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# Promoted hydrogen activation and spillover over Pt/Co<sub>3</sub>O<sub>4</sub> by facet engineering of Co<sub>3</sub>O<sub>4</sub> 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/Co<sub>3</sub>O<sub>4</sub>-x catalysts are fabricated with similar Pt nanoparticle sizes, identical metal loadings, and tailored Co<sub>3</sub>O<sub>4</sub> crystal facets (x = o, t, c; where "o", "t", and "c" denote Co<sub>3</sub>O<sub>4</sub> exposing predominantly (111), mixed (111)/(100), and (100) facets, respectively). The electronic structure of Pt nanoparticles and the hydrogen spillover capability of Pt/Co<sub>3</sub>O<sub>4</sub> are modulated by exposing different crystal facets of Co<sub>3</sub>O<sub>4</sub>. For the 4-nitrophenol (4-NP) hydrogenation reaction with H<sub>2</sub> as the hydrogen source, the Pt/Co<sub>3</sub>O<sub>4</sub>-o catalyst with more Pt<sup>0</sup> species and stronger hydrogen spillover capability exhibits the best hydrogenation activity with a turnover frequency (TOF) of 164.2 h<sup>-1</sup>. Mechanistic studies indicate that, compared with Pt/Co<sub>3</sub>O<sub>4</sub>-c, the Pt/Co<sub>3</sub>O<sub>4</sub>-o exhibits weaker adsorption and activation of the nitro group, while its ability to activate H<sub>2</sub> is stronger. The enhanced catalytic activity of Pt/Co<sub>3</sub>O<sub>4</sub>-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,<sup>1,2</sup> particularly for the degradation of persistent organic pollutants such as 4-nitrophenol (4-NP),<sup>3</sup> a common toxic contaminant in wastewater.<sup>4-6</sup> Supported metal catalysts, especially platinum-based systems, have garnered significant attention due to their exceptional hydrogen activation capability.<sup>7,8</sup> 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.<sup>9-14</sup> 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.<sup>15-18</sup>

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,<sup>19-22</sup> facilitating support-mediated reactant activation processes,<sup>23,24</sup> inducing interfacial charge transfer dynamics,<sup>25,26</sup> 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.<sup>27</sup> By constructing sandwich-structured ZIF-8<sub>x</sub>@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<sub>c</sub>@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.<sup>28</sup> 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 Pd<sub>1</sub>/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 Co<sub>3</sub>O<sub>4</sub>-supported Pt catalysts. Three distinct Co<sub>3</sub>O<sub>4</sub> 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 H<sub>2</sub> as the hydrogen source, the Pt/Co<sub>3</sub>O<sub>4-x</sub> (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/Co<sub>3</sub>O<sub>4-o</sub> > Pt/Co<sub>3</sub>O<sub>4-t</sub> > Pt/Co<sub>3</sub>O<sub>4-c</sub>. Detailed analyses indicate that, the Pt/Co<sub>3</sub>O<sub>4-o</sub> with more Pt<sup>0</sup> species has stronger hydrogen activation and spillover capacity and thus significantly accelerates the catalytic hydrogenation performance.

## Results and discussion

### Catalyst characterization

A series of Co<sub>3</sub>O<sub>4</sub> 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 Co<sub>3</sub>O<sub>4</sub>, the corresponding exposed crystal facets are distinct. Specifically, the octahedron Co<sub>3</sub>O<sub>4</sub> (Co<sub>3</sub>O<sub>4-o</sub>) and cube Co<sub>3</sub>O<sub>4</sub> (Co<sub>3</sub>O<sub>4-c</sub>) are enclosed with (111) and (100) facets, respectively, while the truncated octahedron Co<sub>3</sub>O<sub>4</sub> (Co<sub>3</sub>O<sub>4-t</sub>) exposes mixed (111) and (100) facets (Fig. S2d–f). Subsequently, the pre-synthesized Pt nanoparticles were supported on the Co<sub>3</sub>O<sub>4-x</sub> (x = o, t, c) supports *via* the colloidal deposition method with ~0.3 wt% Pt loading (determined by ICP-OES, Table S1), yielding Pt/Co<sub>3</sub>O<sub>4-o</sub>, Pt/Co<sub>3</sub>O<sub>4-t</sub>, and Pt/Co<sub>3</sub>O<sub>4-c</sub>. SEM images of Pt/Co<sub>3</sub>O<sub>4-x</sub> (x = o, t, c) show that the size and morphology of the original Co<sub>3</sub>O<sub>4-x</sub> (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/Co<sub>3</sub>O<sub>4-x</sub> (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 Co<sub>3</sub>O<sub>4-x</sub> (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/Co<sub>3</sub>O<sub>4-x</sub> (x = o, t, c) (Fig. 1d, h and l) are 0.23 nm, corresponding to the (111) planes of Pt. N<sub>2</sub> adsorption–desorption experiments indicate that the Brunauer–Emmett–Teller (BET) surface areas of Pt/Co<sub>3</sub>O<sub>4-o</sub>, Pt/Co<sub>3</sub>O<sub>4-t</sub>, and Pt/Co<sub>3</sub>O<sub>4-c</sub> are 2.4, 3.4, and 3.4 m<sup>2</sup> g<sup>-1</sup>, respectively, indicating similar surface areas (Table S1).

X-ray diffraction (XRD) was used to investigate the crystal structures of Co<sub>3</sub>O<sub>4-x</sub> and Pt/Co<sub>3</sub>O<sub>4-x</sub> (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 Co<sub>3</sub>O<sub>4</sub>, respectively (PDF#43-1003). The intensity ratio of the (111) to (400) peaks for Co<sub>3</sub>O<sub>4-x</sub> (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 Co<sub>3</sub>O<sub>4-x</sub> (x = o, t, c) supports, the Pt-loaded counterparts (Pt/Co<sub>3</sub>O<sub>4-x</sub>) 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 Co<sub>3</sub>O<sub>4</sub> 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/Co<sub>3</sub>O<sub>4-o</sub>, -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 Co<sub>3</sub>O<sub>4-x</sub> and Pt/Co<sub>3</sub>O<sub>4-x</sub> (x = o, t, c), respectively. The peaks at ~780.2 and 795.4 eV are assigned to Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub>, respectively. The peaks of Co 2p<sub>3/2</sub> can be deconvoluted into two peaks at ~780.0 and 781.4 eV, indicating the coexistence of Co<sup>3+</sup> and Co<sup>2+</sup>.<sup>29</sup> Notably, compared to the pristine Co<sub>3</sub>O<sub>4-x</sub> (x = o, t, c) supports, the Pt-loaded counterparts (Pt/Co<sub>3</sub>O<sub>4-x</sub>) with the same morphologies show an

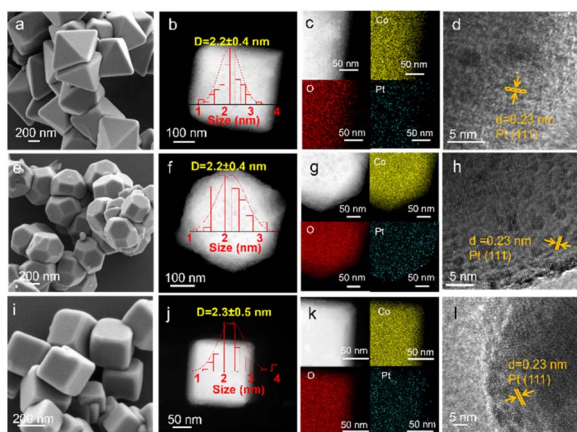


Fig. 1 (a, e, and i) SEM images, (b, f and j) HAADF-STEM images, (c, g, and k) STEM-EDS elemental mappings, and (d, h, and l) HRTEM images of Pt/Co<sub>3</sub>O<sub>4-o</sub>, Pt/Co<sub>3</sub>O<sub>4-t</sub>, and Pt/Co<sub>3</sub>O<sub>4-c</sub>, respectively.

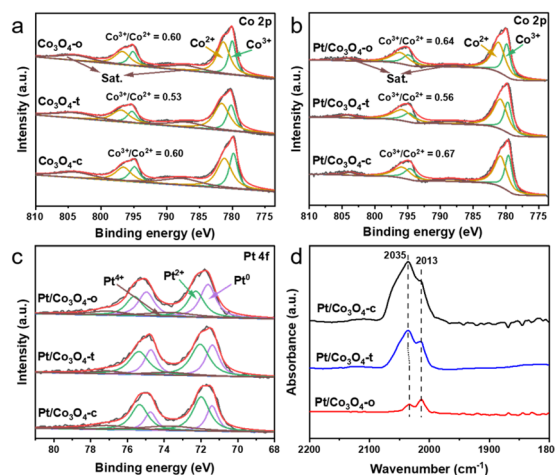


Fig. 2 XPS spectra of Co 2p for (a) Co<sub>3</sub>O<sub>4-x</sub> and (b) Pt/Co<sub>3</sub>O<sub>4-x</sub> (x = o, t, c). (c) XPS spectra of Pt 4f and (d) CO-DRIFTS spectra for Pt/Co<sub>3</sub>O<sub>4-x</sub> (x = o, t, c).



increase in the  $\text{Co}^{3+}/\text{Co}^{2+}$  ratio, implying the transfer of electrons from Co to Pt.<sup>30</sup> Moreover, the XPS spectra of Pt 4f for Pt/ $\text{Co}_3\text{O}_4$ -x (x = o, t, c) show two peaks located at  $\sim 71.7$  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  $\text{Pt}^0$ ,  $\text{Pt}^{2+}$ , and  $\text{Pt}^{4+}$ .<sup>31</sup> The fitting results reveal that the  $\text{Pt}^0$  content follows the order: Pt/ $\text{Co}_3\text{O}_4$ -o (44.7%) > Pt/ $\text{Co}_3\text{O}_4$ -t (39.4%) > Pt/ $\text{Co}_3\text{O}_4$ -c (26.1%) (Table S3), suggesting the differentiated electronic states of Pt nanoparticles with varied  $\text{Co}_3\text{O}_4$  facets. To gain insight into the state of Pt under reaction conditions, quasi-in situ XPS analysis was performed after  $\text{H}_2$  treatment at  $40^\circ\text{C}$ . Intriguingly, although the  $\text{Pt}^0$  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/ $\text{Co}_3\text{O}_4$ -x (x = o, t, c), as shown in Fig. 2d. Two absorption bands observed at  $2033$ – $2035$  and  $2013$   $\text{cm}^{-1}$  are assigned to the linear absorption of CO on the terrace and step sites of Pt nanoparticles, respectively.<sup>32</sup> Compared to the Pt/ $\text{Co}_3\text{O}_4$ -t and Pt/ $\text{Co}_3\text{O}_4$ -c, the CO adsorption peak at the terrace sites of Pt/ $\text{Co}_3\text{O}_4$ -o shifts to a lower wavenumber (from  $2035$  to  $2033$   $\text{cm}^{-1}$ ). Additionally, the relative intensity of the CO signal adsorbed at the step sites follows the order: Pt/ $\text{Co}_3\text{O}_4$ -o > Pt/ $\text{Co}_3\text{O}_4$ -t > Pt/ $\text{Co}_3\text{O}_4$ -c. These results suggest that the Pt species on Pt/ $\text{Co}_3\text{O}_4$ -o surfaces are in a lower valence state,<sup>33</sup> 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 ( $\text{H}_2$ -TPR) was carried out to investigate the reducibility of  $\text{Co}_3\text{O}_4$ -x and Pt/ $\text{Co}_3\text{O}_4$ -x (x = o, t, c), as shown in Fig. 3a and b.  $\text{H}_2$ -TPR profiles show no reduction peak below  $100^\circ\text{C}$  for any Pt/ $\text{Co}_3\text{O}_4$ -x catalyst, confirming the metallic state ( $\text{Pt}^0$ ) 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  $\text{Co}_3\text{O}_4$  support. The shift to lower temperatures (by  $\sim 50^\circ\text{C}$ ) compared to bare  $\text{Co}_3\text{O}_4$  demonstrates that metallic  $\text{Pt}^0$  promotes support reduction *via* hydrogen spillover.<sup>34,35</sup>

To detect spilled hydrogen, hydrogen temperature-programmed desorption coupled with mass spectrometry ( $\text{H}_2$ -TPD-MS) measurements of Pt/ $\text{Co}_3\text{O}_4$ -x were performed. As shown in Fig. 3c and S5, the MS signals reveal that the major desorption products are  $\text{H}_2\text{O}$  ( $m/z = 18$ ) and OH species ( $m/z = 17$ ), with no significant molecular  $\text{H}_2$  ( $m/z = 2$ ) detected. This indicates that active hydrogen species generated on  $\text{Pt}^0$  sites spill over onto the  $\text{Co}_3\text{O}_4$  support and react with lattice oxygen to form surface hydroxyl groups, which subsequently recombine and decompose upon heating.<sup>36,37</sup> 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

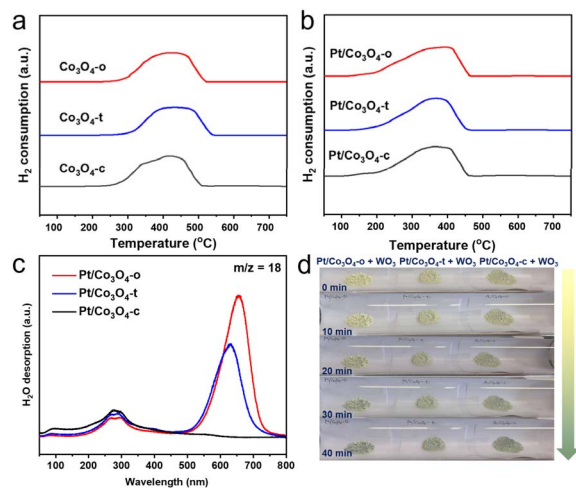


Fig. 3  $\text{H}_2$ -TPR profiles of (a) the as-prepared  $\text{Co}_3\text{O}_4$ -x and (b) Pt/ $\text{Co}_3\text{O}_4$ -x (x = o, t, c) catalysts. (c)  $\text{H}_2$ -TPD profiles of the as-prepared Pt/ $\text{Co}_3\text{O}_4$ -x (x = o, t, c). (d) Photographs of samples made with  $\text{WO}_3$  (300 mg) mixed with the Pt/ $\text{Co}_3\text{O}_4$ -x (x = o, t, c) catalysts (1 mg) before treatment and after treatment with 10%  $\text{H}_2/\text{Ar}$  at  $25^\circ\text{C}$  for different times.

lattice. Critically, the intensity of the high-temperature peak follows the order: Pt/ $\text{Co}_3\text{O}_4$ -o > Pt/ $\text{Co}_3\text{O}_4$ -t > Pt/ $\text{Co}_3\text{O}_4$ -c. This provides direct evidence that the (111) facet of  $\text{Co}_3\text{O}_4$  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/ $\text{Co}_3\text{O}_4$ -x catalysts and 300 mg of  $\text{WO}_3$  nanowires, the original color of the mixtures is light yellow. After being exposed to hydrogen atmosphere, the mixture of Pt/ $\text{Co}_3\text{O}_4$ -o and  $\text{WO}_3$  exhibits the most pronounced color change within 40 minutes, implying the strongest hydrogen spillover effect over Pt/ $\text{Co}_3\text{O}_4$ -o. This result aligns with the  $\text{H}_2$ -TPD-MS data and is attributed to the stronger metal-support interaction in Pt/ $\text{Co}_3\text{O}_4$ -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/ $\text{Co}_3\text{O}_4$ -x (x = o, t, c) for 4-NP hydrogenation

The catalytic performance of Pt/ $\text{Co}_3\text{O}_4$ -x (x = o, t, c) was evaluated by the 4-NP reduction. The reduction process using  $\text{H}_2$  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-aminobenzol (4-AP) (Fig. S8). Among the Pt/ $\text{Co}_3\text{O}_4$ -o, Pt/ $\text{Co}_3\text{O}_4$ -t, and Pt/ $\text{Co}_3\text{O}_4$ -c catalysts, the Pt/ $\text{Co}_3\text{O}_4$ -o exhibited the shortest reaction time with nearly 100% conversion (Fig. S9). Furthermore, Fig. 4d shows a logarithmic plot of the



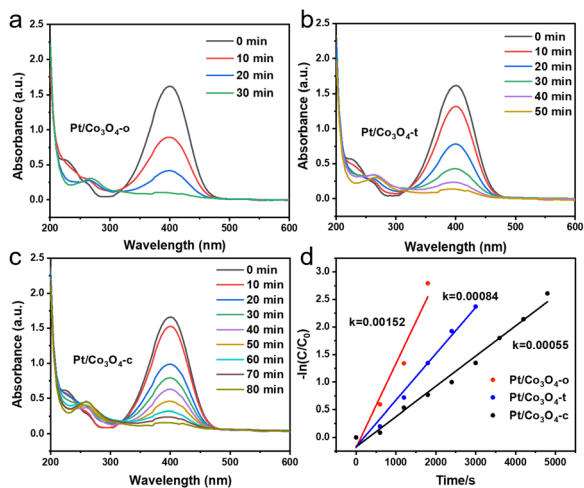


Fig. 4 Time-dependent UV-vis spectra of 4-NP reduced by (a) Pt/Co<sub>3</sub>O<sub>4</sub>-o, (b) Pt/Co<sub>3</sub>O<sub>4</sub>-t, and (c) Pt/Co<sub>3</sub>O<sub>4</sub>-c. (d) The kinetics plots of  $-\ln(C_t/C_0)$  against the reaction time for the reduction of 4-NP over different Pt/Co<sub>3</sub>O<sub>4</sub>-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 ( $\ln(C_t/C_0) = -k_{app}t$ ).<sup>38</sup> Compared to the Pt/Co<sub>3</sub>O<sub>4</sub>-t and Pt/Co<sub>3</sub>O<sub>4</sub>-c catalysts ( $8.4 \times 10^{-4}$  and  $5.5 \times 10^{-4} \text{ s}^{-1}$ , respectively), the Pt/Co<sub>3</sub>O<sub>4</sub>-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 Co<sub>3</sub>O<sub>4</sub> 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/Co<sub>3</sub>O<sub>4</sub>-o ( $164.2 \text{ h}^{-1}$ ) > Pt/Co<sub>3</sub>O<sub>4</sub>-t ( $115.2 \text{ h}^{-1}$ ) > Pt/Co<sub>3</sub>O<sub>4</sub>-c ( $75.6 \text{ h}^{-1}$ ) (Table S4). Subsequently, the apparent activation energy ( $E_a$ ) experiment was performed (Fig. S11). The  $E_a$  values follow the order: Pt/Co<sub>3</sub>O<sub>4</sub>-o ( $23.0 \text{ kJ mol}^{-1}$ ) < Pt/Co<sub>3</sub>O<sub>4</sub>-t ( $25.3 \text{ kJ mol}^{-1}$ ) < Pt/Co<sub>3</sub>O<sub>4</sub>-c ( $55.2 \text{ kJ mol}^{-1}$ ). The significantly lower  $E_a$  for Pt/Co<sub>3</sub>O<sub>4</sub>-o accounts for its superior catalytic activity. More importantly, we establish a quantitative correlation between the Co<sub>3</sub>O<sub>4</sub>(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/Co<sub>3</sub>O<sub>4</sub>-o > Pt/Co<sub>3</sub>O<sub>4</sub>-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 Co<sub>3</sub>O<sub>4</sub> supports.

The Pt/Co<sub>3</sub>O<sub>4</sub>-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 Co<sub>3</sub>O<sub>4</sub> 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/Co<sub>3</sub>O<sub>4</sub>-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/Co<sub>3</sub>O<sub>4</sub>-o demonstrates a competitive turnover frequency ( $164.2 \text{ h}^{-1}$ ) under an exceptionally mild condition ( $40 \text{ }^\circ\text{C}$ ,  $1 \text{ bar H}_2$ ). Many reported systems require significantly higher H<sub>2</sub> 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/Co<sub>3</sub>O<sub>4</sub>-o, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was first used to investigate the adsorption behavior of 4-NP on Pt/Co<sub>3</sub>O<sub>4</sub>-o and Pt/Co<sub>3</sub>O<sub>4</sub>-c as model catalysts, as shown in Fig. S19. The spectra of Pt/Co<sub>3</sub>O<sub>4</sub>-o and Pt/Co<sub>3</sub>O<sub>4</sub>-c show two bands at  $1578$  and  $1316 \text{ cm}^{-1}$ , corresponding to asymmetric stretching and symmetric stretching vibrations of the nitro group, respectively.<sup>39</sup> Compared with the Pt/Co<sub>3</sub>O<sub>4</sub>-c catalyst, Pt/Co<sub>3</sub>O<sub>4</sub>-o exhibits a weaker peak intensity at  $1578 \text{ cm}^{-1}$ , suggesting a weaker adsorption capability for the nitro group. Further, the adsorption and activation capability of Pt/Co<sub>3</sub>O<sub>4</sub>-o and Pt/Co<sub>3</sub>O<sub>4</sub>-c for 4-NP and H<sub>2</sub> 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/Co<sub>3</sub>O<sub>4</sub>-o (0.81) than for Pt/Co<sub>3</sub>O<sub>4</sub>-c (0.75), implying that it is more difficult for Pt/Co<sub>3</sub>O<sub>4</sub>-o to activate the nitro group. This is consistent with the result of DRIFTS. For the adsorption and activation of H<sub>2</sub> (Fig. 5b), the reaction order of Pt/Co<sub>3</sub>O<sub>4</sub>-o (0.41) is lower than that of Pt/Co<sub>3</sub>O<sub>4</sub>-c (0.53), indicating that it is easier for Pt/Co<sub>3</sub>O<sub>4</sub>-o to activate H<sub>2</sub>.

To gain theoretical insight, DFT calculations were conducted. Pt<sub>4</sub> clusters supported on Co<sub>3</sub>O<sub>4</sub>-(111) and Co<sub>3</sub>O<sub>4</sub>-(100) (labeled as Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(111) and Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(100), respectively) were constructed to mimic the Pt/Co<sub>3</sub>O<sub>4</sub>-o and Pt/Co<sub>3</sub>O<sub>4</sub>-c catalysts based on the distinct exposed facets of Co<sub>3</sub>O<sub>4</sub> supports: the octahedral Co<sub>3</sub>O<sub>4</sub>-o predominantly exposes the (111) facet, whereas the cubic Co<sub>3</sub>O<sub>4</sub>-c preferentially exposes the (100) facet (Fig. S20a and b). First, when Pt<sub>4</sub> clusters were anchored on different Co<sub>3</sub>O<sub>4</sub> model surfaces, the electron transfer from Co<sub>3</sub>O<sub>4</sub> to Pt<sub>4</sub> was about  $-1.65|e|$  for Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(111) and  $-0.74|e|$  for Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(100), respectively (Fig. S20c and d, Table S7). The



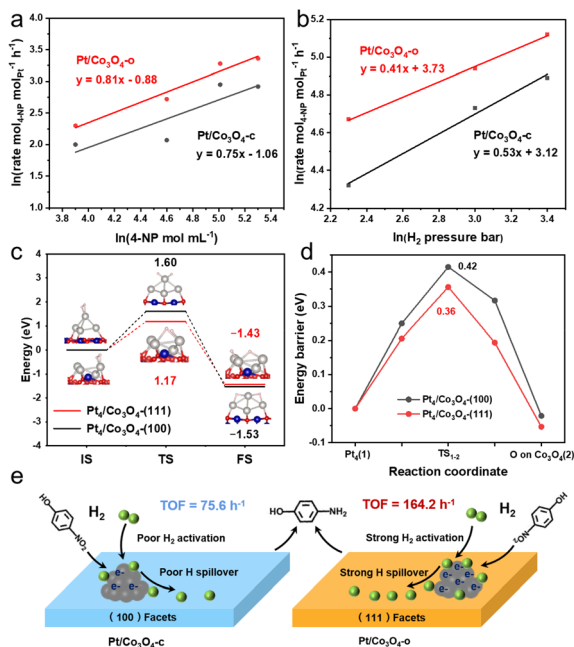


Fig. 5 Kinetic experiments of 4-NP hydrogenation over the Pt/Co<sub>3</sub>O<sub>4</sub>-o and Pt/Co<sub>3</sub>O<sub>4</sub>-c catalysts: the reaction order for (a) 4-NP and (b) H<sub>2</sub>. The reaction rates were determined at conversions below 30%. (c) Potential energy profiles of H<sub>2</sub> dissociation on the Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(100) and Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(111) model surfaces. (d) Potential energy profiles for hydrogen atom migration from Pt<sub>4</sub> to Co<sub>3</sub>O<sub>4</sub> across the interface on the Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(100) and Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(111) model surfaces. (e) Schematic illustration of possible mechanisms on Pt/Co<sub>3</sub>O<sub>4</sub>-c and Pt/Co<sub>3</sub>O<sub>4</sub>-o for 4-NP hydrogenation.

charge density differences indicate that more electrons transfer from Co<sub>3</sub>O<sub>4</sub> to Pt for Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(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 Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(111) and Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(100) surfaces. The adsorption energy results presented in Fig. S21e indicate that the Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(111) exhibits the weaker capability for facilitating the nitro group activation. Further, Fig. 5c reveals the adsorption and activation of H<sub>2</sub> on the Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(111) and Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(100) surfaces, in which the energy barrier (1.17 eV) of H<sub>2</sub> dissociation on Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(111) is lower than that on Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(100) (1.6 eV), implying that the activation of H<sub>2</sub> by Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(111) is easier. These results are consistent with the kinetics results. Furthermore, for hydrogen-atom migration from Pt to Co<sub>3</sub>O<sub>4</sub> across the interface, the energy barrier on the Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(111) (0.36 eV) is lower than that on the Pt<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>-(100) (0.42 eV), indicating kinetically more favourable hydrogen spillover on Co<sub>3</sub>O<sub>4</sub>-(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, H<sub>2</sub> activation ability, as well as active hydrogen spillover.<sup>40,41</sup> With Pt/Co<sub>3</sub>O<sub>4</sub>-o and Pt/Co<sub>3</sub>O<sub>4</sub>-c as model catalysts, the kinetic experiments and DFT calculations illustrate that compared with Pt/Co<sub>3</sub>O<sub>4</sub>-c, the adsorption/activation of 4-NP on the Pt/Co<sub>3</sub>O<sub>4</sub>-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/Co<sub>3</sub>O<sub>4</sub>-o has a stronger H<sub>2</sub> dissociation ability and lower hydrogen-migration barrier. The accelerated hydrogen dissociation on electron-rich Pt sites, coupled with enhanced hydrogen spillover to the Co<sub>3</sub>O<sub>4</sub> support, establishes a dynamic hydrogen supply chain that maximizes the utilization of active hydrogen species. The 4-NP adsorbed on Pt or near Pt-Co<sub>3</sub>O<sub>4</sub> 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/Co<sub>3</sub>O<sub>4</sub>-x (x = o, t, c) catalysts with tailored Co<sub>3</sub>O<sub>4</sub> crystal facets have been successfully constructed for the hydrogenation of 4-nitrophenol. Owing to the crystal facet effect, the Pt nanoparticles in Pt/Co<sub>3</sub>O<sub>4</sub>-o are more negatively charged than those in Pt/Co<sub>3</sub>O<sub>4</sub>-c and Pt/Co<sub>3</sub>O<sub>4</sub>-t, and Pt/Co<sub>3</sub>O<sub>4</sub>-o exhibits the strongest hydrogen spillover capability. For the 4-nitrophenol (4-NP) hydrogenation reaction, the Pt/Co<sub>3</sub>O<sub>4</sub>-o has the best catalytic activity with a TOF value of 164.2 h<sup>-1</sup>. 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/Co<sub>3</sub>O<sub>4</sub>-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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