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Promoted hydrogen activation and spillover over Pt/Co₃O₄ by facet engineering of Co₃O₄ for enhanced catalytic hydrogenation

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The exposed facets of supported metal catalysts play a crucial role in catalytic hydrogenation performance. However, the internal relationship between the support crystal facet and catalytic performance needs to be further explored. Herein, a series of well-defined Pt/Co₃O₄-x catalysts are fabricated with similar Pt nanoparticle sizes, identical metal loadings, and tailored Co₃O₄ crystal facets (x = o, t, c; where "o", "t", and "c" denote Co₃O₄ exposing predominantly (111), mixed (111)/(100), and (100) facets, respectively). The electronic structure of Pt nanoparticles and the hydrogen spillover capability of Pt/Co₃O₄ are modulated by exposing different crystal facets of Co₃O₄. For the 4-nitrophenol (4-NP) hydrogenation reaction with H₂ as the hydrogen source, the Pt/Co₃O₄-o catalyst with more Pt⁰ species and stronger hydrogen spillover capability exhibits the best hydrogenation activity with a turnover frequency (TOF) of 164.2 h⁻¹. Mechanistic studies indicate that, compared with Pt/Co₃O₄-c, the Pt/Co₃O₄-o exhibits weaker adsorption and activation of the nitro group, while its ability to activate H₂ is stronger. The enhanced catalytic activity of Pt/Co₃O₄-o is attributed to promoted hydrogen activation and spillover. This work highlights support crystal facet engineering for regulating the electronic structure and hydrogen spillover effect, which provides in-depth insight into catalyst design and hydrogenation mechanism.

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Introduction

Catalytic hydrogenation plays a pivotal role in environmental protection and industrial processes,^{1,2} particularly for the degradation of persistent organic pollutants such as 4-nitrophenol (4-NP),³ a common toxic contaminant in wastewater.⁴⁻⁶ Supported metal catalysts, especially platinum-based systems, have garnered significant attention due to their exceptional hydrogen activation capability.^{7,8} However, the catalytic performance of such systems is intricately linked not only to the active metal sites but also to the structural and electronic properties of the support material.⁹⁻¹⁴ Previous extensive research has predominantly focused on elucidating the internal relationship between metal nanoparticle characteristics (including size regulation, alloy composition, and morphological engineering) and the catalytic hydrogenation performance.¹⁵⁻¹⁸

The microstructures of support, particularly the exposed crystal facet, have been recognized as a critical influencing factor for catalytic hydrogenation performance by modulating the geometric/electronic configurations of metal nanoparticles,¹⁹⁻²² facilitating support-mediated reactant activation processes,^{23,24} inducing interfacial charge transfer dynamics,^{25,26} and so on. For example, Gao *et al.* reported a study on tailoring the electronic states of Pd nanoparticles by

modulating the exposed crystal facets of ZIF-8 supports.²⁷ By constructing sandwich-structured ZIF-8_x@Pd@ZIF-8 composites, where distinct facets were engineered, the electron density of Pd nanoparticles was precisely controlled. The (100) facet induced electron-deficient Pd species (ZIF-8_c@Pd@ZIF-8) could preferentially adsorb the electron-rich nitro group of *p*-chloronitrobenzene, achieving excellent catalytic activity and selectivity in the hydrogenation of *p*-chloronitrobenzene to *p*-chloroaniline. Moreover, the facet engineering of nanocatalysts has proven critical for optimizing hydrogen spillover processes for selective hydrogenation. Jiang *et al.* reported a groundbreaking study on tailoring the catalytic performance of highly diluted Pd single-atom catalysts through facet engineering of Cu supports.²⁸ By dispersing Pd atoms onto Cu nanosheets (exposing (111) facets) and nanocubes (exposing (100) facets), the authors revealed a striking facet-dependent behavior in the semi-hydrogenation of alkynes. While hydrogen spillover occurred on both facets, only Pd₁/Cu(100) exhibited exceptional activity and selectivity even at ultralow Pd loadings (50 ppm). Despite advances in catalyst design, the role of the support facet in modulating electronic states and hydrogen spillover efficiency remains poorly understood.

Herein, we systematically investigate the facet-dependent behavior of Co₃O₄-supported Pt catalysts. Three distinct Co₃O₄ morphologies—octahedral (exposing (111) facets), cubic (exposing (100) facets), and truncated intermediates (co-exposing (111) and (100) facets)—were synthesized to anchor

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Pt nanoparticles with similar sizes and loadings. For the 4-nitrophenol (4-NP) hydrogenation with H₂ as the hydrogen source, the Pt/Co₃O_{4-x} (x = o, t, c) catalysts present a notable dependence of catalytic activity on exposed facets of supports. And the catalytic activity follows the order: Pt/Co₃O_{4-o} > Pt/Co₃O_{4-t} > Pt/Co₃O_{4-c}. Detailed analyses indicate that, the Pt/Co₃O_{4-o} with more Pt⁰ species has stronger hydrogen activation and spillover capacity and thus significantly accelerates the catalytic hydrogenation performance.

Results and discussion

Catalyst characterization

A series of Co₃O₄ supports with different morphologies were synthesized by hydrothermal method (Fig. S1). Their scanning electron microscopy (SEM) images demonstrate that the synthesized nanoparticles exhibit good morphology (Fig. S2a–c). For different morphologies of Co₃O₄, the corresponding exposed crystal facets are distinct. Specifically, the octahedron Co₃O₄ (Co₃O_{4-o}) and cube Co₃O₄ (Co₃O_{4-c}) are enclosed with (111) and (100) facets, respectively, while the truncated octahedron Co₃O₄ (Co₃O_{4-t}) exposes mixed (111) and (100) facets (Fig. S2d–f). Subsequently, the pre-synthesized Pt nanoparticles were supported on the Co₃O_{4-x} (x = o, t, c) supports *via* the colloidal deposition method with ~0.3 wt% Pt loading (determined by ICP-OES, Table S1), yielding Pt/Co₃O_{4-o}, Pt/Co₃O_{4-t}, and Pt/Co₃O_{4-c}. SEM images of Pt/Co₃O_{4-x} (x = o, t, c) show that the size and morphology of the original Co₃O_{4-x} (x = o, t, c) are almost maintained after Pt loading (Fig. 1a, e, and i).

The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) with energy dispersive X-ray spectroscopy (EDS) elemental mapping was further employed to characterize Pt/Co₃O_{4-x} (x = o, t, c). As shown in Fig. 1b, f, and j, obvious bright spots of Pt nanoparticles are observed. Pt nanoparticles are uniformly dispersed on the Co₃O_{4-x} (x = o, t, c) supports (Fig. 1c, g, and k). And the average diameters of Pt nanoparticles are similar, about 2.2 nm. Furthermore, the lattice fringes measured in the high-

resolution TEM (HRTEM) images of Pt/Co₃O_{4-x} (x = o, t, c) (Fig. 1d, h and l) are 0.23 nm, corresponding to the (111) planes of Pt. N₂ adsorption–desorption experiments indicate that the Brunauer–Emmett–Teller (BET) surface areas of Pt/Co₃O_{4-o}, Pt/Co₃O_{4-t}, and Pt/Co₃O_{4-c} are 2.4, 3.4, and 3.4 m² g⁻¹, respectively, indicating similar surface areas (Table S1).

X-ray diffraction (XRD) was used to investigate the crystal structures of Co₃O_{4-x} and Pt/Co₃O_{4-x} (x = o, t, c), as shown in Fig. S3a. All XRD patterns show the diffraction peaks located at 19.0°, 31.3°, 36.9°, 38.6°, 44.9°, 55.7°, 59.4°, and 65.3°, which correspond to the (111), (220), (311), (222), (400), (422), (511), and (440) planes of Co₃O₄, respectively (PDF#43-1003). The intensity ratio of the (111) to (400) peaks for Co₃O_{4-x} (x = o, t, c) decreases in order of octahedron (0.9) > truncated octahedron (0.7) > cube (0.5) (Fig. S3b), suggesting morphology-dependent facet exposure. Compared to bare Co₃O_{4-x} (x = o, t, c) supports, the Pt-loaded counterparts (Pt/Co₃O_{4-x}) exhibit similar trends in the (111)/(400) peak intensity ratios (Fig. S3c), implying that Pt deposition does not significantly perturb the predominant facet distribution of the Co₃O₄ supports. A semi-quantitative analysis based on the XRD intensity ratios estimates the relative abundance of the (111) facet to be ~100%, ~57%, and ~0% for Pt/Co₃O_{4-o}, -t, and -c, respectively, providing a quantitative structural descriptor for the catalyst series (Table S2). No characteristic diffraction peaks belonging to crystalline Pt nanoparticles are observed, which can be attributed to the low loading and/or small size of Pt species.

X-ray photoelectron spectroscopy (XPS) was employed to reveal the surface chemical states of Pt and Co. Fig. 2a and b show the Co 2p spectra of Co₃O_{4-x} and Pt/Co₃O_{4-x} (x = o, t, c), respectively. The peaks at ~780.2 and 795.4 eV are assigned to Co 2p_{3/2} and Co 2p_{1/2}, respectively. The peaks of Co 2p_{3/2} can be deconvoluted into two peaks at ~780.0 and 781.4 eV, indicating the coexistence of Co³⁺ and Co²⁺.²⁹ Notably, compared to the pristine Co₃O_{4-x} (x = o, t, c) supports, the Pt-loaded counterparts (Pt/Co₃O_{4-x}) with the same morphologies show an

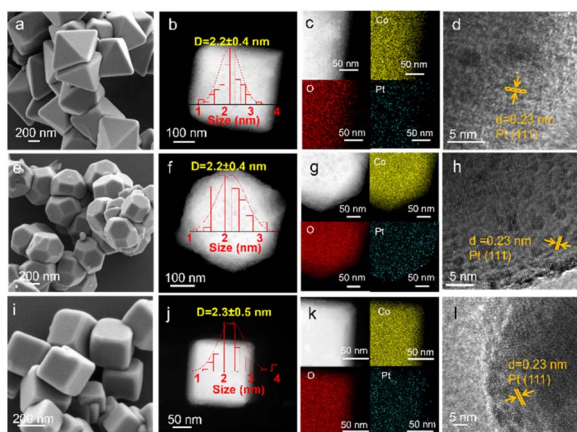


Fig. 1 (a, e, and i) SEM images, (b, f and j) HAADF-STEM images, (c, g, and k) STEM-EDS elemental mappings, and (d, h, and l) HRTEM images of Pt/Co₃O_{4-o}, Pt/Co₃O_{4-t}, and Pt/Co₃O_{4-c}, respectively.

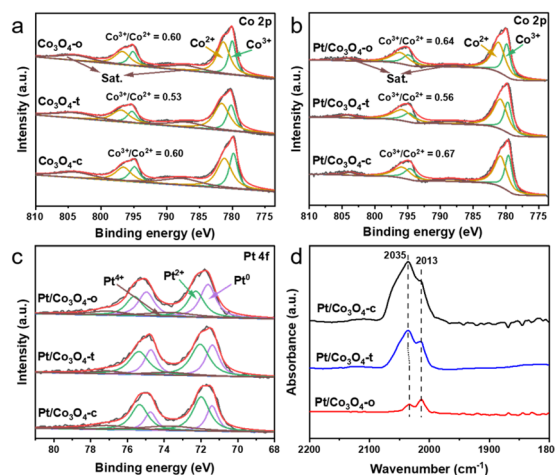


Fig. 2 XPS spectra of Co 2p for (a) Co₃O_{4-x} and (b) Pt/Co₃O_{4-x} (x = o, t, c). (c) XPS spectra of Pt 4f and (d) CO-DRIFTS spectra for Pt/Co₃O_{4-x} (x = o, t, c).



increase in the $\text{Co}^{3+}/\text{Co}^{2+}$ ratio, implying the transfer of electrons from Co to Pt.³⁰ Moreover, the XPS spectra of Pt 4f for Pt/ Co_3O_4 -x (x = o, t, c) show two peaks located at ~ 71.7 and 75.0 eV, which are attributed to Pt $4f_{7/2}$ and $4f_{5/2}$, respectively (Fig. 2c). And the Pt 4f spectra were fitted by Pt^0 , Pt^{2+} , and Pt^{4+} .³¹ The fitting results reveal that the Pt^0 content follows the order: Pt/ Co_3O_4 -o (44.7%) > Pt/ Co_3O_4 -t (39.4%) > Pt/ Co_3O_4 -c (26.1%) (Table S3), suggesting the differentiated electronic states of Pt nanoparticles with varied Co_3O_4 facets. To gain insight into the state of Pt under reaction conditions, quasi-in situ XPS analysis was performed after H_2 treatment at 40°C . Intriguingly, although the Pt^0 content increased for all catalysts, the facet-dependent order remained unchanged (Fig. S4, Table S3), suggesting that the intrinsic electronic modulation by the support facet is preserved under a reducing atmosphere.

Further, diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) of CO chemisorption was performed to evaluate the electronic states of surface Pt species in Pt/ Co_3O_4 -x (x = o, t, c), as shown in Fig. 2d. Two absorption bands observed at 2033 – 2035 and 2013 cm^{-1} are assigned to the linear absorption of CO on the terrace and step sites of Pt nanoparticles, respectively.³² Compared to the Pt/ Co_3O_4 -t and Pt/ Co_3O_4 -c, the CO adsorption peak at the terrace sites of Pt/ Co_3O_4 -o shifts to a lower wavenumber (from 2035 to 2033 cm^{-1}). Additionally, the relative intensity of the CO signal adsorbed at the step sites follows the order: Pt/ Co_3O_4 -o > Pt/ Co_3O_4 -t > Pt/ Co_3O_4 -c. These results suggest that the Pt species on Pt/ Co_3O_4 -o surfaces are in a lower valence state,³³ which aligns with the XPS result. The observed charge transfer and modified electronic state of Pt (Fig. 2) confirm that a facet-dependent metal-support interaction is effectively established through our colloidal deposition process, even in the absence of high-temperature treatment.

Hydrogen temperature-programmed reduction (H_2 -TPR) was carried out to investigate the reducibility of Co_3O_4 -x and Pt/ Co_3O_4 -x (x = o, t, c), as shown in Fig. 3a and b. H_2 -TPR profiles show no reduction peak below 100°C for any Pt/ Co_3O_4 -x catalyst, confirming the metallic state (Pt^0) of the pre-synthesized nanoparticles. The prominent peaks observed at higher temperatures ($\sim 370^\circ\text{C}$) are therefore attributed solely to the reduction of the Co_3O_4 support. The shift to lower temperatures (by $\sim 50^\circ\text{C}$) compared to bare Co_3O_4 demonstrates that metallic Pt^0 promotes support reduction *via* hydrogen spillover.^{34,35}

To detect spilled hydrogen, hydrogen temperature-programmed desorption coupled with mass spectrometry (H_2 -TPD-MS) measurements of Pt/ Co_3O_4 -x were performed. As shown in Fig. 3c and S5, the MS signals reveal that the major desorption products are H_2O ($m/z = 18$) and OH species ($m/z = 17$), with no significant molecular H_2 ($m/z = 2$) detected. This indicates that active hydrogen species generated on Pt^0 sites spill over onto the Co_3O_4 support and react with lattice oxygen to form surface hydroxyl groups, which subsequently recombine and decompose upon heating.^{36,37} The profiles show two main desorption regions: a peak at $\sim 280^\circ\text{C}$ attributed to the removal of weakly-bound hydroxyls, and another more intense peak at $\sim 650^\circ\text{C}$ associated with strongly-bound hydroxyls likely formed from hydrogen that has migrated deeper into the oxide

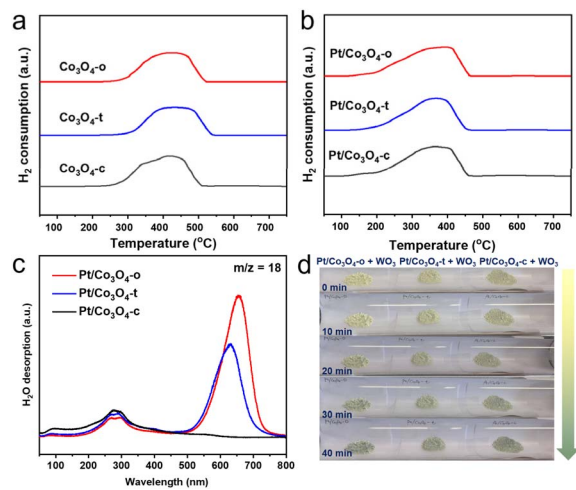


Fig. 3 H_2 -TPR profiles of (a) the as-prepared Co_3O_4 -x and (b) Pt/ Co_3O_4 -x (x = o, t, c) catalysts. (c) H_2 -TPD profiles of the as-prepared Pt/ Co_3O_4 -x (x = o, t, c). (d) Photographs of samples made with WO_3 (300 mg) mixed with the Pt/ Co_3O_4 -x (x = o, t, c) catalysts (1 mg) before treatment and after treatment with 10% H_2/Ar at 25°C for different times.

lattice. Critically, the intensity of the high-temperature peak follows the order: Pt/ Co_3O_4 -o > Pt/ Co_3O_4 -t > Pt/ Co_3O_4 -c. This provides direct evidence that the (111) facet of Co_3O_4 is the most effective in stabilizing and incorporating spilled hydrogen.

Further, a color change experiment was conducted to visually evaluate the hydrogen spillover effect (Fig. 3d). By mixing 1 mg of Pt/ Co_3O_4 -x catalysts and 300 mg of WO_3 nanowires, the original color of the mixtures is light yellow. After being exposed to hydrogen atmosphere, the mixture of Pt/ Co_3O_4 -o and WO_3 exhibits the most pronounced color change within 40 minutes, implying the strongest hydrogen spillover effect over Pt/ Co_3O_4 -o. This result aligns with the H_2 -TPD-MS data and is attributed to the stronger metal-support interaction in Pt/ Co_3O_4 -o, which facilitates the generation and transfer of active hydrogen species (Fig. 2c and d and S6). Further, a parallel experiment conducted in aqueous reaction conditions (Fig. S7) also yielded a distinct color change, confirming that hydrogen spillover persists in the liquid environment relevant to catalysis.

Catalytic performance of Pt/ Co_3O_4 -x (x = o, t, c) for 4-NP hydrogenation

The catalytic performance of Pt/ Co_3O_4 -x (x = o, t, c) was evaluated by the 4-NP reduction. The reduction process using H_2 as hydrogen source was monitored by UV-vis spectroscopy every ten minutes, and the intensity of the UV absorption peak at 400 nm was used to quantify the concentration of 4-NP. As shown in Fig. 4a–c, the peak intensity at 400 nm gradually decreased as the reaction proceeded. Simultaneously, a new peak appeared at 257 nm, which was ascribed to the formation of 4-aminobenzenol (4-AP) (Fig. S8). Among the Pt/ Co_3O_4 -o, Pt/ Co_3O_4 -t, and Pt/ Co_3O_4 -c catalysts, the Pt/ Co_3O_4 -o exhibited the shortest reaction time with nearly 100% conversion (Fig. S9). Furthermore, Fig. 4d shows a logarithmic plot of the



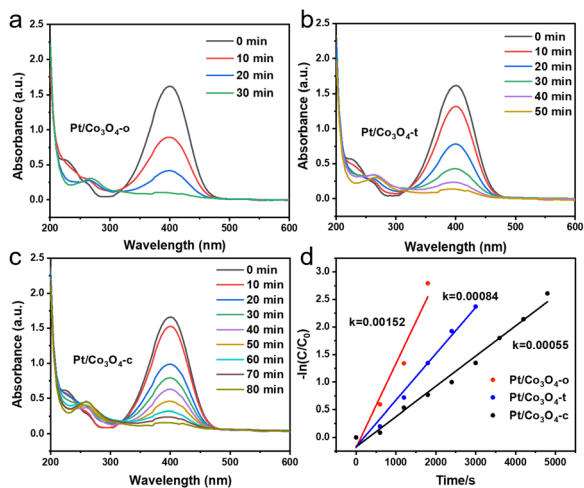


Fig. 4 Time-dependent UV-vis spectra of 4-NP reduced by (a) Pt/Co₃O₄-o, (b) Pt/Co₃O₄-t, and (c) Pt/Co₃O₄-c. (d) The kinetics plots of $-\ln(C_t/C_0)$ against the reaction time for the reduction of 4-NP over different Pt/Co₃O₄-x (x = o, t, c) catalysts.

concentration ($-\ln(C/C_0)$) versus reaction time for different catalysts. The concentration ($-\ln(C/C_0)$) is proportional to the reaction time, and thus the apparent kinetic rate constant (k_{app}) can be estimated based on slope regression of the logarithmic graph ($\ln(C_t/C_0) = -k_{app}t$).³⁸ Compared to the Pt/Co₃O₄-t and Pt/Co₃O₄-c catalysts (8.4×10^{-4} and $5.5 \times 10^{-4} \text{ s}^{-1}$, respectively), the Pt/Co₃O₄-o has the highest k_{app} value ($1.52 \times 10^{-3} \text{ s}^{-1}$), indicating its superior catalytic activity. Under identical reaction conditions, the bare Co₃O₄ support exhibited negligible catalytic activity (Fig. S10).

To further evaluate the intrinsic activity per Pt site, the turnover frequency (TOF) was determined based on CO chemisorption measurements. The calculated TOF values follow the same trend: Pt/Co₃O₄-o (164.2 h^{-1}) > Pt/Co₃O₄-t (115.2 h^{-1}) > Pt/Co₃O₄-c (75.6 h^{-1}) (Table S4). Subsequently, the apparent activation energy (E_a) experiment was performed (Fig. S11). The E_a values follow the order: Pt/Co₃O₄-o (23.0 kJ mol^{-1}) < Pt/Co₃O₄-t (25.3 kJ mol^{-1}) < Pt/Co₃O₄-c (55.2 kJ mol^{-1}). The significantly lower E_a for Pt/Co₃O₄-o accounts for its superior catalytic activity. More importantly, we establish a quantitative correlation between the Co₃O₄(111) facet exposure and the TOF (Fig. S12). This linear correlation directly demonstrates that the abundance of the (111) facet is the predominant factor governing the catalytic hydrogenation activity.

For comparison, control catalysts were also prepared *via* a conventional impregnation-chemical reduction method. While the same activity order (Pt/Co₃O₄-o > Pt/Co₃O₄-c) was preserved, the catalytic activities of the impregnation-prepared catalysts were substantially lower than their colloidal-deposition counterparts (Fig. S13). This lower activity is consistent with the larger and less uniform Pt nanoparticles formed by the impregnation method (Fig. S14), demonstrating the advantage of the colloidal deposition route for achieving high Pt dispersion on our low-surface-area Co₃O₄ supports.

The Pt/Co₃O₄-o was reused to test the stability for 4-NP hydrogenation. The catalytic activity was well maintained after five cycles (Fig. S15), indicating its high catalytic stability. Post-reaction characterizations (XRD, TEM, and XPS) confirm that the Pt nanoparticle size, dispersion, and chemical state, as well as the Co₃O₄ crystal facets, remain essentially unchanged after cycling (Fig. S16 and Table S3). Together with the minimal Pt leaching (<0.2%) confirmed by ICP-MS (Table S5), these results demonstrate the robust structural and compositional stability of the catalyst. When nitrobenzene was employed as the substrate, the Pt/Co₃O₄-o still exhibited the superior catalytic activity (Fig. S17 and S18).

Compared with state-of-the-art catalysts for 4-NP hydrogenation (Table S6), the optimal Pt/Co₃O₄-o demonstrates a competitive turnover frequency (164.2 h^{-1}) under an exceptionally mild condition ($40 \text{ }^\circ\text{C}$, 1 bar H_2). Many reported systems require significantly higher H₂ pressures or temperatures to achieve comparable activity. This combination of high intrinsic activity, low activation barrier, robust stability, and facet-dependent performance underscores the practical promise and fundamental insight offered by our facet-engineered catalyst.

Catalytic mechanism

To elucidate the origin of the superior catalytic performance of Pt/Co₃O₄-o, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was first used to investigate the adsorption behavior of 4-NP on Pt/Co₃O₄-o and Pt/Co₃O₄-c as model catalysts, as shown in Fig. S19. The spectra of Pt/Co₃O₄-o and Pt/Co₃O₄-c show two bands at 1578 and 1316 cm^{-1} , corresponding to asymmetric stretching and symmetric stretching vibrations of the nitro group, respectively.³⁹ Compared with the Pt/Co₃O₄-c catalyst, Pt/Co₃O₄-o exhibits a weaker peak intensity at 1578 cm^{-1} , suggesting a weaker adsorption capability for the nitro group. Further, the adsorption and activation capability of Pt/Co₃O₄-o and Pt/Co₃O₄-c for 4-NP and H₂ was explored through kinetic experiments. Fig. 5a displays the kinetic behavior for 4-NP adsorption and activation. The reaction order with respect to 4-NP is higher for Pt/Co₃O₄-o (0.81) than for Pt/Co₃O₄-c (0.75), implying that it is more difficult for Pt/Co₃O₄-o to activate the nitro group. This is consistent with the result of DRIFTS. For the adsorption and activation of H₂ (Fig. 5b), the reaction order of Pt/Co₃O₄-o (0.41) is lower than that of Pt/Co₃O₄-c (0.53), indicating that it is easier for Pt/Co₃O₄-o to activate H₂.

To gain theoretical insight, DFT calculations were conducted. Pt₄ clusters supported on Co₃O₄-(111) and Co₃O₄-(100) (labeled as Pt₄/Co₃O₄-(111) and Pt₄/Co₃O₄-(100), respectively) were constructed to mimic the Pt/Co₃O₄-o and Pt/Co₃O₄-c catalysts based on the distinct exposed facets of Co₃O₄ supports: the octahedral Co₃O₄-o predominantly exposes the (111) facet, whereas the cubic Co₃O₄-c preferentially exposes the (100) facet (Fig. S20a and b). First, when Pt₄ clusters were anchored on different Co₃O₄ model surfaces, the electron transfer from Co₃O₄ to Pt₄ was about $-1.65|e|$ for Pt₄/Co₃O₄-(111) and $-0.74|e|$ for Pt₄/Co₃O₄-(100), respectively (Fig. S20c and d, Table S7). The



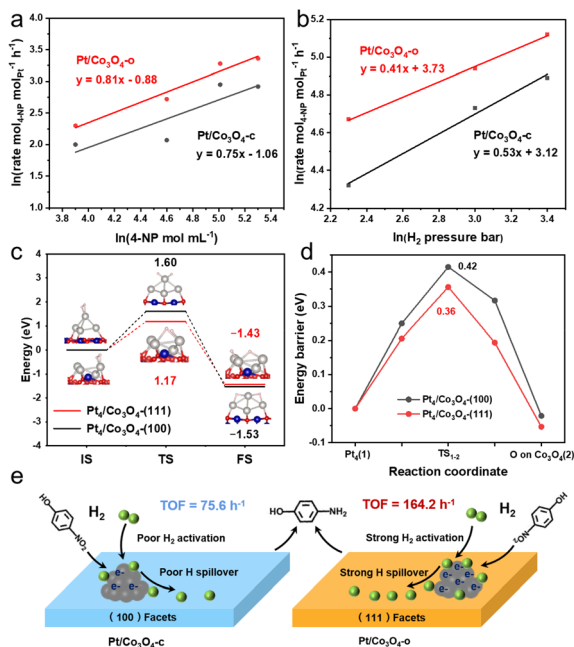


Fig. 5 Kinetic experiments of 4-NP hydrogenation over the Pt/Co₃O₄-o and Pt/Co₃O₄-c catalysts: the reaction order for (a) 4-NP and (b) H₂. The reaction rates were determined at conversions below 30%. (c) Potential energy profiles of H₂ dissociation on the Pt₄/Co₃O₄-(100) and Pt₄/Co₃O₄-(111) model surfaces. (d) Potential energy profiles for hydrogen atom migration from Pt₄ to Co₃O₄ across the interface on the Pt₄/Co₃O₄-(100) and Pt₄/Co₃O₄-(111) model surfaces. (e) Schematic illustration of possible mechanisms on Pt/Co₃O₄-c and Pt/Co₃O₄-o for 4-NP hydrogenation.

charge density differences indicate that more electrons transfer from Co₃O₄ to Pt for Pt₄/Co₃O₄-(111), leading to a lower oxidation state of Pt. This is also confirmed by the XPS results. Next, Fig. S21a–d shows the optimized adsorption structures of 4-NP on the Pt₄/Co₃O₄-(111) and Pt₄/Co₃O₄-(100) surfaces. The adsorption energy results presented in Fig. S21e indicate that the Pt₄/Co₃O₄-(111) exhibits the weaker capability for facilitating the nitro group activation. Further, Fig. 5c reveals the adsorption and activation of H₂ on the Pt₄/Co₃O₄-(111) and Pt₄/Co₃O₄-(100) surfaces, in which the energy barrier (1.17 eV) of H₂ dissociation on Pt₄/Co₃O₄-(111) is lower than that on Pt₄/Co₃O₄-(100) (1.6 eV), implying that the activation of H₂ by Pt₄/Co₃O₄-(111) is easier. These results are consistent with the kinetics results. Furthermore, for hydrogen-atom migration from Pt to Co₃O₄ across the interface, the energy barrier on the Pt₄/Co₃O₄-(111) (0.36 eV) is lower than that on the Pt₄/Co₃O₄-(100) (0.42 eV), indicating kinetically more favourable hydrogen spillover on Co₃O₄-(111) (Fig. 5d and S22).

Based on the above results, the possible promotion mechanism is proposed (Fig. 5e). For the hydrogenation reaction, the activity of a catalyst is strongly related to the substrate activation ability, H₂ activation ability, as well as active hydrogen spillover.^{40,41} With Pt/Co₃O₄-o and Pt/Co₃O₄-c as model catalysts, the kinetic experiments and DFT calculations illustrate that compared with Pt/Co₃O₄-c, the adsorption/activation of 4-NP on the Pt/Co₃O₄-o is weaker, indicating that the adsorption/

activation of 4-NP is not the key factor contributing to the difference in activity in this reaction. However, the Pt/Co₃O₄-o has a stronger H₂ dissociation ability and lower hydrogen-migration barrier. The accelerated hydrogen dissociation on electron-rich Pt sites, coupled with enhanced hydrogen spillover to the Co₃O₄ support, establishes a dynamic hydrogen supply chain that maximizes the utilization of active hydrogen species. The 4-NP adsorbed on Pt or near Pt-Co₃O₄ interfaces can continuously consume active hydrogen species, and the hydrogenation reaction can be promoted in a dynamic process.

Conclusions

In summary, a series of well-defined Pt/Co₃O₄-x (x = o, t, c) catalysts with tailored Co₃O₄ crystal facets have been successfully constructed for the hydrogenation of 4-nitrophenol. Owing to the crystal facet effect, the Pt nanoparticles in Pt/Co₃O₄-o are more negatively charged than those in Pt/Co₃O₄-c and Pt/Co₃O₄-t, and Pt/Co₃O₄-o exhibits the strongest hydrogen spillover capability. For the 4-nitrophenol (4-NP) hydrogenation reaction, the Pt/Co₃O₄-o has the best catalytic activity with a TOF value of 164.2 h⁻¹. Detailed analyses reveal that the negatively charged Pt sites are favorable to the activation of hydrogen rather than the nitro group. Therefore, the enhanced catalytic activity of Pt/Co₃O₄-o is attributed to the promoted hydrogen activation and spillover. This work highlights crystal facet engineering of support to regulate the electronic structure and hydrogen spillover effect, which provides in-depth insight into the catalyst design and hydrogenation mechanism.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Hui Yun: investigation, validation, visualization, data curation, formal analysis, methodology, writing – original draft. Jiao Feng: visualization, writing – review & editing. Wanying Peng: visualization, writing – review & editing. Mi Xiong: conceptualization, funding acquisition, supervision, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article has been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5sc09402j>.

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