Crystal shape controlled H$_2$ storage rate in nanoporous carbon composite with ultra-fine Pt nanoparticle

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This study demonstrates that the hydrogen storage rate (HSR) of nanoporous carbon supported platinum nanocatalysts (NC) is determined by their heterojunction and geometric configurations. The present NC is synthesized in an average particle size of ~1.5 nm by incipient wetness impregnation of Pt$^{4+}$ on carbon support followed by annealing in H$_2$ ambient at 102–105 °C. Among the steps in hydrogen storage, decomposition of H$_2$ molecule into 2 H atoms on Pt NC surface is the deciding factor in HSR that is controlled by the thickness of Pt NC. For the best condition, HSR of Pt NC in 1–2 atomic layers thick (4.7 μg/g min) is 2.6 times faster than that (1.3 μg/g min) of Pt NC with higher than 3 atomic layers thick.

Hydrogen is one of the most effective energy forms in terms of power density and conversion efficiency for keeping human civilization sustainable. However, in current development of technologies, the capacity of hydrogen storage is often too low to be used as a daily energy supply, except for carbon supported Pt nanocatalyst (NC). This material has been classified as a potential means to the on-board hydrogen storage material according to the Department of Energy (DOE), U.S.A. The hydrogen storage capacity of this material is influenced by chemical and physical properties in both carbon support (defect density, ligand identity, porosity) and the supported NC (composition, shape, and configuration). Among existing pathways, the spillover is considered to be a predominant mechanism in decomposition and subsequent storage of hydrogen in the interfaces of Pt NC$^{1,2}$. Although many studies and applications have been devoted to spillover mechanism, the difficulty to reproduce the earlier results indicates that gaps between experiment and fundamental theory in heterogeneous catalysis still exist$^{3–5}$.

Our previous work adopted inelastic neutron scattering analysis to reveal the fundamental pathways for H$_2$ storage on Pt NC$^{6–8}$. On Pt NC surface, hydrogen molecules are dissociated into hydrogen atoms that are either bound to neighboring defect sites or trapped by pi-electron resonance on surface of the nanoporous carbon. A complementary XPS analysis shows that formation of C-H bonds results in 1.2–1.5% mass fraction of hydrogen storage on Pt decorated single walled carbon nanotube$^9$.

Although the spillover pathways are getting clear, little is known about the impacts of geometric configuration of nanoporous carbon supported Pt clusters on H$_2$ storage rate (HSR)/capacity. To elucidate the effects of crystal shape on HSR of Pt/AC, this study employs several methods, including small angle X-ray scattering (SAXS), X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), and density functional theory calculation (DFT). Our finding shows that the rate of H$_2$ decomposition is controlled by the crystal thickness of carbon supported Pt NC. For the best condition, HSR of Pt NC in 1–2 atomic layers thick (4.7 μg/g min) is 2.6 times faster than...
that (1.3 μg/g min) of Pt NC with higher than 3 atomic layers thick. Details of configuration and surface energy determination in relation to the HSR of Pt/AC are given in the following sections.

Results

From theoretical geometrical calculation, surface-to-bulk ratio of NC with a known size is proportional to the crystal shape. The step-by-step strategy for determining the impacts of crystal shape on HSR of Pt NC is (1) XRD and SAXS analyses on the coherent length and geometrical asymmetry of NC in carbon support, (2) surface-to-bulk ratio determination by cross-referencing results of XAS and geometrical calculation, and finally (3) adsorption energy calculation on Pt-H bondings at Pt NC with thickness determined by structure characterizations.

Crystal structure and nanostructure of active carbon supported Pt nanocatalyst (Pt NC).

Crystal structure of Pt/AC and carbon support are revealed by using XRD analysis. Figure 1 demonstrates the XRD pattern of INER_A (1a) and INER_B (1b) before and after conducting the H_2 purged High-pressure Thermogravimetric analyzer (HP-TGA). As indicated in Fig. 1, peak D is the characteristic line of (002) facet for active carbon (AC) while peak X represents the lines of (111)/(220) facets for metallic Pt and (110) facet for PtO (or (002) facet for PtO_2). For freshly prepared NC, the average coherent length (h_{avg}) of metallic phase at Pt (111)/(200) facets is 9.2/10.2 Å for INER_A and 11.1/11.2 Å for INER_B. After HP_TGA treatment, h_{avg} of Pt(111)/Pt(200) in INER_A is decreased/increased by 17.4%/11.8%. In INER_B, h_{avg} of Pt(111)/Pt(200) is increased by 8.1/9.8% after exposed to the same treatment. In this condition, h_{avg} of Pt metal oxide phase is decreased by 9.0% in INER_A and is increased by 10.7% in INER_B.

Average particle size (D_{avg}), particle size distribution (P_R), and particle shape of Pt NC are characterized by SAXS analysis. In general, features of SAXS spectra result from the interference between incident X-ray and both inter-particle (Q < 0.07 Å^{-1}) and intra-particle (Q > 0.07 Å^{-1}) structures. Inter-particle structure that is also called structure factor (S(Q)) include inter-particle distance as well as the size and packing density of inter-particle agglomerates. Known as form factor (P(Q)), intra-particle structure consists of the shape, dimension, and configuration of NC. This study only focuses on the discussions related to P(Q) of SAXS spectra because of the dominant role of intra-particle structures in H_2 decomposition activity of NC. Figure 2a compares the SAXS spectra of the experimental Pt/AC with least-square fitting curves calculated by the model of polydispersed spheres with bimodal Schulz distribution (ESI); where background scattering of pure AC powder was subtracted for extracting the contribution of metallic NCs. In the low q range, the scattering hump at q_i with a width (W_i) and a height (H_i) results from scattering interferences of among X-ray and intra-particle structures of NC. The ratio of W_i/H_i is proportional to surface roughness and polydispersity (P) of NC; subscripts A and B denote respectively parameters of INER_A and INER_B.

In INER_A spectrum, as compared to that of INER_B, shift of oscillation hump (from q_B to q_A) to low q and reduction of W_i/H_i ratio indicate a larger geometrical asymmetry of NC. Figure 2b shows particle size distribution (Schulz distribution) of experimental Pt NCs. Accordingly, the average radius of both INER_A and INER_B is ~6.9 Å (i.e., D_{avg} ~ 14 Å). Compared to P_B, a broadened P_A (~35.2%) with an asymmetrical profile (tailing to high R region) implies a high aspect ratio of NC in INER_A.
Chemical composition and surface oxidation ratio of Pt NC affected by pre-metal doping treatment on active carbon support. Figure 3a compares Pt L$_3$-edge X-ray absorption near-edge spectra (XANES) of experimental Pt NCs and standard samples (CNT supported Pt NC and Pt foil). In a L$_3$-edge spectrum, the inflection point position (i.e., 1$^{\text{st}}$ deviation maximum ($E_0$) at arrow X of XANES spectra in Fig. S1) refers to the minimum energy of photoelectron for initiating electron transitions from 2p$_{3/2}$ to 5d$_{5/2}$ orbitals. Intensity ($h_B$) and width ($W$) of near-edge absorption peak (arrow B) denote respectively the 2p$_{3/2}$ to 5d$_{5/2}$ transition probability and band width of 5d orbital of Pt atoms. As depicted in Fig. 3a, the strongest $h_B$ shows the highest p-d transition of Pt atoms in INER_A among all the samples. In the meantime, flattened post-edge hump (i.e. $h_C/W_C$ ratio) refers to local disordering of severe Pt oxidation in INER_A. On the other hand, in INER_B, a significantly decreased $h_B$ accounts for the presence of metallic Pt clusters. Chemical composition of experimental Pt NCs is further illustrated by linear combination fitting (LCF) method. As shown in Table 2, Pt oxide (PtO and PtO$_2$) ratio is 79.7% in INER_A and 42.9% in INER_B.

Figure 3b compares Fourier transformed EXAFS spectra (i.e., radial functions) of experimental Pt NCs and CNT supported Pt. Accordingly, Pt oxide and metal characters are evident in INER_B as revealed respectively by...
the radial peak ranging from 1.0 to 1.75 Å (Pt-O bond pair) and that from 2.2 to 3.15 Å (Pt–Pt bond pair). The results of model analysis (Table 3) show that the coordination number (CN) of Pt oxide (Pt-O, CN \( \text{Pt-O} \)) is 1.31 (\( R_{\text{Pt-O}} = 1.922 \) Å) and that of metallic Pt-Pt bond (CN \( \text{Pt-Pt} \)) is 2.01 (\( R_{\text{Pt-Pt}} = 2.754 \) Å). In INER_A, peak A results from the X-ray interference with Pt-O1 (1.922 Å) and Pt-O2 (2.079 Å) bonds. In the event, CN of Pt-O1 is 1.86 and that of Pt-O2 is 2.87 for PtO2 phase in experiment NC. Compared to CN of ideal PtO2 crystal, CNs of Pt-O1 and Pt-O2 are both reduced but to different extent. CN\( _{\text{Pt-O1}} \) decreases by ~7% while CN\( _{\text{Pt-O2}} \) falls by ~28.2%. The uneven reduction explains the growth of asymmetrical 2D Pt crystal in INER_A.

Surface-to-bulk ratio determination by chemical composition of Pt NC. To confirm crystal shape, the surface-to-bulk ratio \( (\eta) \) of experimental NCs is compared with that of ideal NCs in different geometries (scheme shown in Fig. 4a). Eqs. 1 and eqn 2 represent the estimation for \( \eta \) of ideal NCs that changes by varying thickness (disk-like crystal, \( \eta_{d} \)) and height (octahedron crystal, \( \eta_{oh} \))

\[
\eta_{d} = \frac{h}{h_d}
\]

\[
\eta_{oh} = \frac{h}{h_{oh}}
\]

Table 1. XRD determined crystal structure parameters of Pt cluster doped nanoporous carbon materials.

| Sample | Peak HP-TGA* X | Index | \( \Delta 20 \text{red} \) | \( h_{\text{avg}} (\text{Å}) \) | \( \Delta h_{\text{avg}} (%) \) | \( d (\text{Å}) \) | \( H_x/H_d \) and \( \Delta (H_x/H_d) \) |
|--------|----------------|-------|-----------------|-----------------|-----------------|----------------|-------------------|
| INER_A | A X 39.7 Pt (111) | 4.779 | 9.2 | −17.4 | 2.28 | H\(_x\)/H\(_d\)-X | 0.28 |
|        | O 39.3 Pt (111) | 5.808 | 7.6 | 2.3 | H\(_x\)/H\(_d\)-O | 0.22 |
| B X 43.2 PtO (110)/PtO\(_2\)(002) | 3.345 | 13.4 | −9.0 | 2.1 | \( \Delta (H_x/H_d) \) | 22.2% |
| O 43.2 PtO (110)/PtO\(_2\)(002) | 3.676 | 12.2 | 2.1 | \( \eta \) |
| C X 46 Pt (200) | 4.522 | 10.2 | 11.8 | 1.98 |
| O 46.3 Pt (200) | 3.97 | 11.4 | 1.97 |
| INER_B | A X 39.4 Pt (111) | 3.97 | 11.1 | 8.1 | 2.3 | H\(_x\)/H\(_d\)-X | 1.67 |
|        | O 39.5 Pt (111) | 3.676 | 12 | 2.29 | H\(_x\)/H\(_d\)-O | 1.08 |
| B X 43.4 PtO (110)/PtO\(_2\)(002) | 3.67 | 12.2 | 10.7 | 2.1 | \( \Delta (H_x/H_d) \) | 35.4% |
| O 43.2 PtO (110)/PtO\(_2\)(002) | 3.309 | 13.5 | 2.11 |
| C X 46.3 Pt (200) | 4.04 | 11.2 | 9.8 | 1.97 |
| O 46.1 Pt (200) | 3.676 | 12.3 | 1.98 |

Figure 4. (a) Schemes for octahedron (h, a, b, c1, c2, and c3 denote the height, two axis in horizontal plan, and side lengths of triangle planes in octahedron) and disk-like (H and D denote the thickness and diameter of disk crystal) and (b) surface to bulk ratio \( (\eta) \) of octahedron and disk like crystals as a function of h or H, where H 1, 2, 3, 6 layers denote \( \eta \) of disk crystal with corresponding atomic layer in thickness.
H/Ar reaction with a displacement of $-0.05 \text{ Å}$ in height. H atoms are located at hollow and bridge sites on Pt layer with indication of Pt-Pt homoatomic bonding distinguished from Pt-C. Rest of the Pt atoms kept at the original positions at low sites with 2–4 bondings with carbon layer. The neighboring Pt atoms which are at high z position (arrows B) of Pt on graphene. In simulation, position of carbon positions is fixed to reproduce the bonding characteristics between bulk graphite and Pt atoms. As depicted in Fig. 5, Pt atoms at corner (arrows A) tend to seat in hollow sites (1PtAC in Fig. 5a) and bridge site as 1PtB, on hollow sites 1PtC, and 1PtAC for pairs at both atop and hollow sites. Average distance between Pt atom and graphene layer is 2.32 Å. The packing structure and energy relaxation profile of two of those stacking sites on graphite surface are built. Configuration with Pt atom on atop position is named as 1PtAC, on bridge site as 1PtB, on hollow sites 1PtC, and 1PtAC for pairs at both atop and hollow sites. Average distance between Pt atom and graphene layer is 2.32 Å. The packing structure and energy relaxation profile of two of those models are shown in Fig. S2a and S2b. Among all configurations, 1PtAC model possesses the lowest binding energy ($E_{\text{dep}}$) of ~0.33 (eV/Pt atom). Therefore, effects of Pt thickness on the H$_2$ binding energy in Pt NC surface are further investigated by DFT calculation with monolayer (1PtAC in Fig. 5a) and two atomic layers (2PtAC in Fig. 5b) of Pt on graphene. In simulation, position of carbon positions is fixed to reproduce the bonding characteristics between bulk graphite and Pt atoms. As depicted in Fig. 5, Pt atoms at corner (arrows A) tend to seat in hollow sites with 2–4 bondings with carbon layer. The neighboring Pt atoms which are at high z position (arrows B) indicate the Pt-Pt homoatomic bonding distinguished from Pt-C. Rest of the Pt atoms kept at the original position with a displacement of $+/−0.05 \text{ Å}$ in height. H atoms are located at hollow and bridge sites on Pt layer with a bond length of 1.540 and 1.750 Å, respectively. The rough Pt surface of 1PtAC implies a high density of dangling bond which is in consistent to the result from spectrum analysis that carbon oxidation supports 1 to 2 atomic layers Pt cluster. For 2PtAC, all Pt atoms at interface form multiple bondings with carbon atoms (arrows C) and atoms tend to agglomerate in 3D cluster as a result of the strong Pt-Pt bond. In this structure, the center Pt atoms are lifted up by 0.1 Å or more in z direction (arrows D) and bond length of Pt-H is 1.804/1.980 Å in hollow sites.
and 1.742/1.836 Å in bridge sites. H atoms locate at bridge and hollow sites of Pt layer where corresponding atoms are at hollow and atop sites of graphene underneath.

Calculation results are given in Table 4. Accordingly, cohesive energy ($E_c$) of 1PtAC is 0.582 eV stronger than that of 2PtAC with a H$_2$ molecule in vacuum. This result accounts for the stronger attraction force to molecular H$_2$ in 2D Pt cluster as compared to that of 3D Pt ones. After relaxation, H atoms are preferentially located at hollow and bridge sites of 1PtAC and at hollow sites of 2PtAC. The coherence energy difference ($\Delta E_c = E'_c - E_c$) between initial and final state is resulted from formation of surface Pt-H bond and is $-0.069$ (eV Pt atom$^{-1}$) for 2PtAC and $-0.255$ for 1PtAC (eV Pt atom$^{-1}$). There are two factors for estimation of $E_c$ including (i) number of Pt atom and (ii) distance/bond strength between H and Pt atoms. In the first factor, $\Delta E_c$ should be doubled by reducing 50% of Pt atoms in DFT model. However, $\Delta E_c$ of 1PtAC is 2.7 times higher than that of 2PtAC. Such an abnormal $\Delta E_c$ could be accounted for the formation of strong Pt-H bond due to the coupling effects between adsorbed H on Pt atom and pi-electron in hollow sites of carbon substrate underneath. Adsorption energy ($E_a$) for H atom on sorption site of 1PtAC (1PtAC-2H model) is $-2.043$ (eV atom$^{-1}$) and 2PtAC-2H is $-1.117$ (eV atom$^{-1}$).

### Discussion

Crystal shape of NC is one of the most influential factors in its HSR because different atomic packing densities of crystal facets will change the activation energy for redox reactions. For nanocrystallite with a known size, surface-to-bulk ratio ($\eta$) is proportional to its crystal shape. The ratio can be estimated by oxidation ratio considering that surface chemisorption of oxygen is a general form of oxide in the outmost layer of Pt NC. Therefore, in determining the correlation between crystal shape to HSR of Pt NC, one should confirm their particle size, oxidation state, and the structure asymmetry by structure characterizations. After that, results of theoretical model calculations on $\eta$ to crystal shape is needed. In this study, X-ray diffraction (XRD), small angle X-ray scattering (SAXS), X-ray absorption spectroscopy (XAS) analyses, and theoretical geometry calculation are employed to reveal the bulk structure parameters, oxidation ratios, as well as $\eta$ in relation to the shape of Pt NC. To investigate the impacts of crystal shape on HSR of Pt NC, density functional theory (DFT) calculation on proper atomic models is performed.

In XRD analysis, ratios of peak X and peak D intensity (H$_X$/H$_D$) are substantially increased from 0.28 (INER$_A$) to 1.67 (INER$_B$), which indicates the increasing of long-term ordering structure in carbon support.
by decreasing Pt content from 0.35 to 0.13 wt%. After HP-TGA test, the further decreased H₂/H₂O implies a disruption of long-term ordering in carbon support. This phenomenon results from intercalation of Pt clusters into carbon support by different extents between INER_A (22.2%) and INER_B (35.4%). In this event, decreasing $\Delta(H_2/H_2O)$ with increasing full width at half maximum (FWHM) of peak D depicts a restructure of Pt atoms into low-dimension Pt clusters on the high dangling bond density surface of INER_A. This hypothesis is further confirmed by uneven changes between average coherent length ($h_{avg}$) of Pt facet (111) (decreased by 17.8%, from 9.2 to 7.6 Å) and (200) facet (increased by 11.8%, from 10.2 to 11.4 Å). Such a phenomenon could be attributed to relocation of atop Pt atoms to carbon sites around metal clusters (Fig. 6).

In the meantime, $h_{avg}$ of Pt oxide phase is decreased by ~9.0% revealing weak Pt-O bonding on Pt atoms directly adjacent to electron rich support (i.e., shielding effects of graphite or graphene). The growth of 2D Pt cluster is further confirmed by the asymmetry SAXS scattering profile of INER_A. On the other hand, $h_{avg}$ of Pt metal and Pt oxide phases in INER_B is increased by 8.1–10.7% after HP-TGA. The growth of both metal and oxide phases is attributed to Pt restructure into 3D cluster by inter-particle coalesce as a result of weak attachment of NC at carbon support. In this event, Pt-O phase is formed in 3D Pt NC surface.

From SAXS analysis, $D_{avg}$ (~1.4 nm) of Pt NCs in INER_A is similar to that of INER_B. Based on XRD analysis, $h_{avg}$ of Pt NCs in the two samples is highly dependent on surface-to-bulk ratio. These observations validate the correlation between $\eta$ and shape of NC with a known size. To identify the crystal shape of experimental NCs, correlations between their oxidation state and $\eta$ are investigated by cross-referencing the results of atomic arrangement, oxidation states, and geometry configurations (VEDO method)\(^{10}\) in INER_A, the content of Pt metal is 20.3% and that of Pt oxide (PtO and PtO₂) is 79.7%. Given that surface oxygen chemisorption is a general form in Pt NCs, their oxidation ratio also refers to surface-to-bulk ratio. Accordingly, $\eta$ of INER_A ($\eta_A$) is 79.7%. This value is higher than $\eta_{Oh}$ of a 1.4 nm octahedron (62%), suggesting the growth of disk-like Pt NCs in a thickness between 1–2 atomic layers. As for INER_B, $\eta_B$ is 42.9% indicating the formation of 3D Pt NCs.

Based on the results of structural analyses and H₂ sorption test, our study shows that Pt atoms tend to stack into 2D NC on active carbon by annealing at 102 °C under H₂ for 2 h (hydrogen reduction) after a metal ion impregnation process. In this condition HSR of carbon supported Pt NC is 4.7 μg/g min. By increasing annealing temperature to 130 °C under H₂, Pt atoms are shaped into 3D polymorph NC on active carbon; the NC HSR becomes 1.3 μg/g min. To clarify the impacts of crystal shape on HSR of Pt NC, H₂ sorption energy of proper atomic stacking scheme is simulated by ab initio DFT calculation. Our hypothesis is further confirmed by the results of binding energy of H atom ($E_b$) in current models. As indicated in Table 4, the endothermic $E_b$ values of H₂ sorption on relevant Pt NCs are higher than $E_b$ of the Pt-H bond in adsorption of H₂ on Pt metal, suggesting the growth of disk-like Pt NCs in a thickness between 1–2 atomic layers. As for INER_B, $\eta_B$ is 42.9% indicating the formation of 3D Pt NCs.

In short, our findings illustrate that Pt atoms tend to aggregate into disk-like NCs with a thickness of 1–2 atomic layers in properly selected carbon support (SSA = 1886 m² g⁻¹). By increasing the hydrogen-reduced temperature to 130 °C and the use of carbon support without acid (function group) treatment, nanoscaled polymorph Pt clusters in 3D are formed on carbon support. We adopt structural characterizations (XRD, SAXS, XAS) and theoretical model calculations to illuminate that HSR for Pt doped nanoporous carbon materials is dominated.
by the crystal shape of supported Pt NC. In a 2D cluster with a thin atomic layer, H₂ molecule will decompose into 2 H atoms. After that, H atoms will be adsorbed in atop sites in the rough surface. In contrast, in a 3D cluster, H atoms tend to locate in hollow sites of Pt surface with a substantially reduced E₀ as compared to that of a 2D cluster. Therefore, the HSR of a 3D Pt cluster is drastically lower than that of a 2D cluster.

### Methods

**Synthesis and the gravimetric hydrogen uptake measurement of Pt doped nanoporous activated carbon composite (Pt NC).** The Supporting Material for growing Pt clusters is a nanoporous active carbon (ACB16) with a BET specific surface area (SSA) of 1886 m² g⁻¹. The Pt clusters were synthesized by incipient wetness impregnation of Pt⁴⁺ ions in ACB16 with a vacuum-attraction system. The subsequent hydrogen reduction was performed at 102°C (rising rate = 5°C min⁻¹) for 2 hours. To reinforce NC attachment, the carbon support was washed in an acid base before Pt impregnation. In this treatment, 10 g nanoporous carbon powder was dispersed in the 500 mL acid solution of H₂SO₄ (95%), HNO₃ (65%) and distilled water. The mixed solution was heated from room temperature to 105°C (rising rate = 0.2°C min⁻¹) and then cooled to room temperature. Details for the experimental procedures are given in our previous works. The samples were named as INER_A (Pt cluster on freshly prepared ACB16) and INER_B (Pt clusters grown on the un-acid-treated carbon ACB17 with SSA = 1857 m² g⁻¹ was hydrogen-reduced 130°C for 2 hours) which respectively contained 0.35 and 0.11 wt% of Pt metal (Table 5). The gravimetric HSRs for the experimental Pt/AC at room temperature were measured by using HP-TGA (Cahn-Thermax-500) of Institute of Nuclear Energy Research, Taiwan. The parameters for preparing the two samples were decided in resulting their optimum HSR. Details of measurement receipt are similar to those given elsewhere. The small angle X-ray scattering (SAXS) spectra were measured using the Bruker Nanostar instrument. The shape of NC was determined by combing the results of Pt oxidation state and the surface ratios of nanocrystallites that vary according to the changes of their sizes in a 3D atomic packing model (VEDO). 

### Density Functional Theory Calculation.

To investigate the H-adsorption on Pt cluster decorated graphite structure, we have carried out first-principles calculations using Vienna Ab initio simulation package (VASP). The calculations were conducted at formsas5 cluster of National Center for High Performance Computing (NCHC), Taiwan. We adopted the projected augmented wave (PAW) pseudopotential method with local density approximation, in which plane-wave energy cutoff of 600 eV and Monkhorst–Pack k-point meshes density of 0.03 Å⁻¹ are used for all calculations. To explore the optimized decoration sites of nano-Pt on graphene, the atop (A), bridge (B), hollow (C) and AB&C mixing sites, and decoration distance from 2.1 Å to 3.7 Å were tested for Pt-decoration sites at atop (A), bridge (B), hollow (C), the supercell’s lattice size was fixed at a = b = 19.68 Å with the optimized C-C bond length of 1.42 Å (128 C + 16Pt atoms). For the mixing decoration sites of AB&C, another supercell was built up with the lattice size fixed at a = 17.0434 Å and b = 25.5651 Å, which ensures the C-C bond length kept at 1.42 Å (144 C + 16 Pt atoms). All the supercells were built up with at least 24 Å vacuum regions in the z-direction to avoid the interaction between adjacent periodic images. To find the most energetically favorable structures, all the Pt atoms were fully relaxed with the supercell size and graphene atoms fixed (stiff graphene without topological change). The ionic relaxation was stopped when the total energy change is below 1 meV.

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### Table 5. Physical Characteristics and hydrogen storage rate (HSR) of experimental Pt doped nanoporous carbon materials.

| Sample   | Pt treatment temperature | SSA (m² g⁻¹) | Pt loading (wt%) | HSR (μg/g min⁻¹) |
|----------|--------------------------|--------------|------------------|-----------------|
| INER_A   | 102°C                    | 1886         | 0.35             | 4.7             |
| INER_B   | 130°C                    | 1857         | 0.11             | 1.3             |

*SSA: BET determined specific surface area, data quoted from previous studies.*

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**Author Contributions**
T.Y.C.* designed the research and wrote this manuscript. All authors contributed to the discussion of the results and edited the manuscript. Y.Z., A.H. and Y.Z. conducted the density functional theory calculation and interpretation. L.G.H. and C.M.F. assisted the X-ray absorption spectroscopy analysis. T.Y.C., C.Y.W., and C.S.T. prepared the carbon supported catalyst and conducted the hydrogen sorption analysis. H.Y.C. measured the X-ray diffraction spectra.

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