1$  had a single absorption peak at 386 nm and  $\text{Pt}_3(\text{C}_{18}\text{H}_{21}\text{P})_5(\text{CO})_2$  had four independent absorption peaks at 323 nm, 377 nm, 417 nm and 491 nm (**Figures S1-S3 in the ESM**). After standing in solution for 15 days, the aforementioned cluster molecules exhibited no significant changes in their characteristic UV-Vis absorption bands, demonstrating excellent solution stability prior to immobilization. For the molecular formulas of Pt<sub>1</sub>, Pt<sub>2</sub> and Pt<sub>3</sub> precursors, electrospray ionization mass spectrometry (ESI-MS) analysis was conducted. As shown in **Figures 1b-1d**, the most intense peak at  $m/z$  1552.29 in Pt<sub>1</sub> precursors corresponded to  $[\text{Pt}_1(\text{C}_{44}\text{H}_{32}\text{P}_2)_2(\text{CO})_4]^+$ , while the strongest peak in Pt<sub>2</sub> precursors is at  $m/z$  1674.65, corresponding to

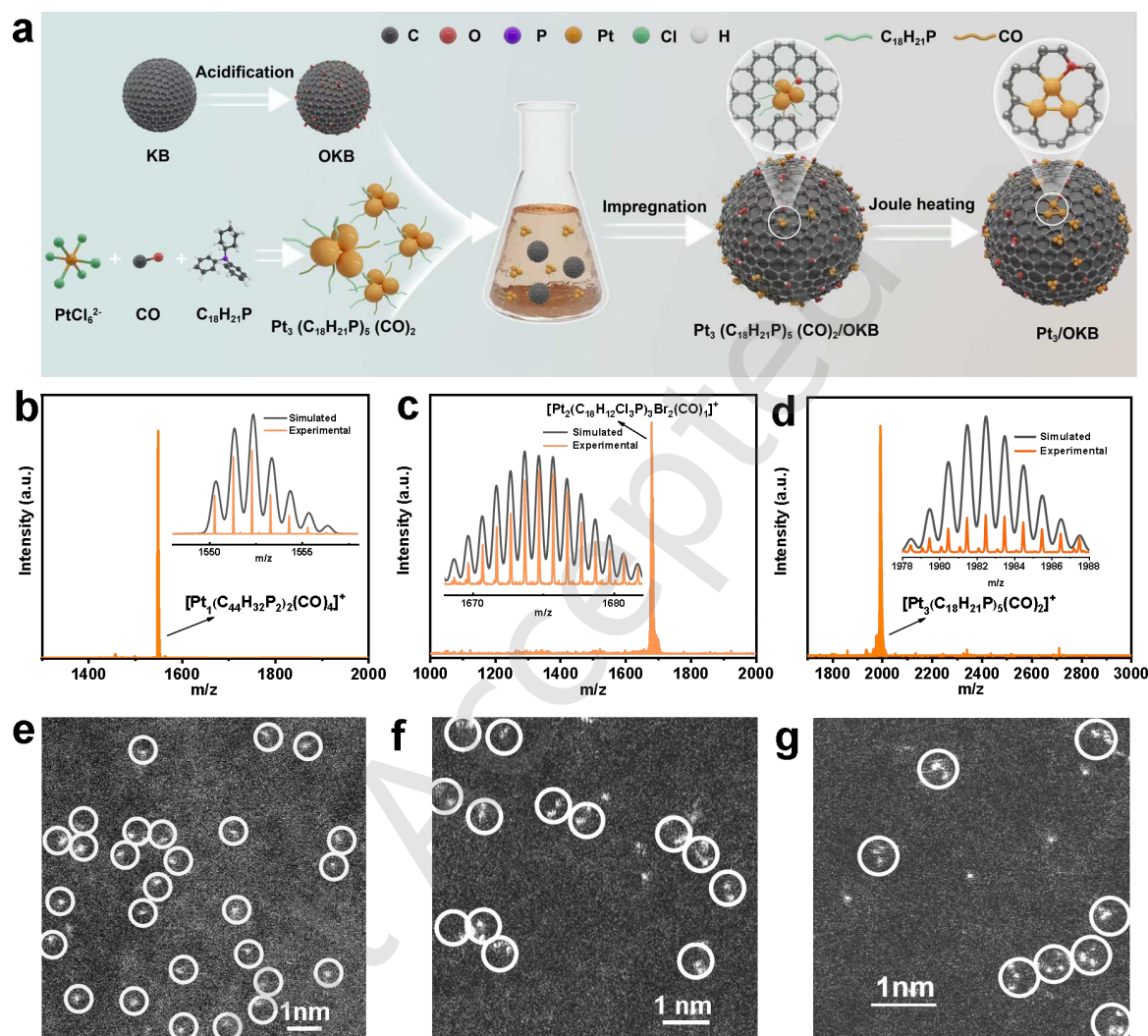
$[\text{Pt}_2(\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P})_3\text{Br}_2(\text{CO})_1]^+$ . In Pt<sub>3</sub> precursors, the peak at  $m/z$  1982.5 corresponded to  $[\text{Pt}_3(\text{C}_{18}\text{H}_{21}\text{P})_5(\text{CO})_2]^+$ . The experimental isotopic distribution pattern closely matched the simulated data (see the inset in **Figures 1b-1d**). FT-IR characterisation revealed that, in contrast to free ligands, the synthesised clusters still exhibited characteristic vibrations of the ligand backbone, demonstrating coordination-based anchoring of the ligands to the platinum center. Moreover, the presence of characteristic responses from both terminal and bridging carbonyl groups in the carbonyl absorption region further corroborates the successful preparation of the mixed-ligand-protected platinum clusters (**Figure S5-S7 in the ESM**).

To achieve precise atom dispersion and maintain structural integrity in the synthesis of atomic multi-phase platinum catalysts, we adopted a precursor engineering strategy by immobilizing ligand-protected  $\text{Pt}_1(\text{C}_{44}\text{H}_{32}\text{P}_2)_2(\text{CO})_4$ ,  $\text{Pt}_2(\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P})_3\text{Br}_2(\text{CO})_1$ , and  $\text{Pt}_3(\text{C}_{18}\text{H}_{21}\text{P})_5(\text{CO})_2$  precursors on OKB (**Figure 1a**) [51]. This process leveraged the  $\pi$ - $\pi$  stacking interactions between the phenyl rings of phosphorus-based ligands and the graphite domains of OKB [52], enhancing the structural stability and uniform dispersion of the precursor. Additionally, the steric hindrance provided by the phosphorus-based ligands played a crucial role in preventing aggregation and promoting effective dispersion and anchoring of the precursor on the support. To prevent metal aggregation during the time-consuming heating process, Joule heating was applied in a nitrogen atmosphere to remove CO and phosphine-based ligands from the precursor loaded on OKB[3,53-55]. This rapid heating process elevated the temperature to the desired level within seconds and maintained it for a specified duration, effectively removing the ligands while strengthening the Pt-C/O interface bonds on the OKB support. The thermal decomposition behaviors of the Pt precursors were evaluated by TGA under N<sub>2</sub> atmosphere (**Figure S8 in the ESM**). Consequently, the final catalysts were sequentially named Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB, and Pt<sub>3</sub>/OKB (see the ESM). X-ray diffraction(XRD) patterns of Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB were all consistent with those of the OKB support, indicating that the platinum species were highly uniformly dispersed. Notably, no characteristic diffraction signals corresponding to platinum nanoparticles were observed. (**Figure S9 in the ESM**). Moreover, TEM images of Pt<sub>3</sub>/OKB after Joule heating showed no detectable Pt nanoparticle aggregation (**Figure S10 in the ESM**). Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis showed that the platinum loading of Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB was 0.56 wt%, 0.96 wt% and 1.19 wt% respectively. By using chloroplatinic acid as a platinum source and immobilizing it into OKB, long-term heating yielded uniformly dispersed nanoparticles (Pt NPs/OKB) with a particle size of approximately 2 nm (**Figure S10 in the ESM**).

Atomic scale structural details were further analyzed using aberration corrected high angle annular dark field scanning transmission electron microscopy (AC HAADF-STEM). For Pt<sub>1</sub>/OKB as shown in **Figure 1e**, the atomic dispersion of a single-atom platinum uniformly anchored on the support, appearing as isolated bright spots. **Figure 1f** showed the

dispersed dual-atom Pt sites in Pt<sub>2</sub>/OKB were clearly visualized as paired bright spots. In the case of Pt<sub>3</sub>/OKB, **Figure 1g** showed the isolated Pt<sub>3</sub> species could be clearly distinguished in the carbon matrix, each precursor consisting of exactly three platinum atoms. Low-magnification HAADF-STEM image further showed a

uniform spatial distribution of Pt species without detectable Pt nanoparticles or large aggregates (**Figure S11 in the ESM**). The additional energy dispersive X-ray spectroscopy (EDS) mapping (**Figure S12 in the ESM**) confirmed the uniform distribution of platinum, carbon, and oxygen on the carbon substrate.



**Figure 1.** Synthesis and structural characterization of Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB catalyst. (a) Schematic diagram of the synthesis route for Pt<sub>3</sub>/OKB. (b) ESI-MS spectrum of Pt<sub>1</sub>, (c) Pt<sub>2</sub> and (d) Pt<sub>3</sub> precursors (recorded in positive mode). Inset: Experimental (orange curve) and simulated (black curve) isotope distribution patterns. (e-g) AC HAADF-STEM images of Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB, respectively.

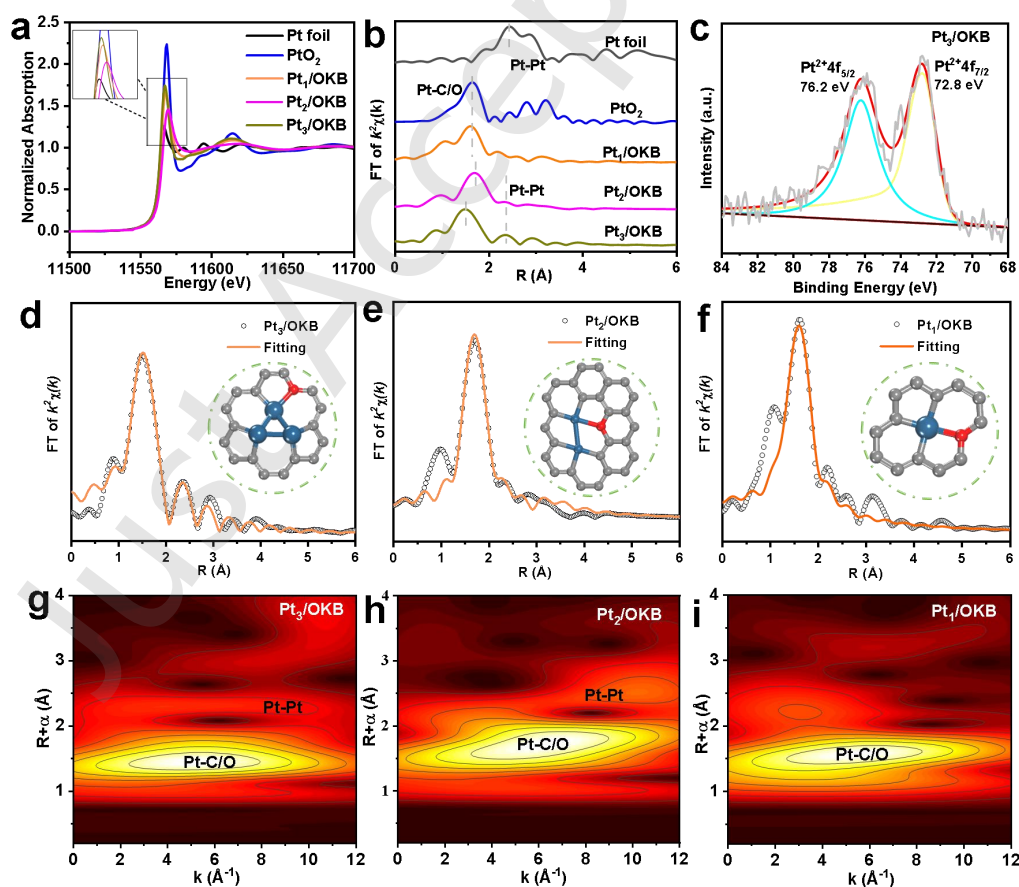
To further elucidate the local atomic and electronic structure of platinum species, X-ray absorption spectroscopy (XAS) measurements were conducted. As shown in **Figure 2a**, the normalized X-ray absorption near edge structure (XANES) spectrum of Pt L<sub>3</sub>-edge indicated that the white line peak intensity of the as-prepared platinum-based catalyst was higher than that of platinum foil but lower than that of PtO<sub>2</sub>. This trend indicated the existence of slightly positively charged Pt<sup>δ+</sup> species, which may be caused by electron transfer between Pt and OKB. It was worth noting that the white-line intensity of Pt<sub>3</sub>/OKB was higher than that of Pt<sub>1</sub>/OKB and Pt<sub>2</sub>/OKB, suggesting

stronger metal-support electronic interaction in the Pt<sub>3</sub>/OKB. In order to verify the chemical state of the platinum species, X-ray photoelectron spectroscopy (XPS) analysis was conducted. The results indicated that the oxidation state of Pt<sup>δ+</sup> in Pt<sub>3</sub>/OKB is close to Pt<sup>2+</sup>-like characteristics (**Figure 2c**) [56-58], which was consistent with the XANES analysis results. The Pt 4f XPS spectra of Pt<sub>1</sub>/OKB and Pt<sub>2</sub>/OKB are shown in **Figure S17-18**, respectively (ESM); their electronic properties are consistent with the XANES results. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy was used to detect the local coordination environment around

platinum atoms. **Figure 2b** showed the  $k^2$ -weighted Fourier transform EXAFS spectra of Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB at the Pt L<sub>3</sub>-edge, as well as the reference spectra of platinum foil and PtO<sub>2</sub>. Three catalysts exhibited distinct absorption peaks at 1.60 Å, 1.68 Å, and 1.51 Å, respectively, corresponding to the scattering paths of Pt-C/O. Notably, an additional distinct signal at approximately 2.35 Å was observed in Pt<sub>3</sub>/OKB and Pt<sub>2</sub>/OKB, attributable to Pt-Pt scattering, indicating the presence of metal bonds in the Pt<sub>2</sub> and Pt<sub>3</sub> atomic species. In order to obtain quantitative structural parameters, EXAFS curve fitting was performed (**Figures 2d-f, S13-S16**), and all fitted coordination parameters were summarized in **Table S1 in the ESM**. The fitting results for Pt<sub>3</sub>/OKB indicated that the average coordination number of Pt-C/O was 2.4, while Pt-Pt was 1.7, which was consistent with the existence of tri-atom Pt. For Pt<sub>2</sub>/OKB, the average coordination number of Pt-Pt was 0.8, while that of Pt-C/O was 3.1, which further confirmed the Pt dimer on OKB. In contrast, no contribution of the Pt-Pt pathway was observed in Pt<sub>1</sub>/OKB, confirming the single-atom dispersion of Pt on the OKB surface, with an average coordination number of 3.6 for the Pt-C/O coordination pathway. The complete removal of the ligands was further confirmed by XPS analysis, which showed no residual

signals for P, Br, or Cl heteroatoms (**Figure S17-S18 in the ESM**). The corresponding wavelet transform (WT) analysis further revealed the characteristics of local structures in real space and reciprocal space (**Figures 2g-i, Fig S19-20 in the ESM**). The wavelet transform of Pt<sub>3</sub>/OKB exhibited two distinct peaks at approximately 5.1 Å<sup>-1</sup> and 9.1 Å<sup>-1</sup>, whereas Pt<sub>2</sub>/OKB displayed peaks at 5.9 Å<sup>-1</sup> and 8.7 Å<sup>-1</sup>, corresponding to Pt-C/O and Pt-Pt scattering, respectively. On the contrary, Pt<sub>1</sub>/OKB only exhibited a major wavelet transform feature at approximately 5.5 Å<sup>-1</sup>, which was only related to Pt-C/O coordination, further confirming the absence of Pt-Pt interaction.

The atomic configurations of the three catalyst samples were further investigated using DFT calculations. Guided by the Pt-C/O and Pt-Pt coordination environments determined from extended X-ray absorption fine structure (EXAFS) spectroscopy, theoretical models of single-atom platinum (Pt<sub>1</sub>), platinum dimers (Pt<sub>2</sub>) and platinum trimers (Pt<sub>3</sub>) were constructed on oxygen-defect-containing graphene substrate (**in the inset of Figure 2d-f**). In these models, the oxygen-containing defect sites serve as anchoring points to immobilise the active platinum species, thereby suppressing the migration and agglomeration of platinum atoms.



**Figure 2.** X-ray absorption spectroscopy of Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB, Pt<sub>3</sub>/OKB, and the references. (a) Normalized Pt L<sub>3</sub>-edge XANES spectra for Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB, Pt<sub>3</sub>/OKB, PtO<sub>2</sub> and Pt foil. (b)  $k^2$ -weighted Fourier-transform Pt L<sub>3</sub>-edge spectra for Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB, Pt<sub>3</sub>/OKB, PtO<sub>2</sub> and Pt foil. (c) High resolution XPS spectra of Pt 4f in Pt<sub>3</sub>/OKB. (d-f) EXAFS fitting curves for Pt<sub>3</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>1</sub>/OKB at R space. Inset: the schematic model of Pt<sub>3</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>1</sub>/OKB. (g-i) WT of the Pt L<sub>3</sub>-edge EXAFS spectra for Pt<sub>3</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>1</sub>/OKB.

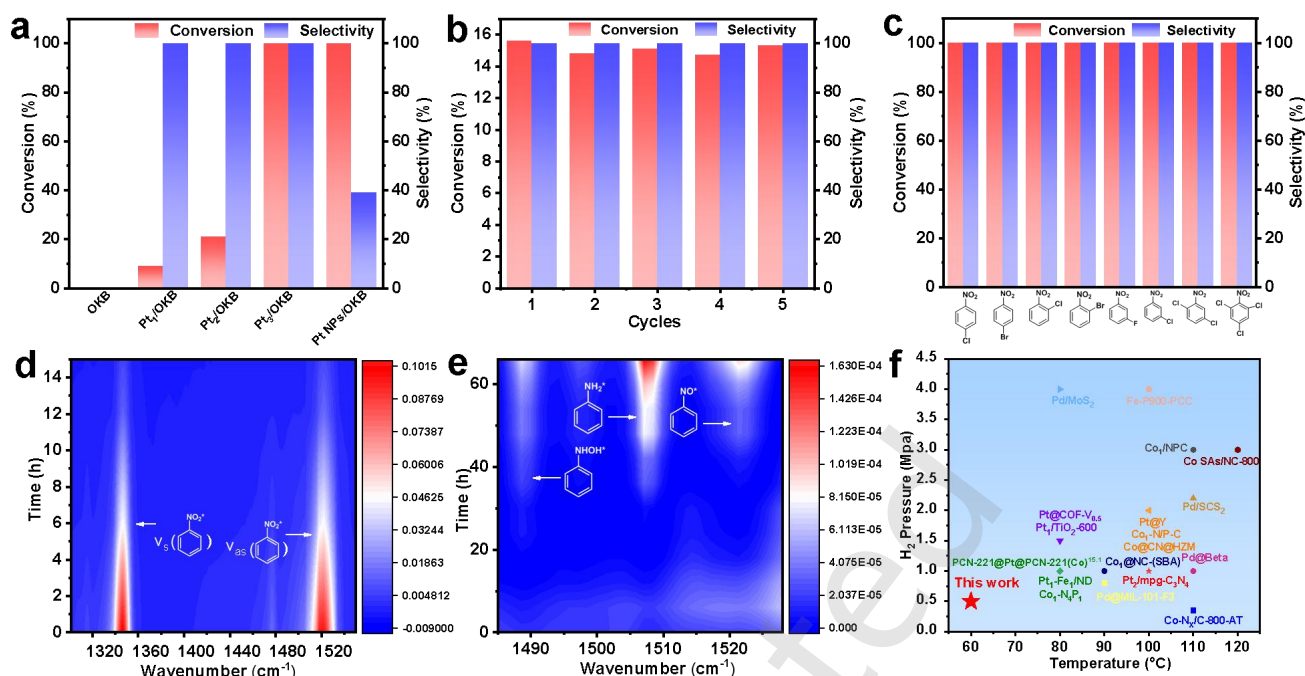
### 3.2 Catalytic Properties of Hydrogenation of Nitroaromatics

Platinum-based catalysts were widely regarded as benchmarks in the field of catalytic hydrogenation due to their outstanding activity [59-61], particularly in the key conversion of nitrobenzene hydrogenation to aniline, which was a key transformation in aromatic amine synthesis. To systematically investigate the influence of platinum structural configuration on catalytic performance, we evaluated and compared the activity and selectivity of Pt<sub>3</sub>/OKB with three reference catalysts of single-atom platinum (Pt<sub>1</sub>/OKB), dual-atom platinum (Pt<sub>2</sub>/OKB) and Pt NPs/OKB catalysts. As shown in **Figure 3a**, under mild reaction conditions (60 °C, 0.5 MPa H<sub>2</sub>), Pt<sub>3</sub>/OKB exhibited excellent catalytic efficiency, achieving complete conversion of nitrobenzene and aniline selectivity exceeding 99%. In contrast, Pt<sub>1</sub>/OKB exhibited significantly lower activity; although it maintains high selectivity for aniline (>99%), its nitrobenzene conversion rate reached only 9%. Although Pt<sub>2</sub>/OKB improved conversion to 21%, the limited Pt-Pt synergistic effect still results in suboptimal activity. This highlighted the crucial role of tri-atom Pt in facilitating H<sub>2</sub> activation kinetics and achieving efficient product desorption through synergistic interatomic effects. To eliminate the effect of the platinum loading, the turnover frequency (TOF) was calculated for each catalyst based on the total number of platinum atoms. **As shown in Figure S21**, the TOF of Pt<sub>3</sub>/OKB reached 409.83 h<sup>-1</sup>, which is 5.2 times and 3.8 times that of Pt<sub>1</sub>/OKB and Pt<sub>2</sub>/OKB, respectively. This indicates that the superior catalytic activity of Pt<sub>3</sub>/OKB does not stem from a higher platinum loading, but rather from the inherently superior catalytic efficiency of the triatomic platinum sites. While Pt NPs/OKB achieved complete conversion of nitrobenzene, it exhibited poor selectivity, producing only 39% aniline, primarily due to non-selective active sites arising from its broad nanoparticle size distribution [15,23-25]. These heterogeneous sites promoted strong adsorption of aromatic rings, leading to excessive hydrogenation and the production of cyclohexylamine as the major byproduct.

In fact, the stability and recyclability of catalysts were critical for industrial applications. We evaluated the recyclability of the Pt<sub>3</sub>/OKB catalyst under 60 °C and 0.5 MPa H<sub>2</sub> conditions at low conversion rates (within 0.5 hours). **Figure 3b** demonstrated the catalyst's outstanding stability during five consecutive cycles. The characterization after the reaction further confirmed this robustness. X-ray diffraction (XRD) (**Figure S22 in the ESM**) patterns showed no detectable reflections characteristic of platinum nanoparticles. In addition, no agglomeration of platinum

nanoparticles was observed in the post-reaction transmission electron microscopy images (**Figure S23 in the ESM**), further confirming the excellent structural stability of the Pt<sub>3</sub>/OKB catalyst. This remarkable stability was attributed to the strong Pt-C/O bonding between tri-atom Pt and oxygen-containing defects on the OKB support, which effectively immobilized the clusters and suppressed migration or sintering during repeated catalytic cycles. To assess substrate versatility and industrial relevance, a series of halogenated nitroaromatics—valuable intermediates in pharmaceutical and agrochemical synthesis, where undesired dehalogenation poses a significant challenge—were tested. As summarized in **Figure 3c**, Pt<sub>3</sub>/OKB exhibited excellent yields (>99%) in all tested substrates, including monohalogenated (such as p-chloronitrobenzene), dihalogenated (such as 2,4-dichloronitrobenzene), and trihalogenated derivatives (such as 2,4,6-trichloronitrobenzene), with no dehalogenation byproducts were detected. The excellent chemical selectivity and wide substrate compatibility of Pt<sub>3</sub>/OKB highlighted its potential as an efficient and sustainable catalyst for the synthesis of fine chemicals in industrial environments.

To elucidate the origin of the high activity of Pt<sub>3</sub>/OKB, in situ DRIFTS was employed to monitor the dynamic evolution of surface species during the nitrobenzene hydrogenation process. As shown in **Figure 3d and 3e**, the initial reaction stage corresponded to strong peaks at 1529 cm<sup>-1</sup> and 1343 cm<sup>-1</sup> representing the asymmetric ( $\nu_{as}(-NO_2)$ ) and symmetric ( $\nu_s(-NO_2)$ ) stretching vibrations of nitro groups, respectively [20]. As the reaction proceeds, these peaks gradually weakened while new peaks appear and intensify at 1520 cm<sup>-1</sup> (nitrosobenzene, PhNO), 1495 cm<sup>-1</sup> (phenylhydroxylamine, PhNHOH) and 1505 cm<sup>-1</sup> (aniline, PhNH<sub>2</sub>), pointing to the process of gradual reduction of nitrobenzene to aniline [19,70]. In contrast, control experiments using Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB, and Pt NPs/OKB (**Figures S24-S26 in the ESM**) showed a significant delay and weaker intensity in the appearance of these intermediate and product peaks. This indicated that Pt<sub>3</sub>/OKB accelerated the rate of each reduction step while improving H<sub>2</sub> activation efficiency and stabilizing key intermediates. Furthermore, a comparative analysis with state-of-the-art catalysts (**Figure 3f, Table S2 in the ESM**), showed that Pt<sub>3</sub>/OKB achieved full conversion and >99% aniline selectivity under notably milder conditions (lower temperature and reduced H<sub>2</sub> pressure) highlighting its superior catalytic competitiveness. The combination of high performance and mild reaction conditions made Pt<sub>3</sub>/OKB a highly competitive catalyst for sustainable nitrobenzene hydrogenation.



**Figure 3.** Hydrogenation performance of nitroaromatics with different catalysts. (a) Catalytic performance of various catalysts for nitrobenzene hydrogenation to aniline. (b) Cycling test of nitrobenzene hydrogenation on Pt<sub>3</sub>/OKB. (c) Hydrogenation of different halogenated nitrobenzenes on Pt<sub>3</sub>/OKB. Reaction conditions: 10 mg catalyst, 0.5 mmol reactant, 2 mL ethanol, 60 °C, 2 h, 0.5 MPa H<sub>2</sub>. (d-e) In-situ DRIFTS spectra of nitrobenzene hydrogenation on Pt<sub>3</sub>/OKB during the reaction. (f) Comparison of reaction conditions for nitroaromatics hydrogenation between Pt<sub>3</sub>/OKB and as-reported supported catalysts.

### 3.3 DFT Calculations

To further investigate the enhanced performance of tri-atomic platinum catalysts, density functional theory calculations were performed to elucidate the mechanism of selective hydrogenation process of nitrobenzene. As shown in **Figure 4a**, at the platinum site, nitrobenzene could be selectively hydrogenated into two different products: aniline or cyclohexylamine. The product selectivity was primarily determined by whether protonation occurs exclusively on the nitro group or concurrently on the carbon atoms of the benzene ring—a process that initiated the ring-hydrogenation pathway [23,62]. To understand the selectivity of products on different platinum sites, a series of atomically defined platinum catalytic models were constructed, including Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB, in which the platinum centers were coordinated by carbon and oxygen atoms, respectively. Based on these platinum sites, we systematically studied the hydrogenation mechanism of nitrobenzene on platinum-based catalysts, Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB, Pt<sub>3</sub>/OKB, and Pt NPs/OKB to elucidate the intrinsic structure-selectivity relationship at the atomic scale (**Figure S27 in the ESM**). Nitrobenzene molecules typically adopted two different adsorption configurations on metal surfaces, vertical adsorption and parallel adsorption. The difference in adsorption structures can significantly affect the subsequent catalytic reaction pathway. To identify the

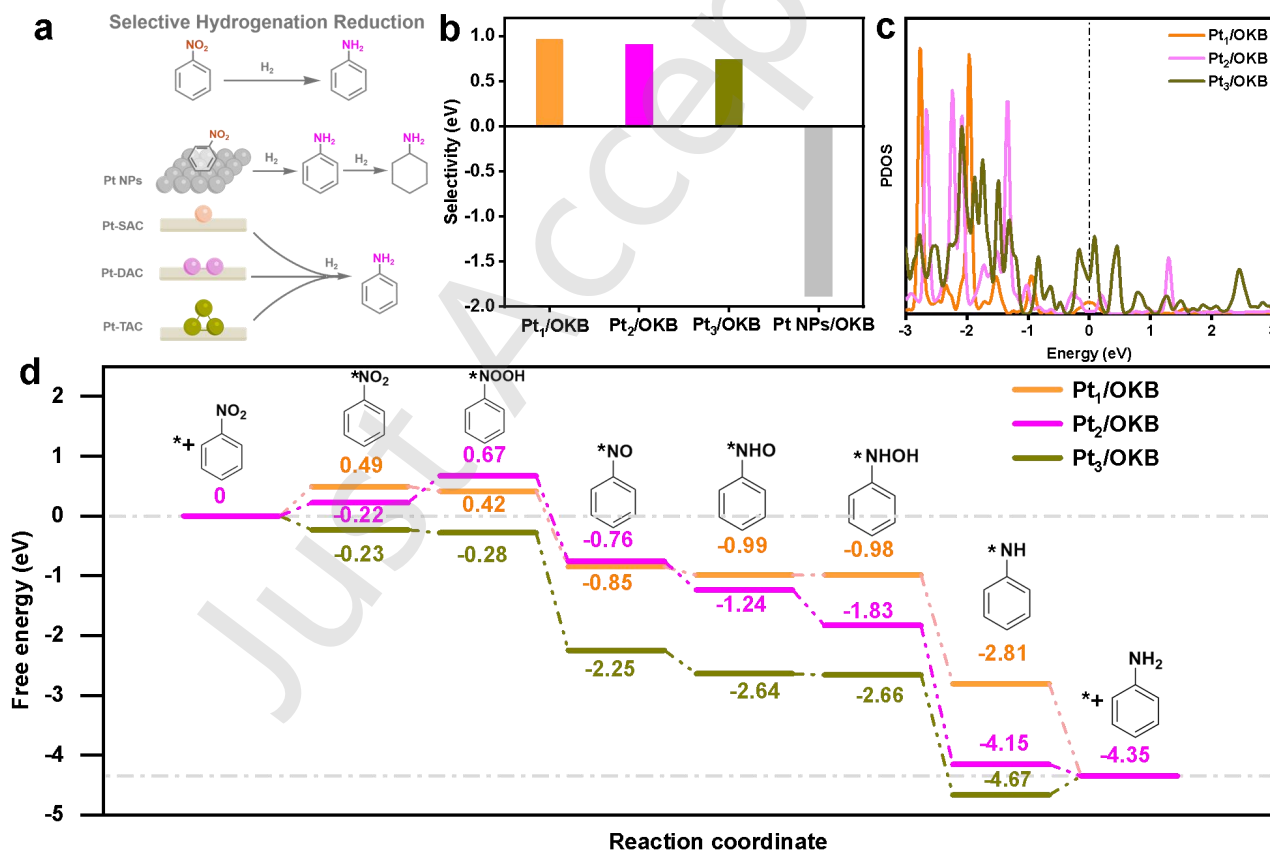
thermodynamically favored adsorption mode on each catalyst, the adsorption energies of both configurations were calculated and compared. The optimized adsorption structures and corresponding adsorption energies were shown in **Figures S28-S32**. These results indicated that the nitrobenzene prefers a parallel adsorption configuration on all catalyst surfaces, as evidenced that catalysts generally tend to adsorb in parallel.

To evaluate the selectivity of the three catalysts, we defined the selectivity as the free energy difference between the formation of cyclohexylamine and the desorption of aniline from the catalyst surface, and calculated for each of catalysts. As shown in **Figure 4b**, Pt NPs/OKB exhibits a negative selectivity value, while Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB, and Pt<sub>3</sub>/OKB show positive selectivity values. This indicated that Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB, and Pt<sub>3</sub>/OKB were more inclined to generate aniline, while Pt NPs/OKB was more likely to form cyclohexylamine. In this system, we define the energy required for benzene ring adsorption and hydrogenation as the benzene ring activation energy. Computational results indicate that the order of benzene ring activation ability from strong to weak is Pt<sub>3</sub>/OKB > Pt<sub>1</sub>/OKB > Pt<sub>2</sub>/OKB (**Table S3 in the ESM**). We observe a clear negative correlation between the state density of the Fermi level (Pt<sub>2</sub>/OKB > Pt<sub>1</sub>/OKB > Pt<sub>3</sub>/OKB) and benzene ring activation ability (**Figure 4c**). Specifically, Pt<sub>3</sub>/OKB exhibits the lowest DOS

intensity at the

Fermi level (0 eV), demonstrating optimal benzene ring activation capability through moderate adsorption. This configuration effectively prevents over-hydrogenation while stabilizing key reaction intermediates. Such a balanced interaction, linked to its intermediate density of states near the Fermi level, enabled Pt<sub>3</sub>/OKB to better coordinate adsorption and desorption processes. As a result, Pt<sub>3</sub>/OKB achieved a superior compromise between catalytic activity and selectivity compared with the other catalysts. To further explain the origin of the difference between Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB, we calculated the reaction free energy profiles of nitrobenzene stepwise hydrogenation by comparing the three parallel adsorption configurations (Figures S33-S35 in the ESM and Figure 4d). The conversion of nitrobenzene to aniline proceeded through \*PhNO<sub>2</sub>, \*PhNOOH, \*PhNO, \*PhNHO, \*PhNHOH, and \*PhNH, and finally yielding \*PhNH<sub>2</sub>. The overall reaction pathways on Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB exhibited distinctly different energetic characteristics. On Pt<sub>1</sub>/OKB, the weak adsorption of nitrobenzene rendered the initial adsorption step the RDS, with a free energy change of up to 0.49 eV.

Although the subsequent hydrogenation steps showed a decreasing free energy trend, the weak adsorption strength limited the overall catalytic efficiency. This indicated that the catalytic activity of Pt<sub>1</sub>/OKB was constrained by its poor binding ability to reaction molecules. The adsorption capacity of Pt<sub>2</sub>/OKB is enhanced by the synergistic effect of bimetallic atoms, but its weak hydrogenation ability makes the first step of nitrobenzene hydrogenation become the reaction kinetic step (RDS), with a free energy change of 0.45 eV, slightly lower than that of Pt<sub>1</sub>/OKB. In contrast, Pt<sub>3</sub>/OKB exhibited a more favorable free energy landscape. Nitrobenzene adsorption was more stable on Pt<sub>3</sub>/OKB, and the energy barriers associated with the hydrogenation of key intermediates were substantially reduced. Notably, on Pt<sub>3</sub>/OKB, the RDS shifted from the initial adsorption to the final desorption of aniline, with a lower free-energy barrier of only 0.32 eV. These results demonstrated that the hydrogenation steps on Pt<sub>3</sub>/OKB proceed more smoothly and that its adsorption strength achieved a more appropriate balance between stabilizing the reaction intermediates and facilitating product desorption.



**Figure 4.** Catalytic mechanism of nitrobenzene hydrogenation with different catalysts. (a) Schematic illustration of selective hydrogenation reactions for four platinum-based catalysts Pt NPs/OKB, Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB. (b) Catalyst selectivity analysis for Pt<sub>3</sub>/OKB, Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt NPs/OKB. (c) Partial density of states (PDOS) distribution maps for the d-orbital components of Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB. (d) Free energy curves of selective hydrogenation reactions for Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB.

## 4 Conclusions

In summary, this work presented a tandem strategy combining ligand protection and precursor engineering to construct the well-defined and uniformly dispersed Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt<sub>3</sub>/OKB catalysts. This approach addressed critical challenges in the synthesis of atomically precise heterogeneous catalyst: ligand-protected precursors maintained the exact atomical number during initial synthesis, while Joule rapid thermal annealing enabled efficient ligand removal without inducing metal aggregation, and simultaneously strengthening Pt-C/O bonds with the OKB support. In the selective hydrogenation of nitrobenzene, Pt<sub>3</sub>/OKB demonstrated exceptional catalytic performance under mild conditions: achieving >99% nitrobenzene conversion and >99% aniline selectivity, outperforming single-atom Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB and Pt NPs/OKB. Beyond this, Pt<sub>3</sub>/OKB exhibited outstanding cycling stability and substrate universality, underscoring its practical applicability in fine chemical synthesis. DFT calculations showed that the superior properties of Pt<sub>3</sub>/OKB are attributed to its well-defined three-atom structure and synergistic Pt-Pt interactions. Specifically, the tri-atom Pt optimized adsorption energetics by facilitating efficient H<sub>2</sub> activation, stabilizing key intermediates, and promoting rapid aniline desorption, thereby overcoming the inherent activity-selectivity trade-off in conventional platinum catalysts. This work not only validates the structural advantages of tri-atomic Pt catalysts in hydrogenation reactions but also provides an innovative, generalizable synthetic paradigm for atomically precise heterogeneous catalysts. This study clarifies the correlation between Pt nuclearity and catalytic hydrogenation performance, and advances the rational design of catalysts for fine chemical synthesis.

**Electronic Supplementary Material:** Supplementary material (Supplementary figures, tables, and experimental details) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909118>.

## Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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measurement.

## Declaration of competing interest

The authors declare no conflicts of interest.

## Author contribution statement

Z. F. Z. and M. L. H.: Experimental design, Data curation, Validation, Writing-manuscript. H. L. J.: Investigation (characterization). Z. Y. W. and M. J. L.: Data curation (DFT calculations), Project administration, Validation, Writing-manuscript. W. B. G.: Data curation (nitrobenzene hydrogenation), Supervision, Validation. R. H. W., X. T. F., and R. J.: Validation. S. J., H. F. J., and Y. Q. Z.: Project administration. S. B. T.: Conceptualization, Project administration, Funding acquisition, Supervision, Writing – review & editing. All the authors have approved the final manuscript.

## Use of AI statement

None.

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## Electronic Supplementary Material

# Tandem synthesis strategy for atomically precise Pt<sub>1</sub>/Pt<sub>2</sub>/Pt<sub>3</sub> catalysts: enhanced nitrobenzene selective hydrogenation via atomic number regulation

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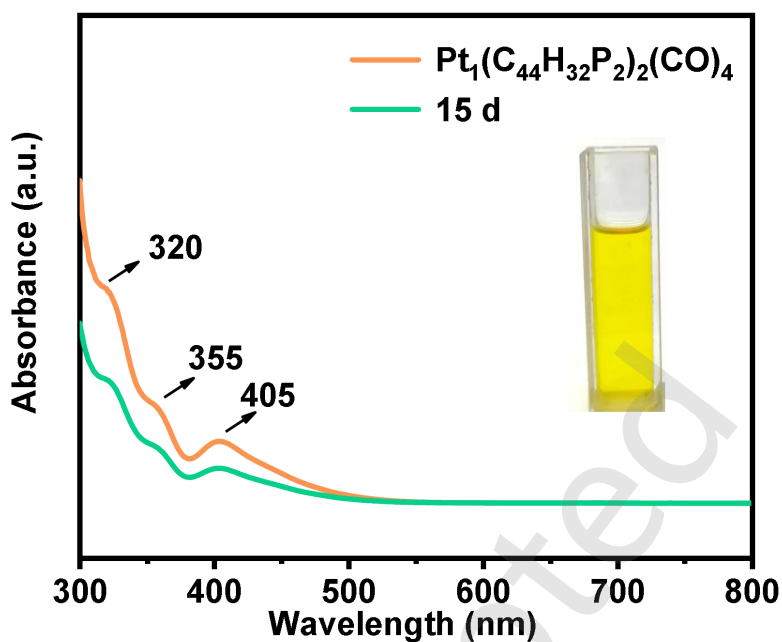
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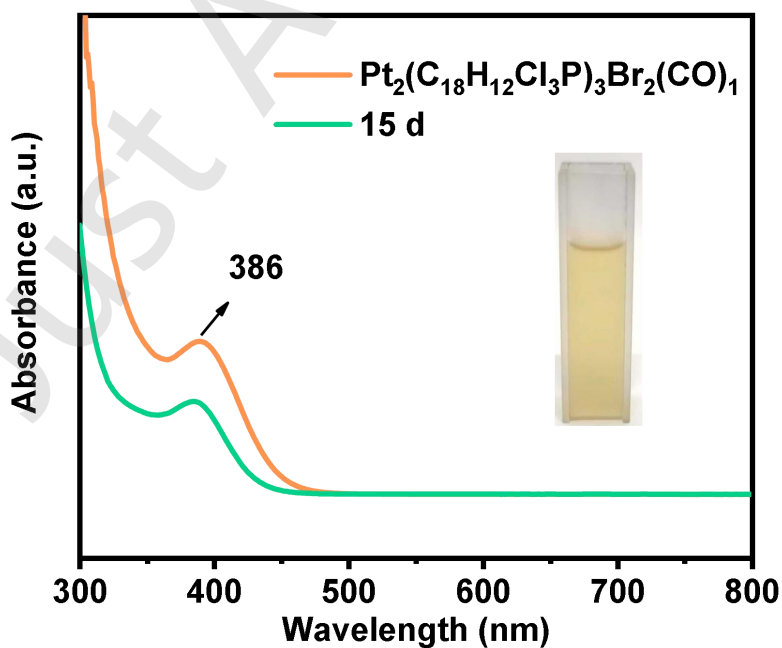
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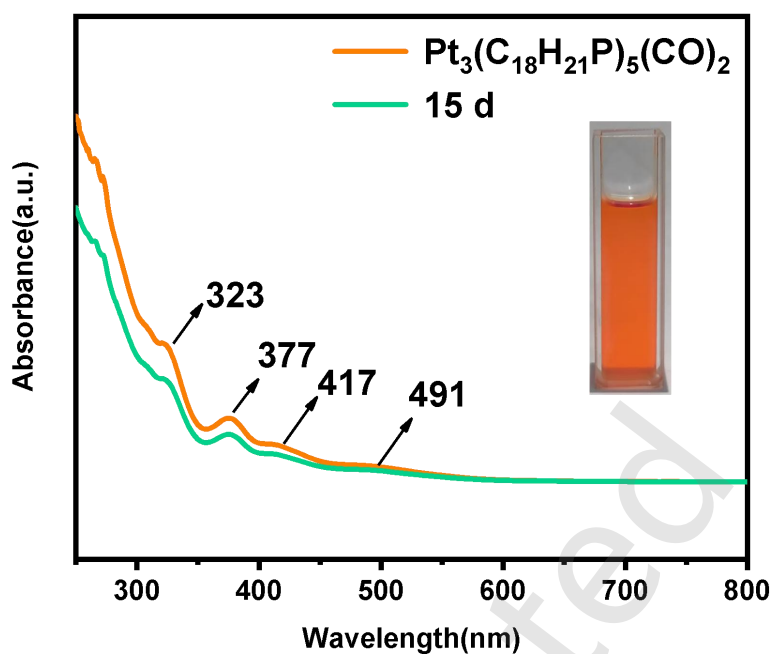
Supporting information to <https://doi.org/10.26599/NR.2026.94909118>



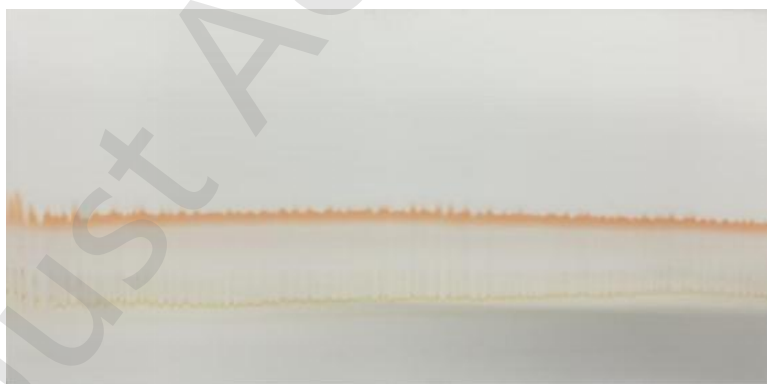
**Figure S1.** UV-vis absorption spectra of the freshly  $\text{Pt}_1$  precursors in DCM and after storage for 15 days at room temperature.(inset: the photograph of  $\text{Pt}_1$  precursors).



**Figure S2.** UV-vis absorption spectra of  $\text{Pt}_2$  precursors in DCM and after storage for 15 days at room temperature.(inset: the photograph of  $\text{Pt}_2$  precursors).



**Figure S3.** UV-vis absorption spectra of  $\text{Pt}_3$  precursors in DCM and after storage for 15 days at room temperature.(inset: the photograph of  $\text{Pt}_3$  precursors).



**Figure S4.** The  $\text{Pt}_3$  nanocluster precursor was purified using thin-layer chromatography (TLC) with a developing solvent of petroleum ether: dichloromethane = 1:1.

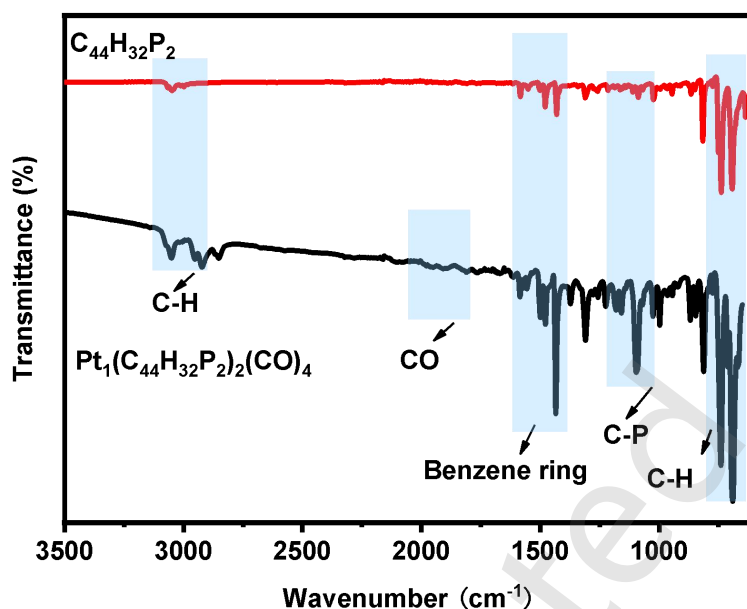


Figure S5. FTIR spectra of the  $Pt_1(C_{44}H_{32}P_2)_2(CO)_4$  precursor and free  $C_{44}H_{32}P_2$  ligand. Major characteristic vibration regions are highlighted in light-blue.

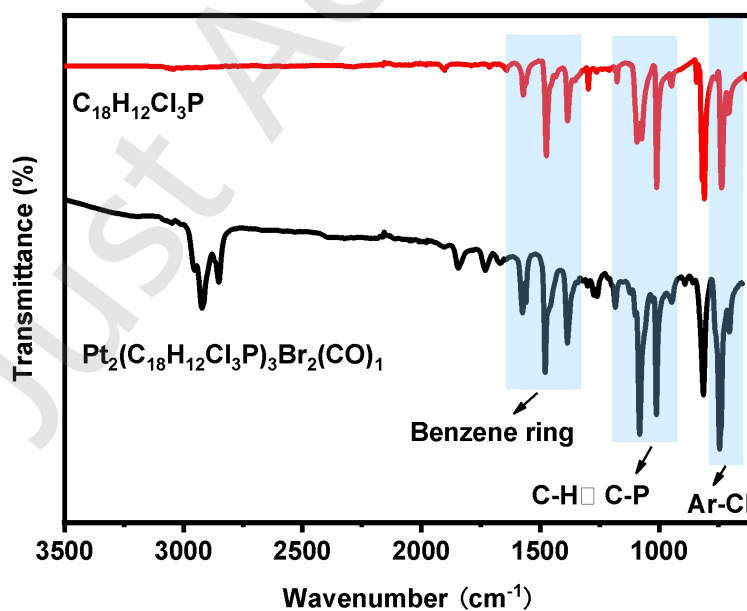


Figure S6. FTIR spectra of the  $Pt_2(C_{18}H_{12}Cl_3P)_3Br_2(CO)_1$  precursor and free  $C_{18}H_{12}Cl_3P$  ligand. Major characteristic vibration regions are highlighted in light-blue.

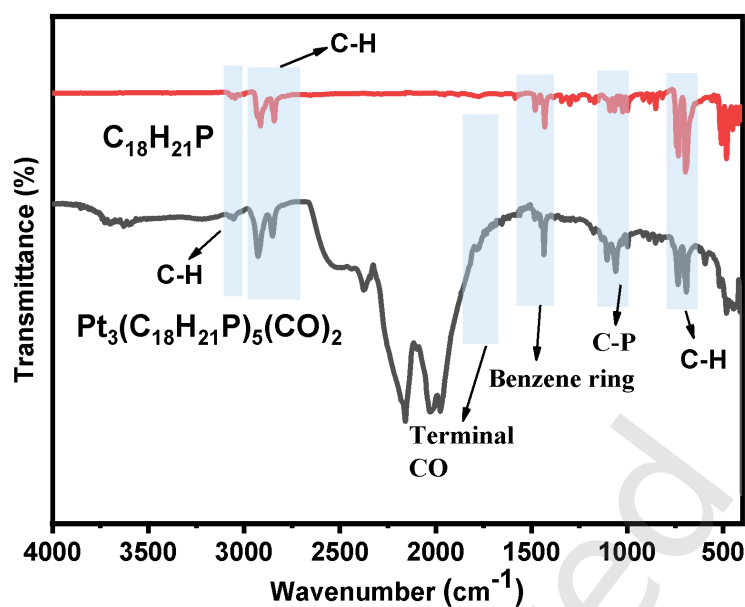


Figure S7. FTIR spectra of the  $\text{Pt}_3(\text{C}_{18}\text{H}_{21}\text{P})_5(\text{CO})_2$  precursor and free  $\text{C}_{18}\text{H}_{21}\text{P}$  ligand. Major characteristic vibration regions are highlighted in light-blue.

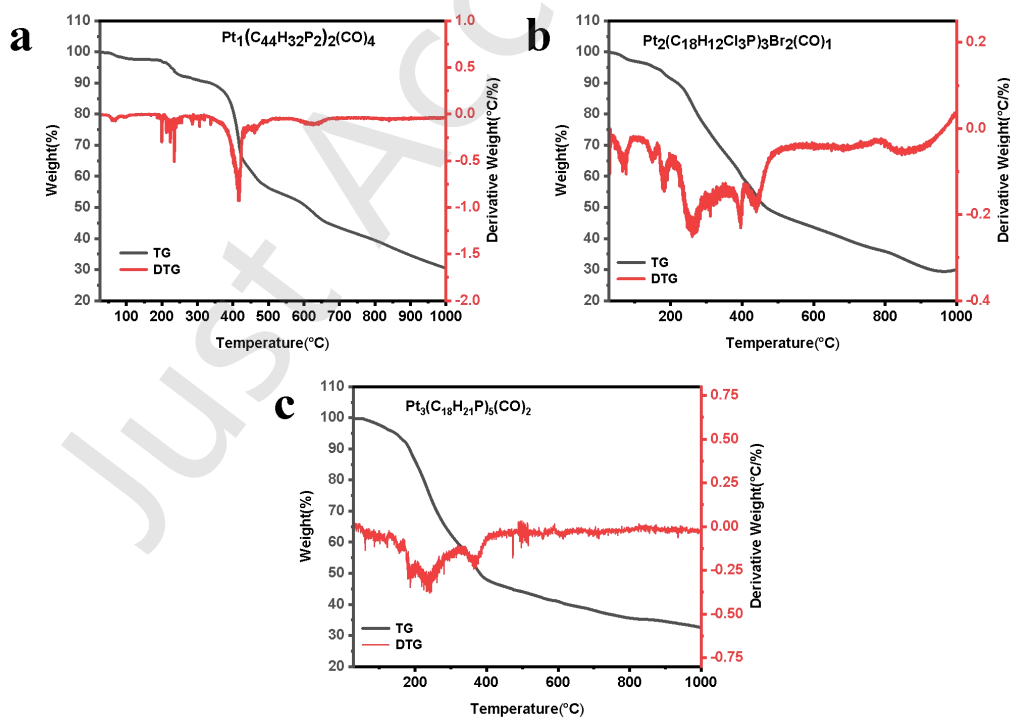


Figure S8. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of (a)  $\text{Pt}_1(\text{C}_{44}\text{H}_{32}\text{P}_2)_2(\text{CO})_4$ , (b)  $\text{Pt}_2(\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P})_3\text{Br}_2(\text{CO})_1$ , and (c)  $\text{Pt}_3(\text{C}_{18}\text{H}_{21}\text{P})_5(\text{CO})_2$  precursors recorded under  $\text{N}_2$  atmosphere.

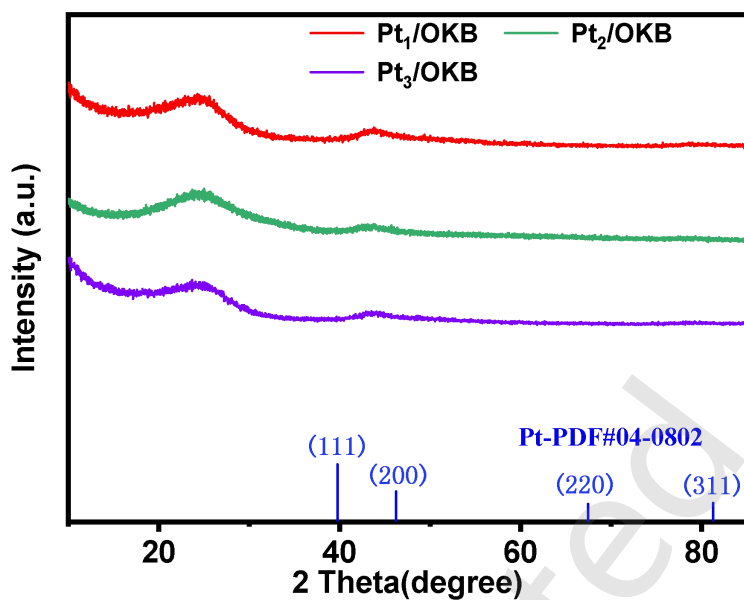


Figure S9. XRD pattern of Pt<sub>1</sub>/OKB, Pt<sub>2</sub>/OKB, Pt<sub>3</sub>/OKB. The blue vertical lines indicate the standard diffraction positions of face-centered cubic Pt, corresponding to the (111), (200), (220), and (311) planes.

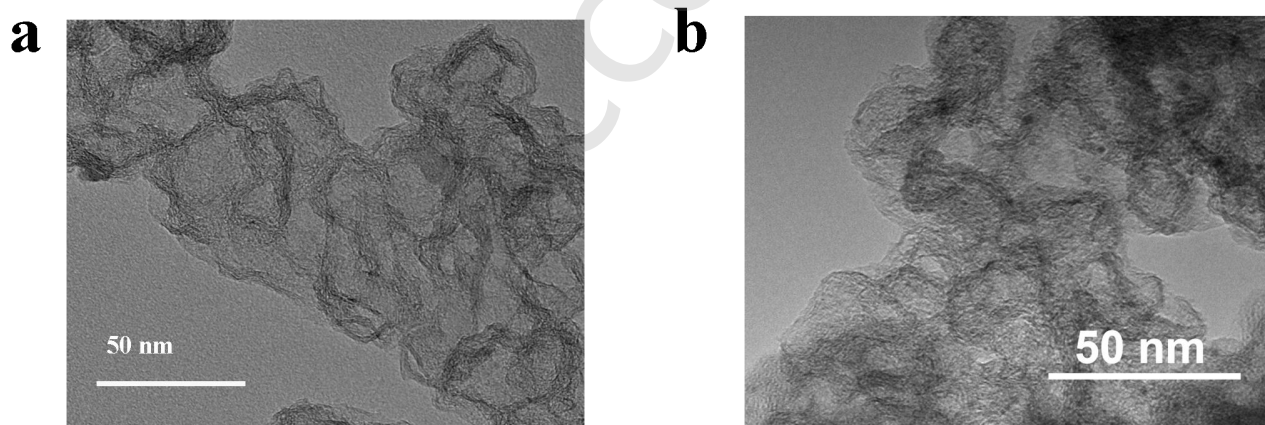


Figure S10. TEM images of (a) Pt<sub>3</sub>/OKB and (b) Pt NPs/OKB.

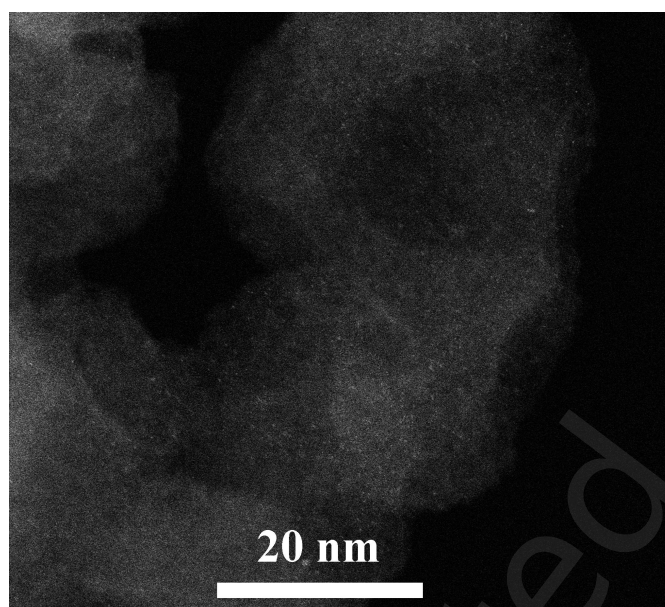


Figure S11. Low-magnification HAADF-STEM images of Pt<sub>3</sub>/OKB.

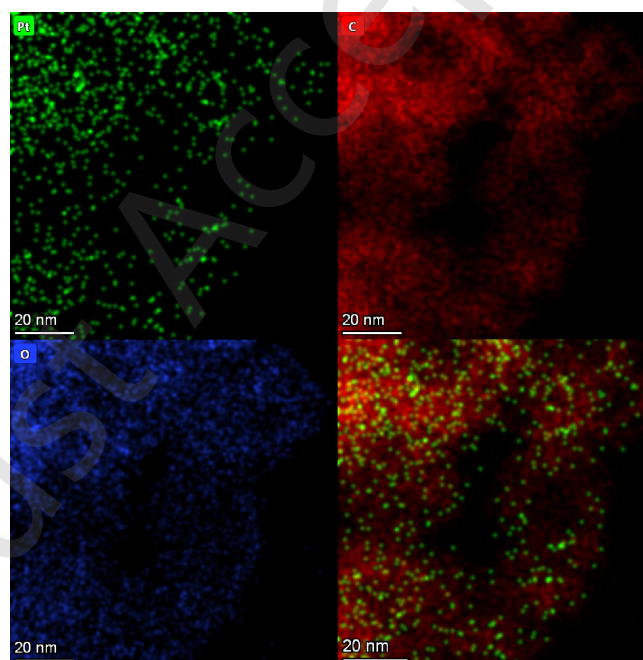


Figure S12. EDS spectrum of Pt<sub>3</sub>/OKB.

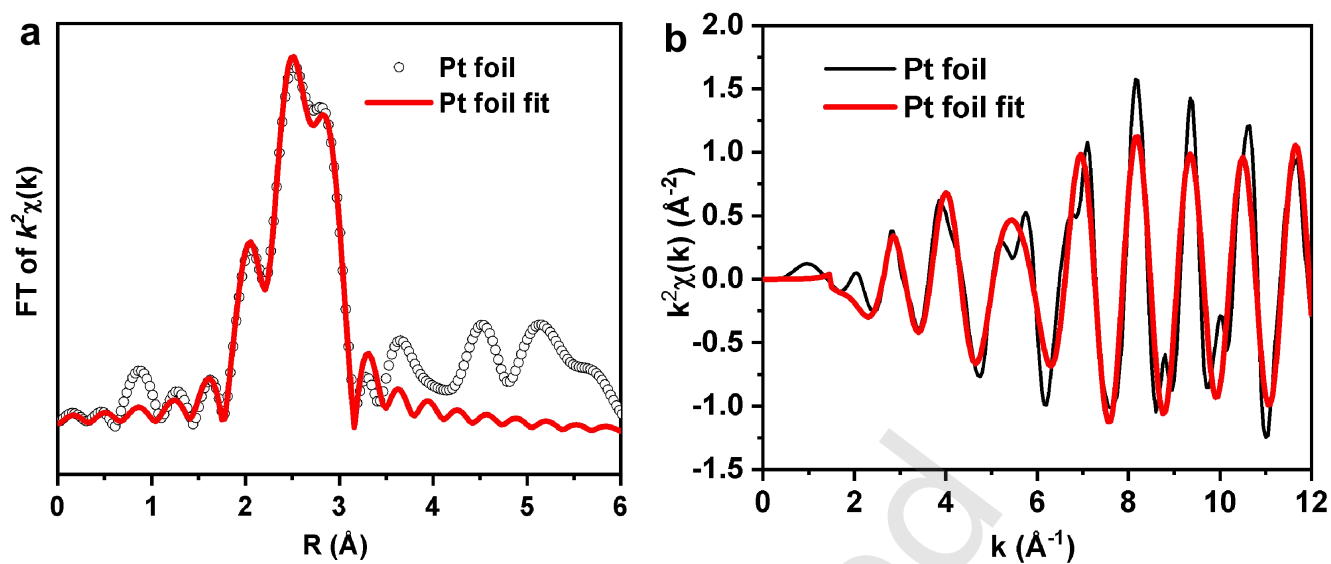


Figure S13. Corresponding EXAFS fitting curves at (a) R-space and (b) k-space of Pt foil.

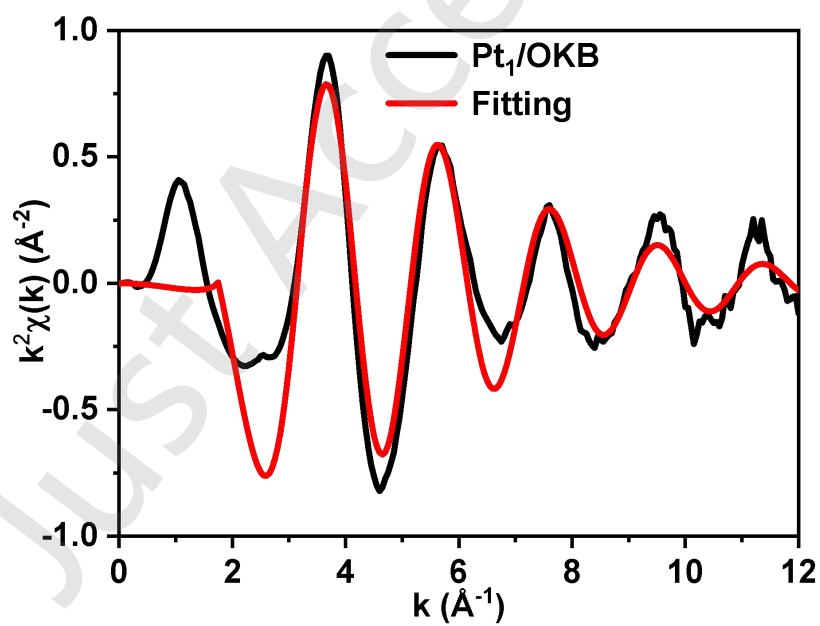
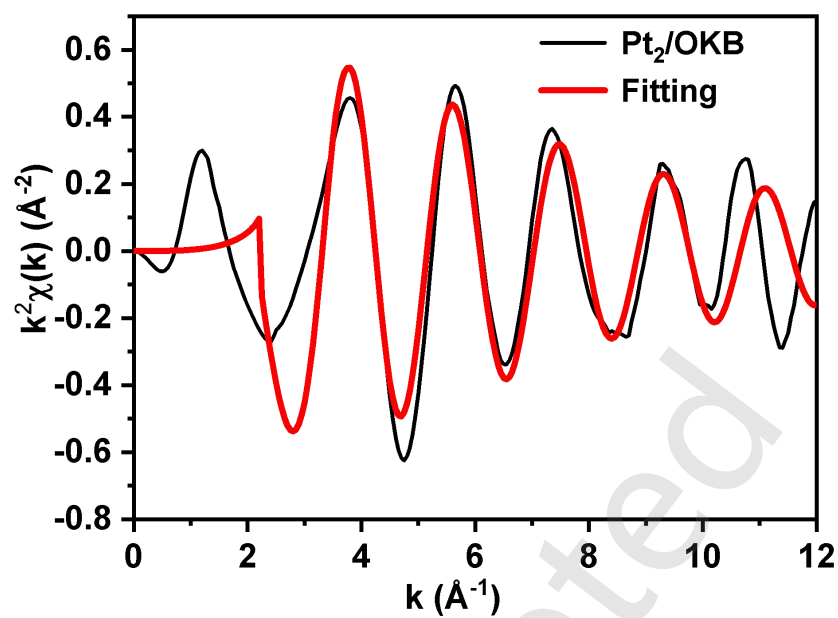
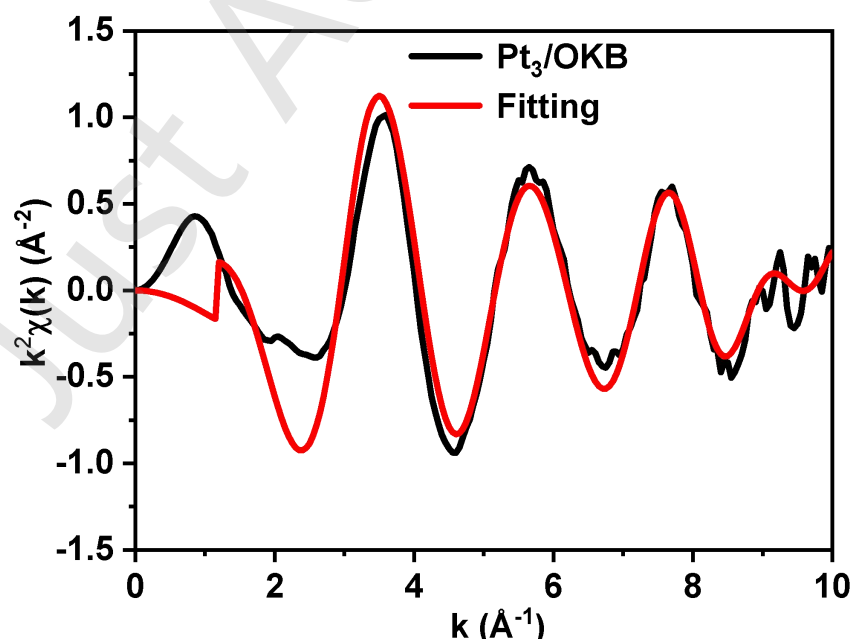


Figure S14. EXAFS spectrum fitting curves of Pt<sub>1</sub>/OKB in k space.

Figure S15. EXAFS spectrum fitting curves of Pt<sub>2</sub>/OKB in k space.Figure S16. EXAFS spectrum fitting curves of Pt<sub>3</sub>/OKB in k space.

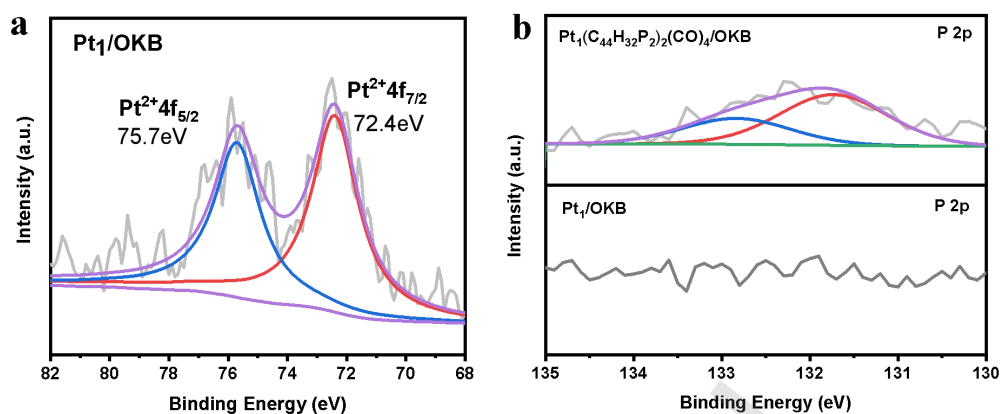


Figure S17. XPS spectra of Pt<sub>1</sub>/OKB before and after Joule heating treatment. (a) Pt 4f spectra of Pt<sub>1</sub>/OKB. (b) P 2p spectra of Pt<sub>1</sub>(C<sub>44</sub>H<sub>32</sub>P<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>/OKB precursor and Pt<sub>1</sub>/OKB after thermal treatment.

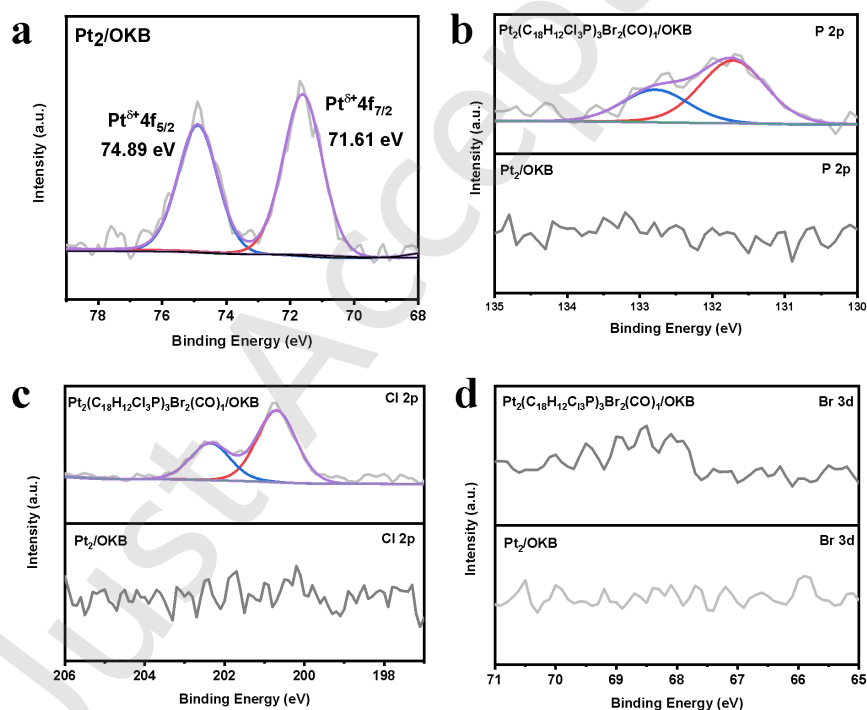
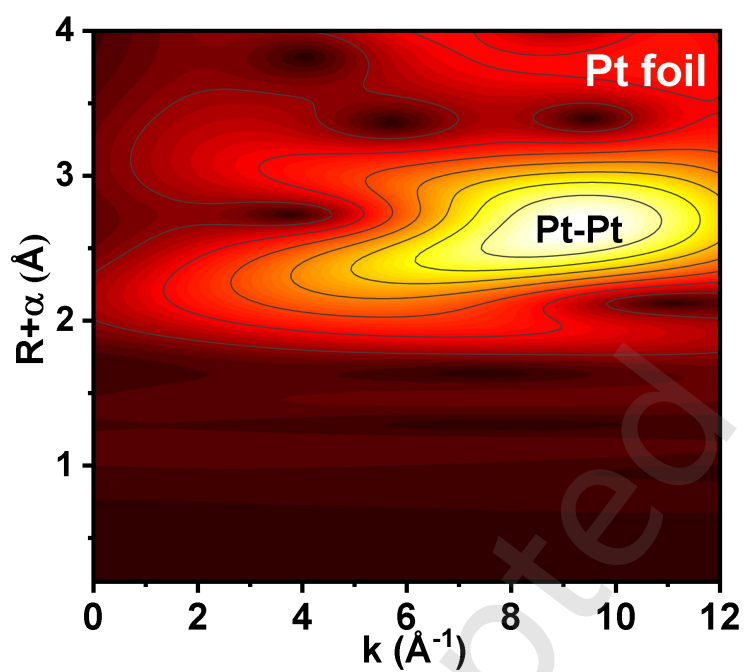
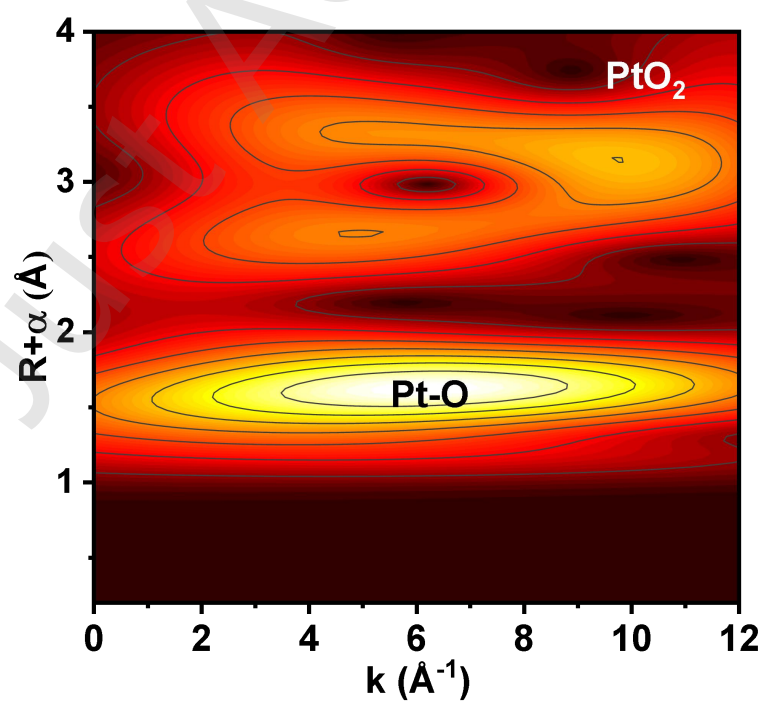


Figure S18. XPS spectra of Pt<sub>2</sub>/OKB before and after Joule heating treatment. (a) Pt 4f spectra of Pt<sub>2</sub>/OKB. (Pt<sup>δ+</sup> < Pt<sup>2+</sup>) (b) P 2p spectra of Pt<sub>2</sub>(C<sub>18</sub>H<sub>12</sub>Cl<sub>3</sub>P)<sub>3</sub>Br<sub>2</sub>(CO)<sub>1</sub>/OKB precursor and Pt<sub>2</sub>/OKB after thermal treatment. (c) Cl 2p spectra of Pt<sub>2</sub>(C<sub>18</sub>H<sub>12</sub>Cl<sub>3</sub>P)<sub>3</sub>Br<sub>2</sub>(CO)<sub>1</sub>/OKB precursor and Pt<sub>2</sub>/OKB after thermal treatment. (d) Br 3d spectra of Pt<sub>2</sub>(C<sub>18</sub>H<sub>12</sub>Cl<sub>3</sub>P)<sub>3</sub>Br<sub>2</sub>(CO)<sub>1</sub>/OKB precursor and Pt<sub>2</sub>/OKB after thermal treatment.

Figure S19. WT of the Pt L<sub>3</sub>-edge EXAFS spectra for Pt foil.Figure S20. WT of the Pt L<sub>3</sub>-edge EXAFS spectra for PtO<sub>2</sub>.

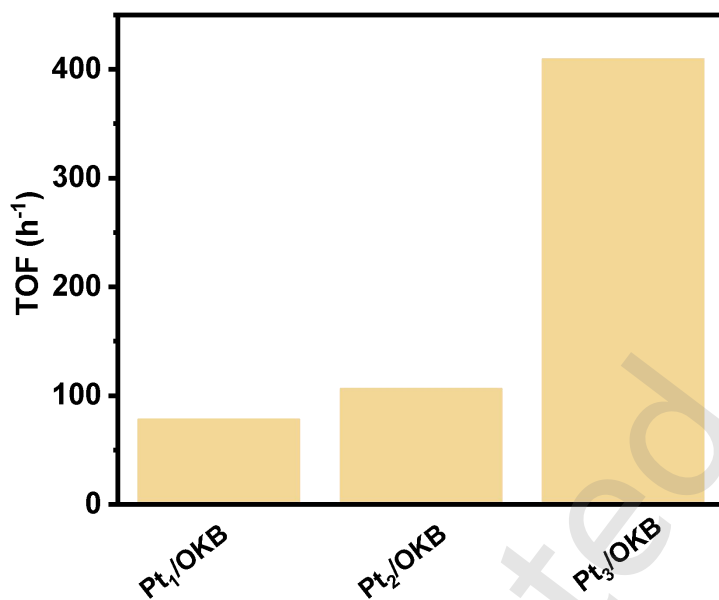


Figure S21. Comparison of TOF values for  $\text{Pt}_1/\text{OKB}$ ,  $\text{Pt}_2/\text{OKB}$  and  $\text{Pt}_3/\text{OKB}$  in nitrobenzene hydrogenation.

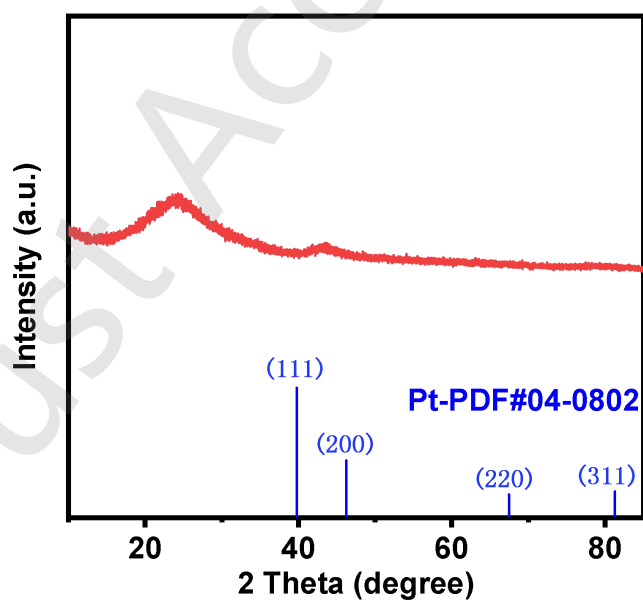


Figure S22. XRD of  $\text{Pt}_3/\text{OKB}$  after the reaction. The blue vertical lines indicate the standard diffraction positions of face-centered cubic Pt, corresponding to the (111), (200), (220), and (311) planes.

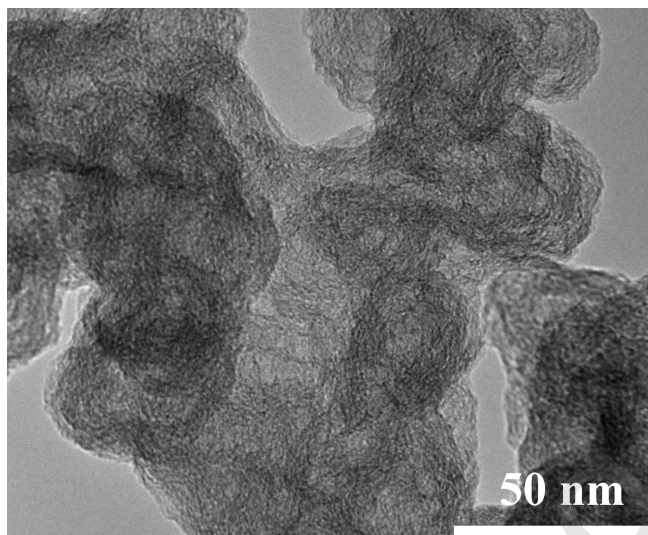


Figure S23. TEM image of Pt<sub>3</sub>/OKB sample after catalytic reaction.

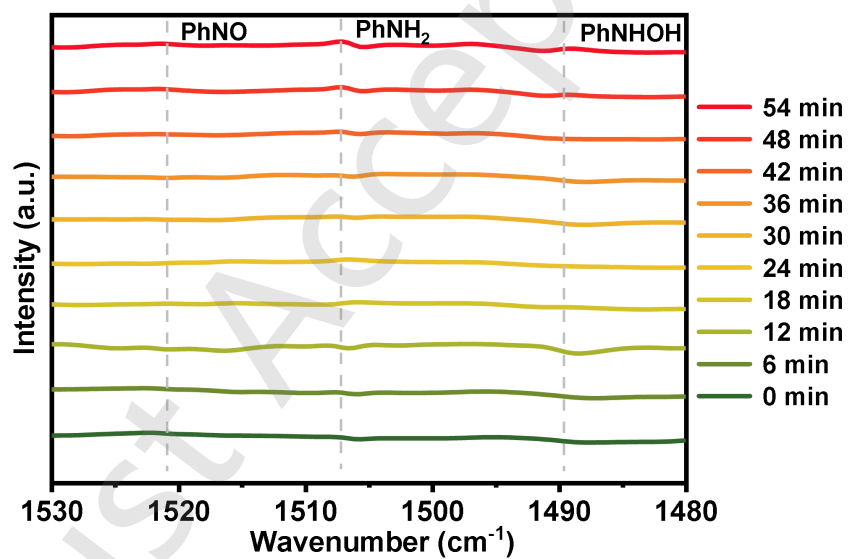


Figure S24. In situ infrared signals of intermediates and products at different times for Pt<sub>1</sub>/OKB.

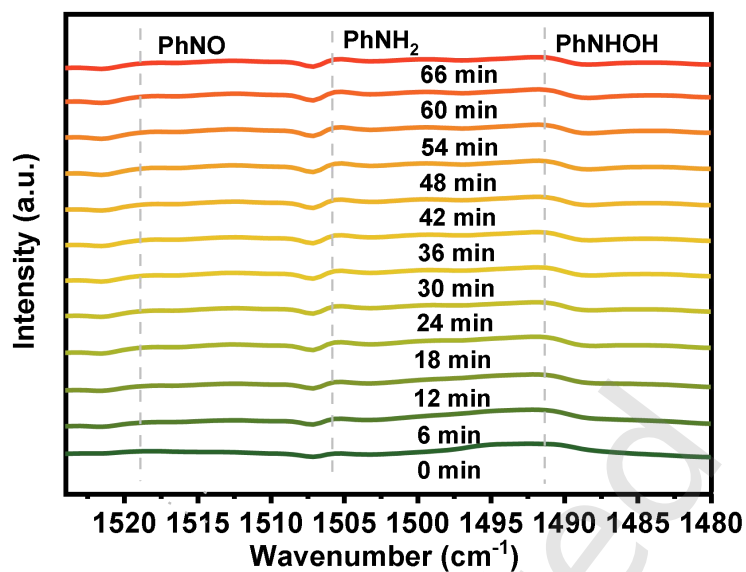


Figure S25. In situ infrared signals of intermediates and products at different times for  $\text{Pt}_2/\text{OKB}$ .

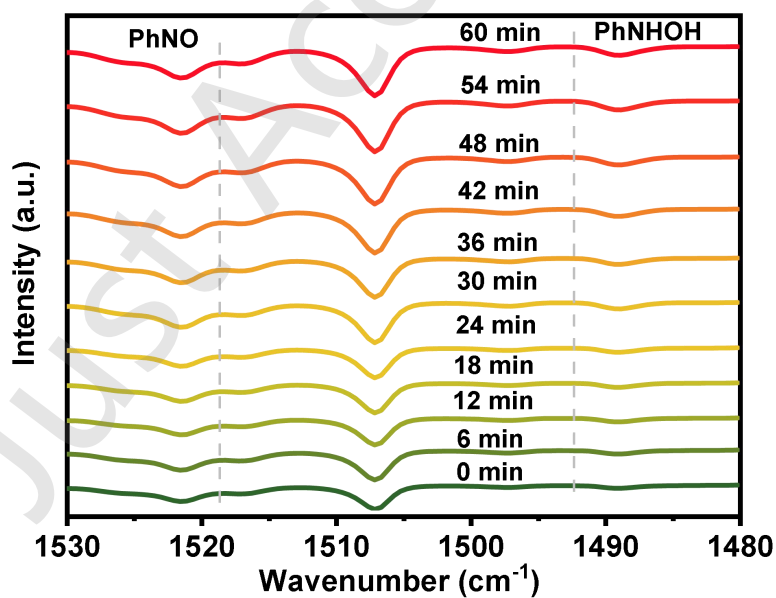


Figure S26. In situ infrared signals of intermediates and products at different times for  $\text{Pt NPs}/\text{OKB}$ .

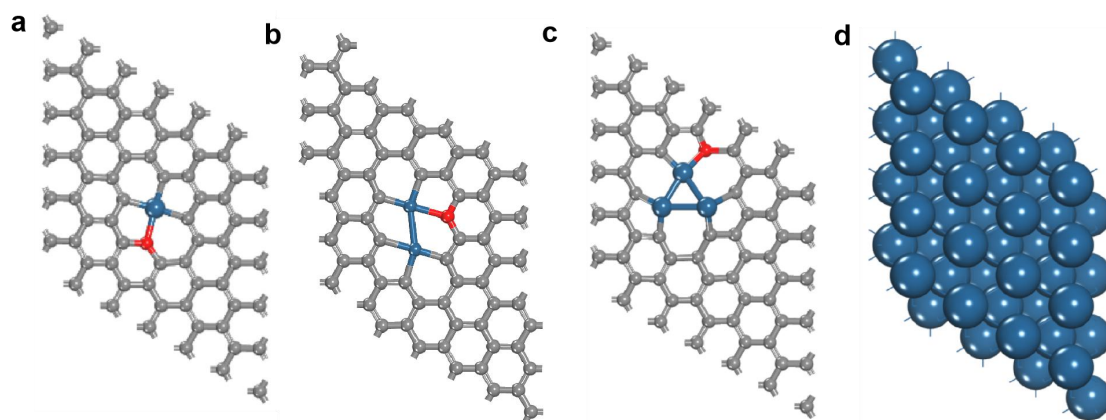


Figure S27. a)  $\text{Pt}_1/\text{OKB}$ , b)  $\text{Pt}_2/\text{OKB}$ , c)  $\text{Pt}_3/\text{OKB}$  and d) (111) surface of Pt NPs/OKB catalytic models. The red, gray, and blue spheres represent oxygen, carbon, and platinum atoms, respectively.

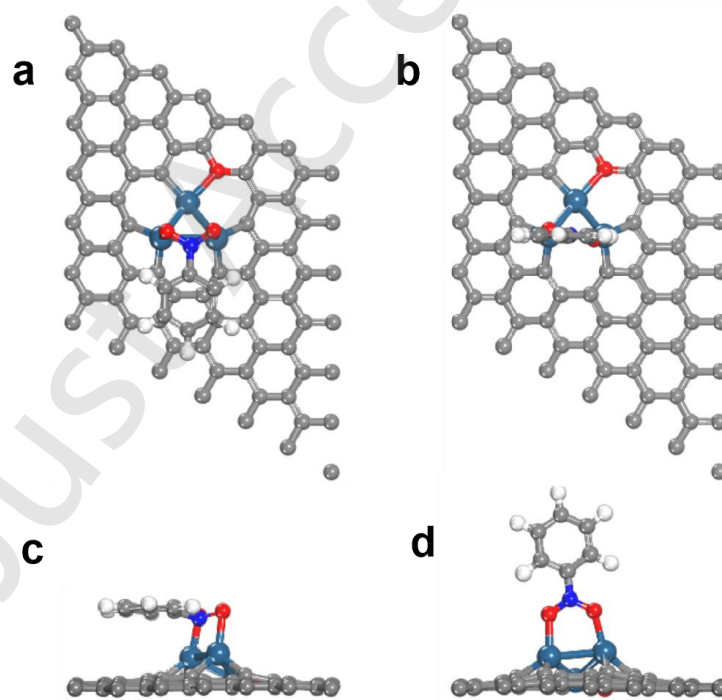


Figure S28. a) and b) illustrate two adsorption modes of nitrobenzene on  $\text{Pt}_3/\text{OKB}$ , while c) and d) show corresponding localized magnifications of these modes.

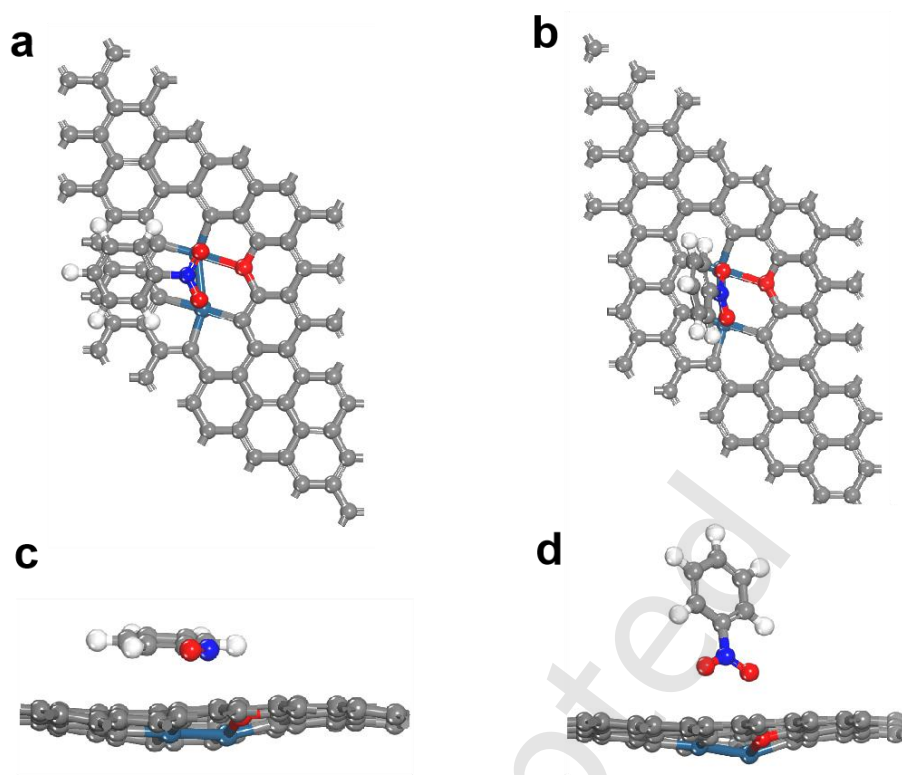


Figure S29. a) and b) illustrate two adsorption modes of nitrobenzene on Pt<sub>2</sub>/OKB, while c) and d) show corresponding localized magnifications of these modes.

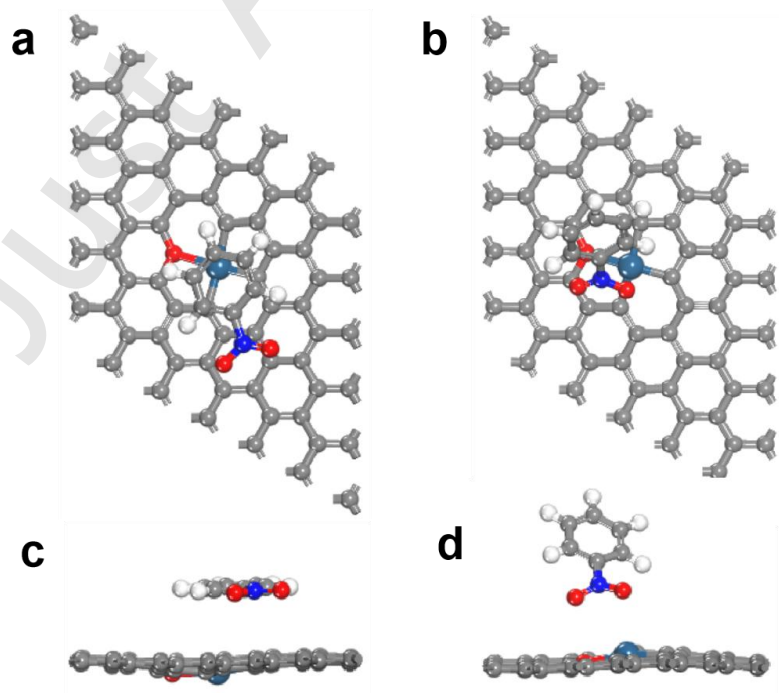


Figure S30. a) and b) illustrate two adsorption modes of nitrobenzene on Pt<sub>1</sub>/OKB, while c) and d) show corresponding localized magnifications of these modes.

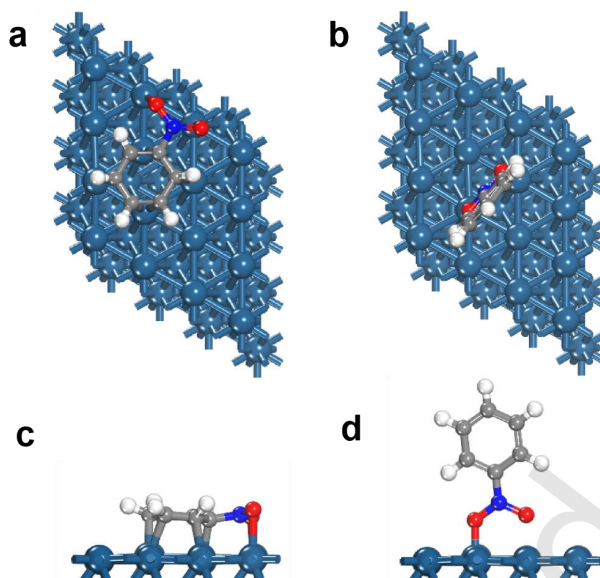


Figure S31. a) and b) illustrate two adsorption modes of nitrobenzene on (111) surface of Pt NPs/OKB, while c) and d) show corresponding localized magnifications of these modes.

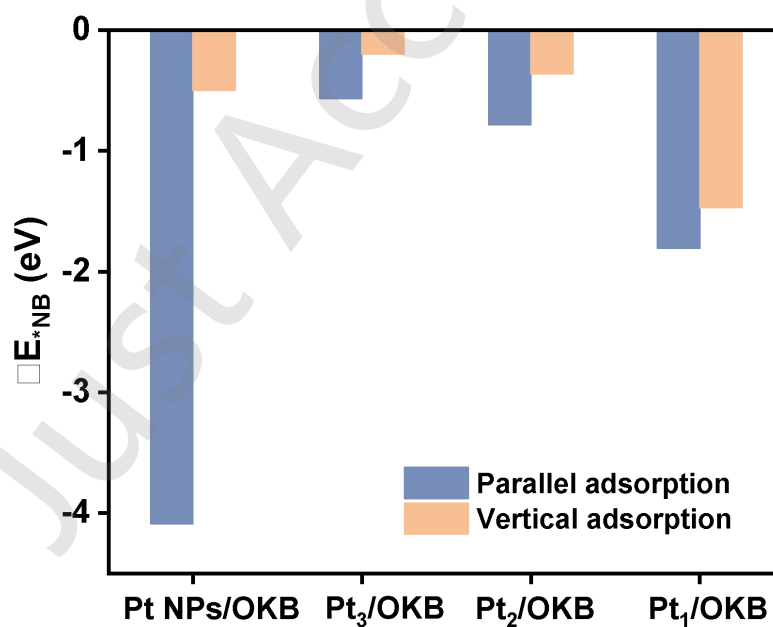


Figure S32. Adsorption energy of two configurations of different catalysts.

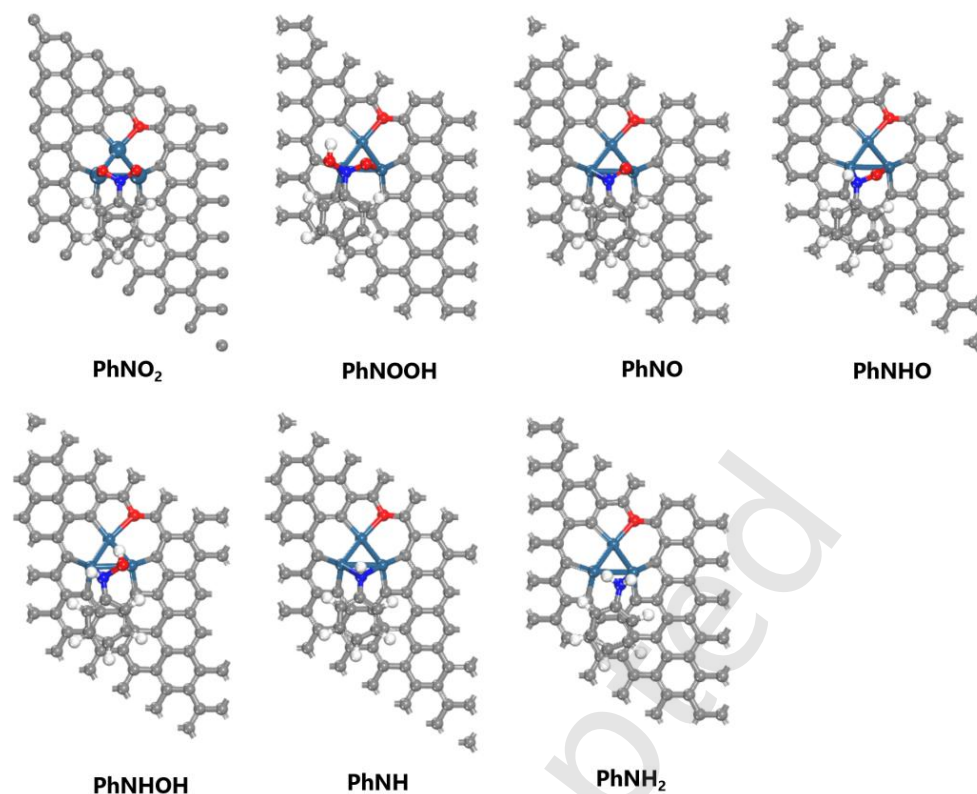


Figure S33. Mechanism of nitrobenzene hydrogenation in Pt<sub>3</sub>/OKB under parallel adsorption configuration.

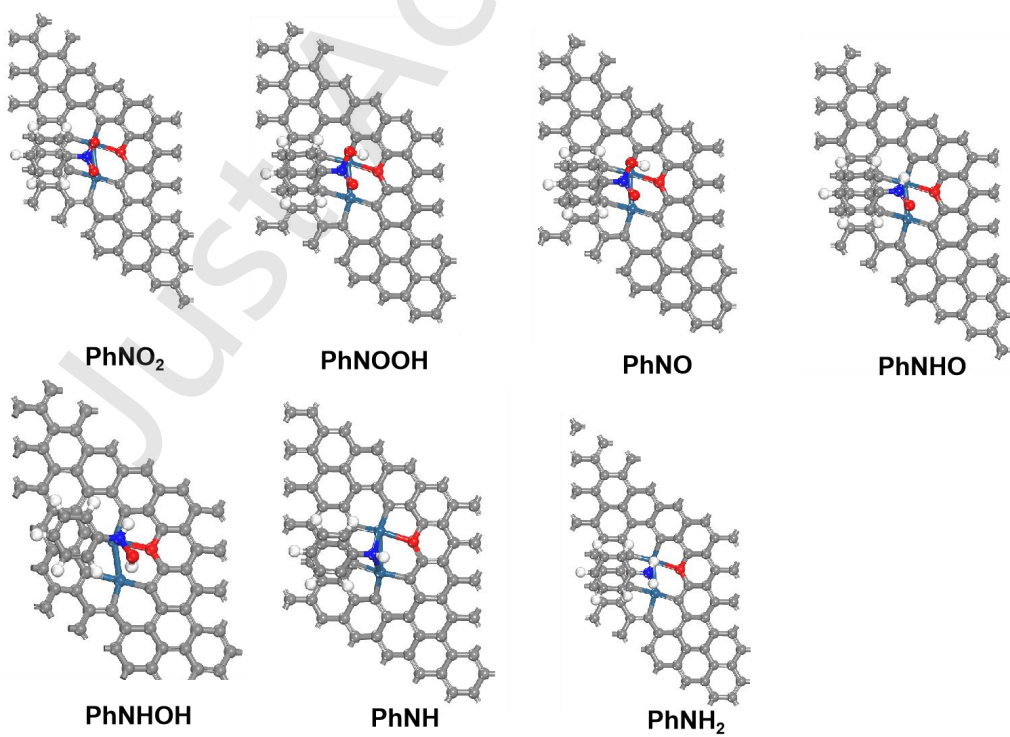


Figure S34. Mechanism of nitrobenzene hydrogenation in Pt<sub>2</sub>/OKB under parallel adsorption configuration.

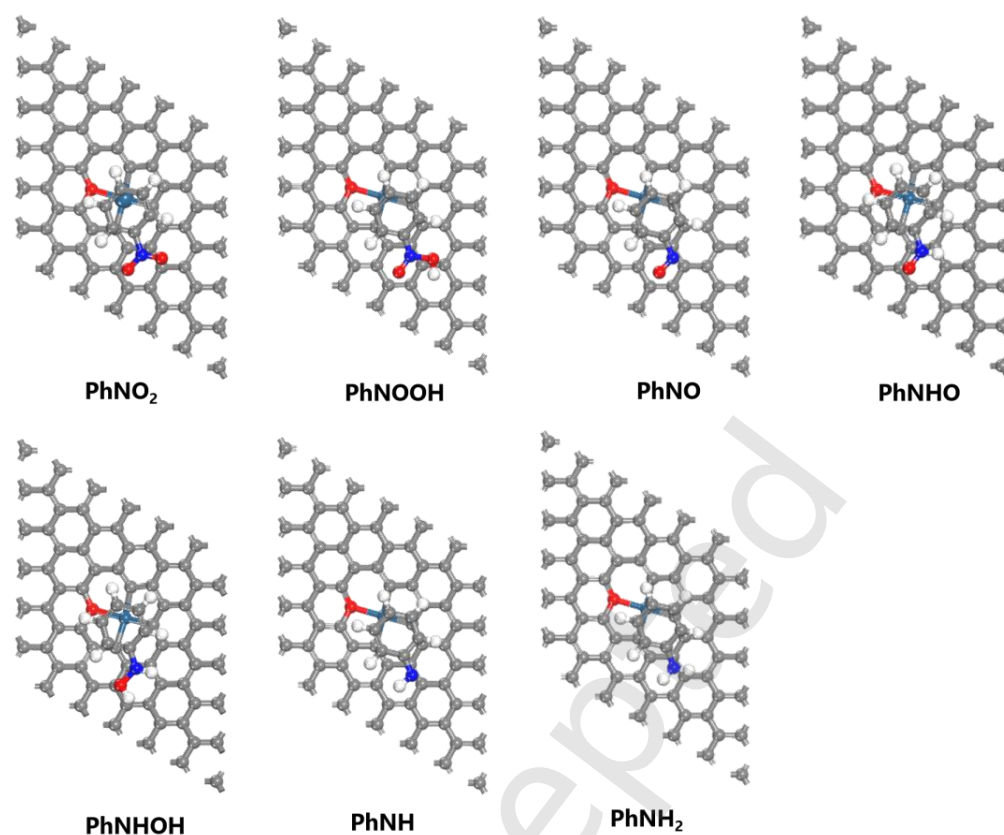


Figure S35. Mechanism of nitrobenzene hydrogenation in Pt<sub>1</sub>/OKB under parallel adsorption configuration.

Table S1. EXAFS fitting parameters at the Pt L-edge various samples ( $S_0^2=0.76$ )

| samples              | path   | C. N. <sup>[a]</sup> | R (Å) <sup>[b]</sup> | $\sigma^2 (\times 10^{-3} \text{ Å}^2)$<br><sup>[c]</sup> | $\Delta E$ (eV) <sup>[d]</sup> | R factor <sup>[e]</sup> |
|----------------------|--------|----------------------|----------------------|-----------------------------------------------------------|--------------------------------|-------------------------|
| Pt foil              | Pt-Pt  | 12*                  | 2.76±0.01            | 4.0±0.4                                                   | 7.7±0.5                        | 0.01                    |
| Pt <sub>1</sub> /OKB | Pt-C/O | 3.6±0.5              | 2.00±0.01            | 6.5±2.0                                                   | 6.0±0.8                        | 0.02                    |
| Pt <sub>2</sub> /OKB | Pt-C/O | 3.1±0.5              | 2.04±0.02            | 1.8±0.8                                                   | 8.9±0.9                        | 0.01                    |
|                      | Pt-Pt  | 0.8±0.3              | 2.78±0.03            | 8.6±1.7                                                   |                                |                         |
| Pt <sub>3</sub> /OKB | Pt-C/O | 2.4±0.4              | 1.99±0.02            | 8.5±2.1                                                   | 1.3±1.8                        | 0.02                    |
|                      | Pt-Pt  | 1.7±0.3              | 2.61±0.02            | 4.3±3.8                                                   |                                |                         |

<sup>a</sup>C. N.: coordination numbers;<sup>b</sup>R: bond distance;<sup>c</sup> $\sigma^2$ : Debye-Waller factors;<sup>d</sup> $\Delta E_0$ : the inner potential correction.<sup>e</sup>R factor: goodness of fit.

\*The experimental EXAFS fit by fixing C. N. as the known crystallographic value.

Table S2. Comparison of hydrogenation catalytic performance of nitroaromatics with Pt<sub>3</sub>/OKB and loaded metal catalysts.

| Catalyst                                                        | Temp.<br>(°C) | P<br>(MPa) | Conv.<br>(%) | Sel.<br>(%) | Substrate            |
|-----------------------------------------------------------------|---------------|------------|--------------|-------------|----------------------|
| Pt <sub>3</sub> /OKB                                            | 60            | 0.5        | >99          | >99         | nitrobenzene         |
| Pt <sub>3</sub> /OKB                                            | 60            | 0.5        | >99          | >99         | p-chloronitrobenzene |
| Pt <sub>3</sub> /OKB                                            | 60            | 0.5        | >99          | >99         | o-chloronitrobenzene |
| Pt <sub>2</sub> /mpg-C <sub>3</sub> N <sub>4</sub> <sup>1</sup> | 100           | 1          | 100          | >99         | nitrobenzene         |
| Pt <sub>1</sub> -Fe <sub>1</sub> /ND <sup>2</sup>               | 80            | 1          | 100          | 100         | p-chloronitrobenzene |
| Pt <sub>1</sub> /TiO <sub>2</sub> -600 <sup>3</sup>             | 80            | 1.5        | >99          | 99          | p-chloronitrobenzene |
| Pt@COF-V <sub>0.5</sub> <sup>4</sup>                            | 80            | 1.5        | >99          | >99         | p-chloronitrobenzene |
| PCN-221@Pt@PCN-221(Co) <sup>15,15</sup>                         | 80            | 1          | >99          | >99         | p-chloronitrobenzene |
| Pt@Y <sup>6</sup>                                               | 100           | 2          | 100          | >99         | o-chloronitrobenzene |
| Pt/CeO <sub>2</sub> -R-300 <sup>7</sup>                         | 25            | 1          | 100          | 65.7        | nitrobenzene         |
| Pd@Beta <sup>8</sup>                                            | 110           | 1          | 100          | 90          | p-chloronitrobenzene |
| Pd@MIL-101-F3 <sup>9</sup>                                      | 90            | 0.8        | 100          | 97          | o-chloronitrobenzene |
| Pd/SCS <sub>2</sub> <sup>10</sup>                               | 110           | 2.2        | 100          | 98.6        | o-chloronitrobenzene |
| Pd/MoS <sub>2</sub> <sup>11</sup>                               | 80            | 4          | 100          | >99         | nitrobenzene         |
| Co <sub>1</sub> @NC-(SBA) <sup>12</sup>                         | 90            | 1          | 99           | 99          | nitrobenzene         |
| Co <sub>1</sub> /NPC <sup>13</sup>                              | 110           | 3          | 100          | 100         | nitrobenzene         |
| Fe-P900-PCC <sup>14</sup>                                       | 100           | 4          | >99          | 98          | nitrobenzene         |
| Co-N <sub>x</sub> /C-800-AT <sup>15</sup>                       | 110           | 0.35       | 100          | 99          | nitrobenzene         |
| Co SAs/NC-800 <sup>16</sup>                                     | 120           | 3          | 100          | 99.8        | nitrobenzene         |
| Co@CN@HBM <sup>17</sup>                                         | 100           | 2          | 99.3         | 100         | nitrobenzene         |
| Co/C-PAQ <sup>18</sup>                                          | 80            | 1          | >99          | >99         | nitrobenzene         |
| Co <sub>1</sub> -N/P-C <sup>19</sup>                            | 100           | 2          | >99          | >99         | nitrobenzene         |
| Co-900 <sup>20</sup>                                            | 25            | 2          | 100          | 100         | p-chloronitrobenzene |
| Co-N <sub>4</sub> P <sub>1</sub> <sup>21</sup>                  | 80            | 0.5        | 83.2         | >99         | p-chloronitrobenzene |

Table S3. Changes in the free energy of benzene ring activation for different catalysts.

| Catalyst             | $\Delta G/\text{eV}$ |
|----------------------|----------------------|
| Pt <sub>1</sub> /OKB | 0.42                 |
| Pt <sub>2</sub> /OKB | 0.67                 |
| Pt <sub>3</sub> /OKB | -0.28                |

Just Accepted

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