



# Heterogeneous catalytic aldehyde-water shift of benzaldehyde into benzoic acid and hydrogen

Xinying Meng<sup>1,†</sup>, Biwei Yan<sup>1,†</sup>, Zening Qi<sup>2</sup>, Min Xie<sup>2</sup>, Yuanyuan Ma<sup>1</sup>, Fangxian Cao<sup>3,\*</sup>, Yongquan Qu<sup>1,\*</sup>

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CeO<sub>2</sub>, Pt, aldehyde-water shift reaction, heterogeneous catalysis, H<sub>2</sub> production

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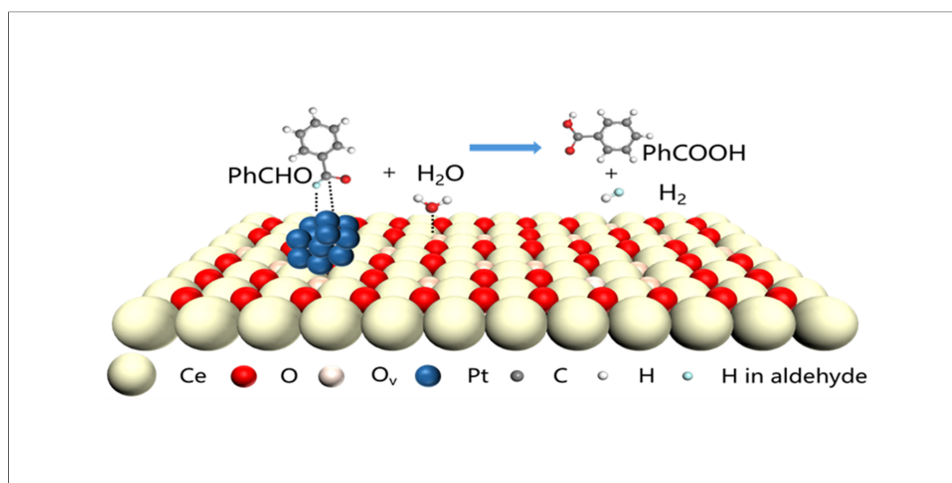
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## Abstract

The “aldehyde-water shift” (AWS) reaction offers a green and sustainable route for producing carboxylic acids with the concomitant release of hydrogen. However, most current AWS processes rely on homogeneous noble metal-based catalysts, facing significant challenges in the separation and recyclability of catalysts. Herein, we present the Pt nanoparticles deposited on highly defective porous CeO<sub>2</sub> nanorods (Pt/PN-CeO<sub>2</sub>) as highly effective catalysts for the production of carboxylic acids and H<sub>2</sub> through the AWS reaction. Isotope investigations have confirmed the occurrence of AWS by tracing the origin of the generated hydrogen with one hydrogen from aldehyde and one hydrogen from water. Further mechanism studies have illustrated that the concentration of oxygen vacancies plays a crucial role in both the activation of the C–H bond in aldehydes and the activation of water. These findings provide valuable insights for designing new catalytic systems by focusing on the construction of heterogeneous catalysts for the AWS reaction.

<sup>1</sup>Key Laboratory of Special Functional and Smart Polymer Materials of Ministry of Industry and Information Technology, School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, Xi'an 710072, Shaanxi, China.

<sup>2</sup>Xi'an Yiwei Putai Environmental Protection Co., LTD, Xi'an 710075, Shaanxi, China.

<sup>3</sup>Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, Yunnan, China.

<sup>†</sup>Authors contributed equally.

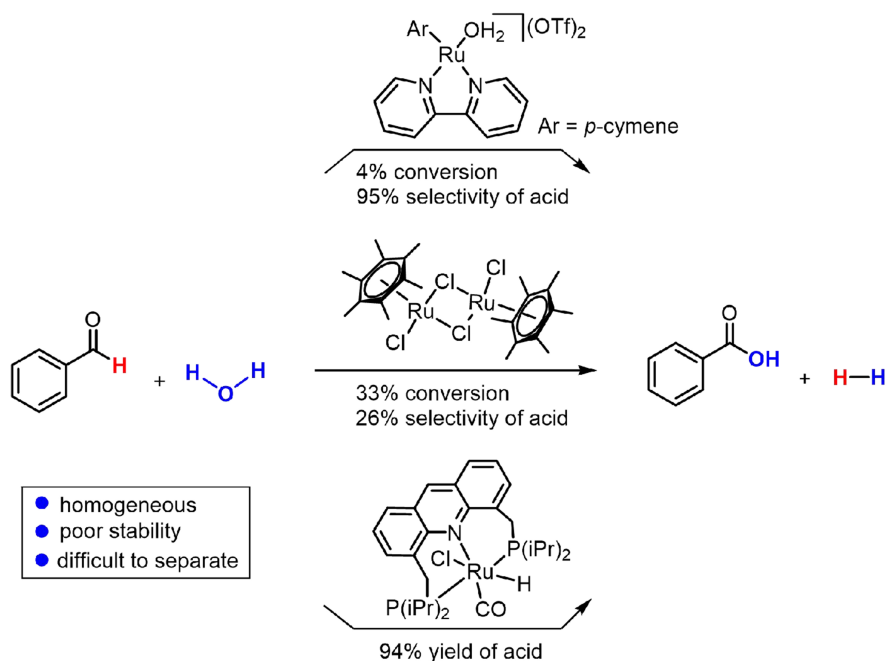
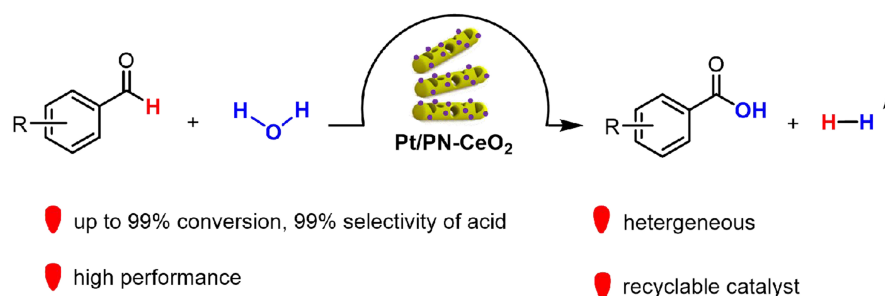
\***Correspondence to:** Prof. Yongquan Qu, Key Laboratory of Special Functional and Smart Polymer Materials of Ministry of Industry and Information Technology, School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, Xi'an 710072, Shaanxi, China. E-mail: yongquan@nwpu.edu.cn; Prof. Fangxian Cao, Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, Yunnan, China, E-mail: cfx\_kust@163.com

## INTRODUCTION

The catalytic dehydrogenation of aldehydes and water into carboxylic acids alongside hydrogen generation represents an atom-economical approach in chemical synthesis<sup>[1-9]</sup>. This transformation, known as the “aldehyde-water shift” (AWS) reaction, has garnered recognition as a green and sustainable approach for the production of various carboxylic acids<sup>[10-12]</sup>. However, the AWS reaction faces thermodynamic challenges due to the high energy nature of H<sub>2</sub> and the high chemical stability of C–H bonds<sup>[13]</sup>. Thus, the pivotal step toward overcoming these obstacles lies in the development of highly efficient catalysts for the AWS reaction. Recently, homogeneous catalysts of metal-based complexes [e.g., iridium, rhodium, ruthenium, platinum (Pt), and copper] have demonstrated their ability to effectively initiate the AWS reaction in the presence of various additives and/or cocatalysts<sup>[14-19]</sup> [Figure 1A]. However, those homogeneous catalysts generally face two significant drawbacks: difficulty in separation and poor recyclability. Consequently, there is an urgent demand to develop high activity and stability heterogeneous catalysts for the AWS reaction. Recently, sporadic yet promising advances have been achieved in developing heterogeneous catalysts, such as copper-based metal oxide and layered double hydroxides (LDH), which have facilitated hydrogen production through the AWS reaction for several active compounds with an aldehyde group (*N,N*-dimethylformamide, formaldehyde, and furfural)<sup>[20-23]</sup>. The Pt/re-Mg<sub>4</sub>Al-LDHs catalysts exhibited remarkable catalytic capability for the selective oxidation of furfural into furoic acid, achieving a conversion rate of 99% and a yield of 97%<sup>[22]</sup>. In this process, the Pt<sup>δ+</sup> sites served as the sites for adsorption and activation of the C=O bond, facilitating the production of H<sub>2</sub>. The Co@CoO heterointerface catalysts delivered a high performance of formaldehyde reforming, in which the Co and CoO components functioned as sites for the activation of C–H and O–H bonds, respectively<sup>[21]</sup>. The pursuit of highly performed heterogeneous catalysts for AWS reaction, capable of producing carboxylic acid and H<sub>2</sub>, remains a highly desirable goal.

Benzoic acid, an important organic compound, has widespread applications in drug synthesis, dye production, bactericides, *etc.*<sup>[24-29]</sup>. Conventionally, carboxylic acids, including benzoic acid, are synthesized through oxidation of alcohol, which involved stoichiometric quantities of harsh oxidants such as acidic potassium permanganate, chromates and hydrogen peroxide<sup>[30]</sup>. However, these traditional oxidation processes often suffer from low atom economy, challenges in the post-reaction treatments, and severe environmental contamination. Consequently, there has been a concerted effort to develop catalytic oxidation routes for the production of benzoic acid, aiming for milder conditions and greater environmental compatibility<sup>[13]</sup>. Inspired by myriad advantages of AWS, the benzaldehyde water shift reaction emerges as a promising alternative to the conventional approach for the eco-friendly synthesis of benzoic acid.

The synergistic and effective co-activation of both the C–H bond in the aldehyde group and the O–H bond in H<sub>2</sub>O are prerequisites for enhancing the performance of AWS. Inspired by the exceptional capability of Pt in activation of C–H bonds<sup>[31-33]</sup> and efficacy of defective CeO<sub>2-x</sub> in the activation of water<sup>[34-37]</sup>, herein, the Pt nanoparticles deposited on highly defective porous CeO<sub>2</sub> nanorods (Pt/PN-CeO<sub>2</sub>) have been rationally designed for the efficiently catalytic AWS reaction of benzaldehyde into benzoic acid, accompanied with the release of hydrogen with high purity [Figure 1B and Figure 2A]. Extensive investigations into the catalytic mechanism have revealed that structural defects of oxygen vacancies (O<sub>v</sub>) play a pivotal role in enhancing the performance of Pt/PN-CeO<sub>2</sub> for the AWS reactions. A high concentration of O<sub>v</sub> not only facilitates the activation of water but also enhances the electron density of Pt. Consequently, this leads to improved activation of the C–H bond in aldehydes. Taking benzaldehyde as a substrate, Pt/PN-CeO<sub>2</sub> delivered remarkable catalytic activity, achieving a benzaldehyde conversion of 99.8% and a benzoic acid selectivity of 99.6%, with a H<sub>2</sub> yield of 85.9%. This innovative approach holds significant promise for the synthesis of benzoic acid and can be extended to catalyze a scope of aldehydes possessing a -CHO group, suggesting its versatility and potential for industrial applications.

**A) Previous work: The AWS of benzaldehyde catalyzed by homogeneous process****B) This work: The AWS of benzaldehyde and derivatives catalyzed by Pt/PN-CeO<sub>2</sub>**

**Figure 1.** (A) The AWS of benzaldehyde catalyzed by homogeneous process; (B) The AWS of benzaldehyde and derivatives catalyzed by Pt/PN-CeO<sub>2</sub>. AWS: Aldehyde-water shift.

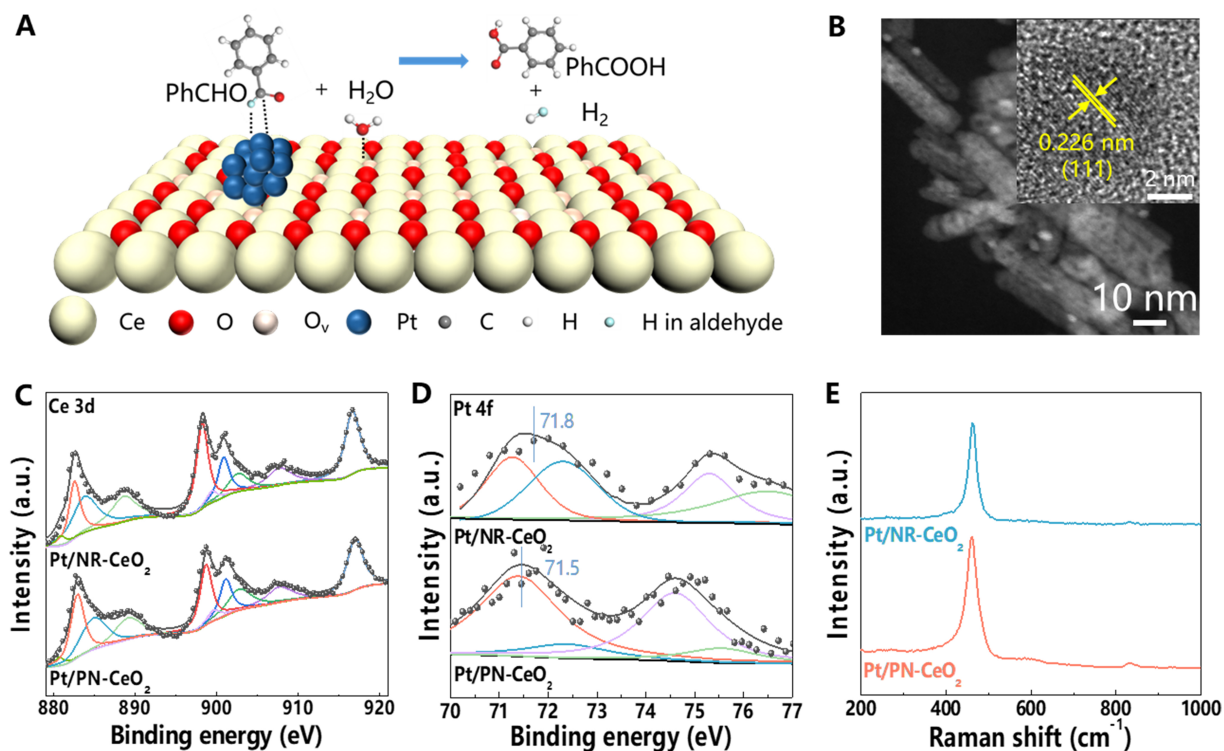
## EXPERIMENTAL

### Preparation of catalysts

A hydrothermal approach was adopted to synthesize both nanorods of CeO<sub>2</sub> (NR-CeO<sub>2</sub>) and porous nanorods of CeO<sub>2</sub> (PN-CeO<sub>2</sub>). Details of the synthesis could be found in our previous reports<sup>[38,39]</sup>. Preparation of Pt/NR-CeO<sub>2</sub> and Pt/PN-CeO<sub>2</sub> underwent a facile impregnation method. Typically, the CeO<sub>2</sub> supports (300 mg) were dispersed in ethanol (30 mL). Then, the desired amount of the aqueous K<sub>2</sub>PtCl<sub>4</sub> solution was added into suspension of the CeO<sub>2</sub>. The solution was stirred for 2 h, and then evaporated at 80 °C. The resulting powder was reduced by a flow of 5 vol% H<sub>2</sub>/Ar at 350 °C for 2 h.

### Characterizations of catalysts

Transmission electron microscope (TEM) characterizations were performed on a JEOL2100F operated. The high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed with a FEI Tecnai F30 microscope (300 kV). X-ray photoelectron spectroscopy (XPS) profiles of various catalysts were analyzed by Thermo Electron Model K-Alpha. The loadings of Pt in various catalysts were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES). The Raman spectra were acquired from an Alpha300R micro-confocal Raman spectrometer.



**Figure 2.** (A) Proposed catalytic process of the Pt/PN-CeO<sub>2</sub> for the AWS reaction of benzaldehyde into benzoic acid and H<sub>2</sub> at the interface between Pt and PN-CeO<sub>2</sub>; (B) Dark-field TEM of Pt/PN-CeO<sub>2</sub> (the insert was the high-resolution dark-field TEM images); XPS analysis of (C) Ce 3d and (D) Pt 4f peaks of Pt/PN-CeO<sub>2</sub> and Pt/NR-CeO<sub>2</sub>; (E) Raman spectra of the Pt/PN-CeO<sub>2</sub> and Pt/NR-CeO<sub>2</sub> catalysts. AWS: Aldehyde-water shift; TEM: transmission electron microscope; XPS: X-ray photoelectron spectroscopy.

### Catalytic AWS reaction

First, 30 mg of catalysts and 1 mmol of benzaldehyde were mixed in a solution of 1, 4-dioxane (1 mL) and H<sub>2</sub>O (0.5 mL) in the presence of various amounts of strong base NaOH. The reaction solution was degassed by bubbling N<sub>2</sub> in a 30 mL autoclave. Then, 0.5 MPa of N<sub>2</sub> was inflated in the autoclave. The temperature of the reaction system quickly increased to 180 °C. After the catalytic reaction was performed for 10 h, the reactor was allowed to cool naturally. A gas sampling bag was used to collect the gas, which was tested by gas chromatography (GC) equipped with a thermal conductivity detector (TCD, North Point GC 901A). Benzaldehyde, benzoic acid, and benzyl alcohol were detected using liquid chromatography (LC, Fuli LC 5090).

## RESULTS AND DISCUSSION

### Synthesis and characterizations of catalysts

NR-CeO<sub>2</sub> and PN-CeO<sub>2</sub> were successfully synthesized through hydrothermal methods, as illustrated in our previous reports. The XRD patterns of both NR-CeO<sub>2</sub> and PN-CeO<sub>2</sub> clearly revealed a well-defined cubic fluorite structure of as-synthesized nanostructures [Supplementary Figure 1]. Dark-field TEM images displayed the nanorod-like characteristics of NR-CeO<sub>2</sub> and the porous nanorod-like characteristics of PN-CeO<sub>2</sub>, respectively [Supplementary Figure 2A and B]. High-resolution TEM images of NR-CeO<sub>2</sub> and PN-CeO<sub>2</sub> [Supplementary Figure 2C and D] exhibited that the predominant crystal face in both NR-CeO<sub>2</sub> and PN-CeO<sub>2</sub> was CeO<sub>2</sub>(110)<sup>[40]</sup>. Analysis of the XPS profiles indicated a significantly higher surface Ce<sup>3+</sup> fraction in PN-CeO<sub>2</sub> (29.2%) over that in NR-CeO<sub>2</sub> (19.8%), suggesting PN-CeO<sub>2</sub> owned higher levels of structural defects of O<sub>v</sub> [Supplementary Figure 3], aligning with our previous findings.

Subsequently, Pt nanoparticles with a theoretical loading of 2.0 wt.% were deposited onto the PN-CeO<sub>2</sub> and NR-CeO<sub>2</sub> via an impregnation process, yielding Pt/PN-CeO<sub>2</sub> and Pt/NR-CeO<sub>2</sub>. As analyzed by ICP-OES, the actual Pt contents in Pt/NR-CeO<sub>2</sub> and Pt/PN-CeO<sub>2</sub> were 1.86 wt.% and 1.89 wt.%, respectively. Dark-field TEM images [Figure 2B and Supplementary Figure 4] revealed that the sizes of Pt nanoparticles on Pt/NR-CeO<sub>2</sub> and Pt/PN-CeO<sub>2</sub> were about 2.15 and 1.83 nm, respectively. XRD patterns of Pt/NR-CeO<sub>2</sub> and Pt/PN-CeO<sub>2</sub> remained similar to the phase of CeO<sub>2</sub>, indicating the preserved cubic fluorite structure of CeO<sub>2</sub> during the synthesis process [Supplementary Figure 1]. Notably, no distinct XRD diffraction peaks for Pt were observed, attributable to the low loadings of Pt in the catalysts.

XPS and Raman spectroscopic analysis were used to further investigate surface properties of Pt/CeO<sub>2</sub>. Specifically, compared to Pt/NR-CeO<sub>2</sub> (Ce<sup>3+</sup> fraction of 20.9% and Ce<sup>3+</sup>-O fraction of 26.4%), Pt/PN-CeO<sub>2</sub> displayed a significantly higher fraction of Ce<sup>3+</sup> (30.7%) and Ce<sup>3+</sup>-O (44.5%), signifying a high concentration of O<sub>v</sub> in Pt/PN-CeO<sub>2</sub> [Figure 2C and Supplementary Figure 5]. Further delving into the electronic structures of Pt in these catalysts, XPS analysis of Pt 4f orbitals revealed a lower binding energy for Pt/PN-CeO<sub>2</sub>, suggesting a stronger metal-support interaction<sup>[39,41,42]</sup> [Figure 2D]. This strengthened interaction correlated with a higher proportion of Pt<sup>0</sup> in Pt/PN-CeO<sub>2</sub> (77.5%) as opposed to 68.6% in Pt/NR-CeO<sub>2</sub>.

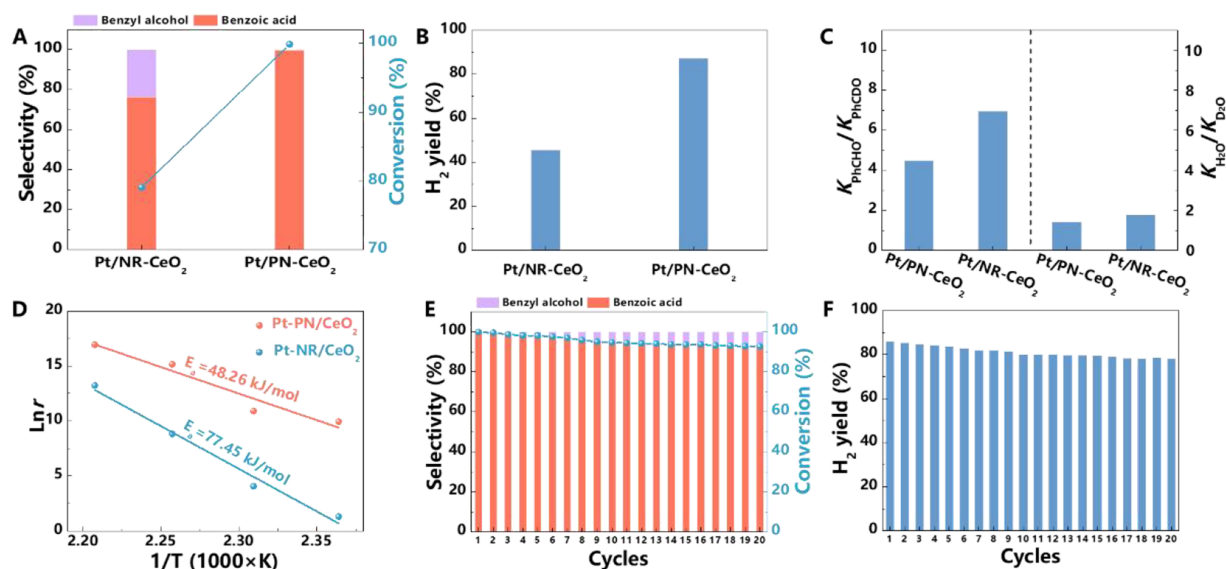
To complement these findings, Raman spectroscopy was used to assess the level of O<sub>v</sub> in Pt/CeO<sub>2</sub> [Figure 2E]. The prominent peak at 460 cm<sup>-1</sup> was attributed to the vibrational mode of the CeO<sub>2</sub> fluorite structure, while the weaker peak around 600 cm<sup>-1</sup> can be attributed to the O<sub>v</sub><sup>[43]</sup>. By calculating the peak area ratio of A<sub>600</sub>/A<sub>460</sub><sup>[44]</sup>, it was evident that Pt/PN-CeO<sub>2</sub> exhibited a higher value of 0.12 compared to 0.05 for Pt/NR-CeO<sub>2</sub>, definitively demonstrating a higher level of structural defects of O<sub>v</sub> in Pt/PN-CeO<sub>2</sub>.

### Catalytic performance

The AWS reaction of benzaldehyde was selected as a model reaction to investigate catalytic behaviors of Pt/CeO<sub>2</sub> catalysts. Initially, we optimized the molar ratio of benzaldehyde to H<sub>2</sub>O, along with the types and amounts of bases, while keeping the temperature at 180 °C and the N<sub>2</sub> pressure at 0.5 MPa [Supplementary Tables 1-3]. When 30 mg of Pt/PN-CeO<sub>2</sub> was used as the catalyst, the optimal conditions for the AWS reaction of benzaldehyde were found to be: 1 mmol of benzaldehyde as the substrate, 2.5 mmol of NaOH, a solvent mixture of 1,4-dioxane (1 mL) and H<sub>2</sub>O (0.5 mL), a temperature of 180 °C, and a pressure of 0.5 MPa N<sub>2</sub>. Under these optimal conditions, Pt/PN-CeO<sub>2</sub> exhibited the highest benzaldehyde conversion (99.8%), benzoic acid selectivity (99.6%), and H<sub>2</sub> yield (85.9%) over a period of 10 h [Figure 3A and B]. Furthermore, we screened the catalytic performance of various metals (Pt, Pd, Ru, *etc.*) deposited on PN-CeO<sub>2</sub> with similar metal loadings for the AWS reaction under the optimized conditions. Among them, Pt/PN-CeO<sub>2</sub> delivered the best catalytic performance [Supplementary Table 4].

### Kinetic investigations

Previously, Pt has been widely acknowledged as an effective catalyst for the activation of the C-H bonds<sup>[45,46]</sup>. Generally, the catalytic performance of metals can be significantly determined by their electronic structures. When the AWS reaction of benzaldehyde was performed under the optimal conditions, Pt/NR-CeO<sub>2</sub> with a 1.86 wt.% Pt loading delivered a much lower catalytic performance with a benzaldehyde conversion of 79.0%, a benzoic acid selectivity of 76.3% and a hydrogen yield of 39.1% [Figure 3A and B]. This can be attributed to the relatively lower electron density of Pt nanocatalysts on NR-CeO<sub>2</sub> than that of Pt on PN-CeO<sub>2</sub> [Figure 2D]. To further examine the roles of Pt nanocatalysts, H/D isotope experiments of benzaldehyde were conducted [Figure 3C]. By replacing benzaldehyde (PhCHO) with benzaldehyde- $\alpha$ -D (PhCDO), there was a significant decrease in both the conversions of benzaldehyde and the generation rates of H<sub>2</sub>. The value of  $k_{\text{PhCHO}}/k_{\text{PhCDO}}$  for Pt/NR-CeO<sub>2</sub> was 7.0, suggesting that the C-H bond activation was a rate-determining step of



**Figure 3.** Catalytic performance of Pt/PN-CeO<sub>2</sub> and Pt/NR-CeO<sub>2</sub> for the AWS of benzaldehyde. (A) Conversions of benzaldehyde and selectivity of benzyl alcohol and benzoic acid; (B) H<sub>2</sub> yields; (C) Ratios of H<sub>2</sub> generation rates from PhCHO to PhCDO as well as the ratios of H<sub>2</sub> generation rates from H<sub>2</sub>O to D<sub>2</sub>O; (D)  $Lnr$ , derived from the H<sub>2</sub> generation rate versus reaction time, as a function of  $1/T$  over various catalysts; (E) and (F) Catalytic stability of the Pt/PN-CeO<sub>2</sub> catalysts for the AWS reaction. Reaction conditions for (A), (B), (D), (E) and (F): PhCHO (1 mmol), H<sub>2</sub>O (0.5 mL), 1, 4-dioxane (1 mL), NaOH (2.5 mmol), catalysts (30 mg), 0.5 MPa N<sub>2</sub>, 180 °C and 10 h. Reaction conditions for (C): PhCHO/PhCDO (1 mmol), H<sub>2</sub>O/D<sub>2</sub>O (0.5 mL), 1, 4-dioxane (1 mL), NaOH (2.5 mmol), catalysts (30 mg), 0.5 MPa N<sub>2</sub>, 180 °C and 10 h. AWS: Aldehyde-water shift.

AWS of benzaldehyde. In contrast, Pt/PN-CeO<sub>2</sub> exhibited a much lower value of  $k_{\text{PhCHO}}/k_{\text{PhCDO}}$  of 4.5, indicating that Pt with a higher electronic density accelerated C-H cleavage.

The presence of O<sub>v</sub> in Pt/CeO<sub>2</sub> not only modulated electronic structures of Pt but also enhanced the activation of H<sub>2</sub>O to generate abundant surface hydroxyls, which facilitated the dehydrogenation of benzaldehyde and the production of H<sub>2</sub>. Then, H<sub>2</sub>O/D<sub>2</sub>O isotope experiments were conducted to assess contributions of O<sub>v</sub> for water activation [Figure 3C]. When H<sub>2</sub>O was replaced with D<sub>2</sub>O, the decreased production rates of H<sub>2</sub> were observed for various Pt/CeO<sub>2</sub> catalysts. The value of  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$  for Pt/PN-CeO<sub>2</sub> was 1.4, slightly lower than that (1.8) for Pt/NR-CeO<sub>2</sub>. Comparing these values with the  $k_{\text{PhCHO}}/k_{\text{PhCDO}}$  ratios, it is evident that the dissociation of H<sub>2</sub>O is not a rate-determining step for AWS reaction of benzaldehyde. Lower impact of D<sub>2</sub>O on H<sub>2</sub> generation rates for Pt/PN-CeO<sub>2</sub> suggested that a higher surface concentration of O<sub>v</sub> delivered a higher capacity for the H<sub>2</sub>O activation.

Next, the reaction orders ( $n$ ) of two Pt/CeO<sub>2</sub> catalysts were investigated to gain insights into their catalytic activity, particularly examining how the substrate coverage at active sites affected the performance of catalysts<sup>[47,48]</sup>. The positive  $n$  values<sup>[49]</sup> with respect to benzaldehyde further implied that activation of C–H bond in benzaldehyde was kinetically relevant step in AWS reaction, typically occurring on the Pt surface. A low value of  $n$  generally indicates the kinetical difficulty for the accessibility of reactants to catalyst surface. Herein, Pt/PN-CeO<sub>2</sub> (0.91) exhibited a higher  $n$  value compared to Pt/NR-CeO<sub>2</sub> (0.85) at the similar Pt loading, demonstrating the better accessibility and catalytic activity of Pt/PN-CeO<sub>2</sub> for the benzaldehyde substrate [Supplementary Figure 6].

Kinetic analysis was then conducted to assess intrinsic catalytic capabilities of Pt/CeO<sub>2</sub> for the AWS reaction at different reaction temperatures. The experiments were conducted within a temperature range of 150 and 180 °C, ensuring that benzaldehyde conversions remained below 30% for all measurements [Figure 3D].

Reaction rate constant  $r$  was calculated from slope of the  $H_2$  generation rates at various reaction temperatures. Activation energy  $E_a$  was determined by slope of linear fit between logarithm of reaction rate constant ( $\ln r$ ) and the reciprocal of the absolute temperature ( $1/T$ ). The derived  $E_a$  value of Pt/PN-CeO<sub>2</sub> was 48.3 kJ·mol<sup>-1</sup>, lower than that of Pt/NR-CeO<sub>2</sub> (77.4 kJ·mol<sup>-1</sup>) [Figure 3D]. This indicated that Pt/PN-CeO<sub>2</sub> possessed a higher capability for catalyzing the AWS of benzaldehyde compared to Pt/NR-CeO<sub>2</sub>, as a lower  $E_a$  generally corresponded to a more favorable reaction pathway and faster reaction rates.

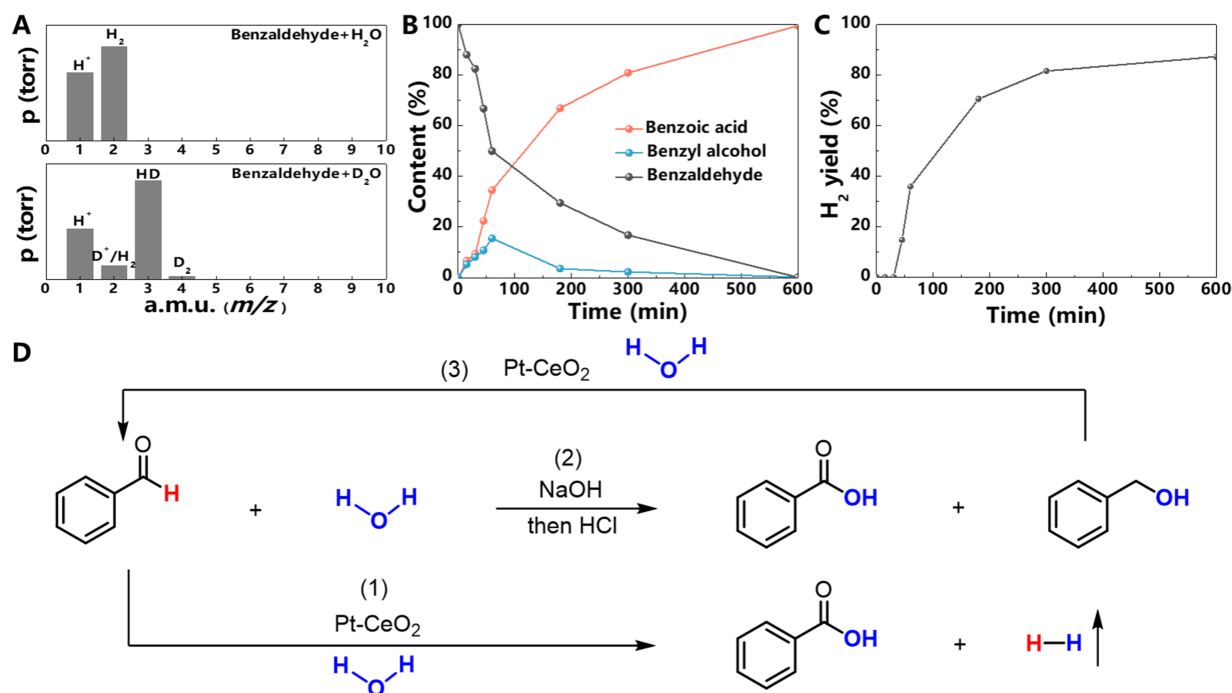
### Catalytic stability

Longer-term stability was conducted [Figure 3E and F]. Even after twenty cycles, there was only a slight decrease in benzaldehyde conversion, benzoic acid selectivity, and  $H_2$  yield, demonstrating the high catalytic stability of the catalysts. After the long-term cycling, there was a reduction in the surface Ce<sup>3+</sup> fraction to 29.8% along with a lower Ce<sup>3+</sup>-O fraction of 40.4% for the used Pt/PN-CeO<sub>2</sub> catalysts [Supplementary Figure 7A and B], compared to as-synthesized catalysts (a Ce<sup>3+</sup> fraction of 30.7% and a Ce<sup>3+</sup>-O fraction of 44.5%). Considering the pivotal role of O<sub>v</sub>, the slight decline in activity and selectivity could potentially be attributed to minimal catalyst loss, along with a slight reduction in the structural defects associated with O<sub>v</sub>. Additionally, morphology, phase and surface properties of the spent Pt/PN-CeO<sub>2</sub> remained well-preserved [Supplementary Figure 7C-E], further confirming the structural robustness of the catalysts.

### Catalytic mechanism

Based on the analysis provided, both Pt nanoparticles and O<sub>v</sub> play crucial roles in activation of the C-H bond and H<sub>2</sub>O. Catalytic activities of Pt/CeO<sub>2</sub> are influenced by varying concentrations of O<sub>v</sub>. As shown in Figure 2D, the higher fraction of Pt<sup>0</sup> in Pt/PN-CeO<sub>2</sub> suggested the increased electronic density of the Pt nanoparticles. The strong electronic metal-support interaction between Pt nanoparticles and PN-CeO<sub>2</sub> constructed more Pt<sup>δ-</sup>-O<sub>v</sub>-Ce<sup>3+</sup> interfacial sites, which was supported by the high concentration of surface defects (a high Ce<sup>3+</sup> fraction of 30.7% and a large Ce<sup>3+</sup>-O fraction of 44.5%) in Pt/PN-CeO<sub>2</sub>. The Pt<sup>δ-</sup>-O<sub>v</sub>-Ce<sup>3+</sup> interfacial sites are active for the C-H dehydrogenation via heterolytic cleavage, according to previous reports<sup>[50-52]</sup>. Moreover, defective CeO<sub>2</sub> has been reported to facilitate H<sub>2</sub>O dissociation<sup>[34,36,38]</sup>, leading to the production of a greater amount of reactive oxygen species, resulting in the acceleration of aldehyde oxidation on Pt/PN-CeO<sub>2</sub>.

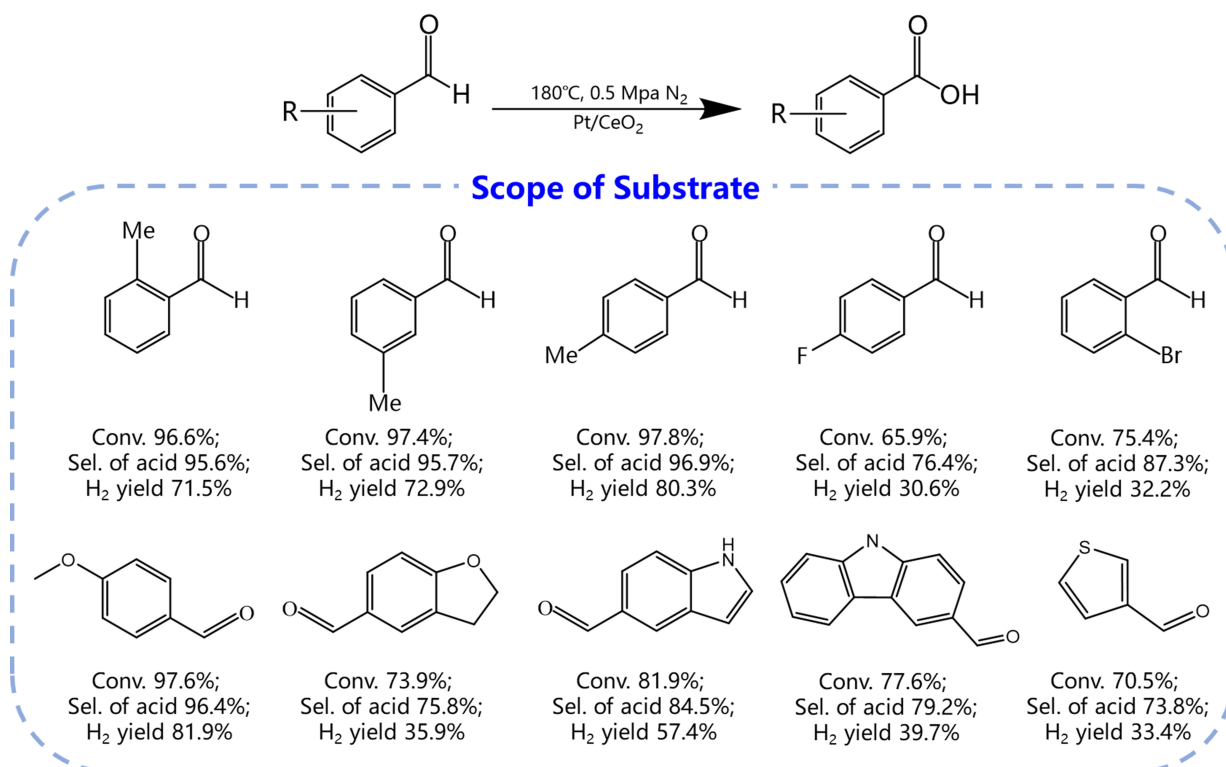
Then, to gain insight into the catalytic mechanism, the isotope experiments were carried out to confirm the origin of  $H_2$  production. By substituting H<sub>2</sub>O with D<sub>2</sub>O, gaseous and liquid products were analyzed by mass spectrometry (MS) and nuclear magnetic resonance hydrogen spectroscopy (<sup>1</sup>H NMR), respectively. When H<sub>2</sub>O was used, MS signals of generated gas were observed at  $m/z$  values of 2 and 1, corresponding to H<sub>2</sub> and H<sup>+</sup>, respectively [Figure 4A]. Comparatively, when D<sub>2</sub>O was utilized, the multiple MS signals were observed at  $m/z$  values ranging from 1 and 4, indicating the involvement of water in the AWS reaction. Notably, the dominant HD peak unambiguously suggested that two H atoms in the generated H<sub>2</sub> originated from water and benzaldehyde, respectively. Additionally, the MS signal at the  $m/z$  value of 4 was observed due to the H/D exchange between benzaldehyde and D<sub>2</sub>O. The <sup>1</sup>H NMR profile of liquid products after the AWS reaction between H<sub>2</sub>O and benzaldehyde gave a signal at approximately 12.3 ppm, which could be assigned to the -OH group of benzoic acid [Supplementary Figure 8]. In contrast, when D<sub>2</sub>O was used for the AWS reaction, the <sup>1</sup>H NMR signal at ~12.3 ppm disappeared, indicating the formation of PhCOOD instead of PhCOOH. These <sup>1</sup>H NMR results confirmed that the -OH group in benzoic acid originated from water. Through these isotope experiments, both the MS and <sup>1</sup>H NMR results provided the unequivocal evidence for the occurrence of the dehydrogenative coupling between water and benzaldehyde, leading to the production of benzoic acid and hydrogen with a high purity.



**Figure 4.** Catalytic mechanism. (A) MS analysis of  $H_2$  generated in the  $Pt/PN-CeO_2/H(D)_2O/benzaldehyde$  systems; (B) Distributions of reactants and products of the AWS of benzaldehyde catalyzed by  $Pt/PN-CeO_2$  at intervals during a period of 10 h; (C)  $H_2$  evolution profile with a time from the reaction mixture; (D) The illustration of benzaldehyde oxidation, benzyl alcohol oxidation, and the disproportionation of aldehyde over the  $Pt/PN-CeO_2$  catalysts. Reaction conditions: PhCHO (1 mmol),  $H_2O/D_2O$  (0.5 mL), 1, 4-dioxane (1 mL), NaOH (2.5 mmol), catalysts (30 mg), 180 °C and 10 h. MS: Mass spectrometry; AWS: aldehyde-water shift.

In principle, the AWS reaction involves one benzaldehyde molecule and one  $H_2O$  molecule to produce one benzoic acid molecule and one  $H_2$  molecule. However, the observed  $H_2$  yields for all catalysts were below this ideal scenario. To understand this phenomenon, both the liquid and gaseous products were monitored at intervals [Figure 4B and C]. Alongside the benzaldehyde dehydrogenative coupling with water to generate benzoic acid and  $H_2$ , the disproportionation of benzaldehyde also occurred to produce benzoic acid and benzyl alcohol. The disproportionation of benzaldehyde led to a quick consumption of aldehyde during the initial stage [Figure 4B]. As depicted in Figure 4C, no release of  $H_2$  was observed during the initial 30 min, indicating a silent period of the AWS reaction and a dominance of the aldehyde disproportionation reaction at the early stage. As anticipated, benzoic acid and benzyl alcohol were detected in a ratio close to 1:1, strongly indicating the occurrence of benzaldehyde disproportionation [Supplementary Figure 9A and B]. Even in the absence of a catalyst under the same conditions, an equimolar amount of benzoic acid and benzyl alcohol was generated, further confirming the benzaldehyde disproportionation under the reaction conditions [Supplementary Figure 9C and D]. Afterward, the generated benzyl alcohol from disproportionation of benzaldehyde was gradually consumed and more benzoic acid was progressively produced, accompanied by the generation of  $H_2$ . The results strongly suggested the occurrence of aqueous-phase reforming of benzyl alcohol and  $H_2O$ . To validate this, aqueous-phase reforming of benzyl alcohol and  $H_2O$  was conducted under the same catalytic conditions as the AWS reaction, in which benzaldehyde was replaced by benzyl alcohol. The production of benzoic acid and  $H_2$  further confirmed the occurrence of this reforming reaction [Supplementary Figure 10].

Based on the aforementioned control experiments, the catalytic AWS reaction of benzaldehyde was outlined as follows [Figure 4D]:



**Figure 5.** Scope of substrates. Reaction conditions: 30 mg of Pt/PN-CeO<sub>2</sub>, 1 mmol of substrate, 2.5 mmol of NaOH, 0.5 mL of H<sub>2</sub>O and 1 mL of 1, 4-dioxane, 180 °C, 0.5 MPa N<sub>2</sub>.

(1) Disproportionation reaction during the initial stage. Benzaldehyde undergoes a predominantly disproportionation reaction under basic catalytic conditions, leading to the formation of benzyl alcohol and benzoic acid [step (2)];

(2) AWS reaction. Following the initial disproportionation, benzaldehyde then undergoes an AWS reaction, yielding benzoic acid and H<sub>2</sub> [step (1)];

(3) Concurrent reforming of benzyl alcohol. Simultaneously, the benzyl alcohol generated from the initial disproportionation reaction reacts with H<sub>2</sub>O in an aqueous-phase reforming process, consuming the benzyl alcohol and producing additional benzoic acid and H<sub>2</sub> [step (3)].

### Catalytic scope

The AWS reactions could be extended to various benzaldehyde derivatives. Under the same catalytic conditions, these derivatives undergo reactions with H<sub>2</sub>O to produce the corresponding acids with the release of H<sub>2</sub> [Figure 5]. Notably, the methyl-substituted benzaldehydes achieved high conversion, selectivity and H<sub>2</sub> yields. However, benzaldehyde derivatives substituted with electron-withdrawing groups (such as F and Br) on the benzene ring displayed moderated activity and selectivity and H<sub>2</sub> fields.

### CONCLUSIONS

In conclusion, the Pt/PN-CeO<sub>2</sub> catalysts have proven to be highly efficient heterogeneous catalysts for AWS reaction, which successfully converts aldehydes and H<sub>2</sub>O into carboxylic acids and H<sub>2</sub>. The monitoring of the reaction process indicated that the catalytic reaction initially involved the disproportionation of aldehydes, followed by the domination of the AWS reactions, leading to an unsatisfactory H<sub>2</sub> yield. Isotope experiments

unveiled the H<sub>2</sub> generation with one H atom from aldehyde and another H atom from water, experimentally demonstrating occurrence of the AWS reaction. Abundant O<sub>v</sub> in Pt/PN-CeO<sub>2</sub> concurrently enhances water activation and boosts electron density of the anchored Pt catalysts, thereby facilitating improved C–H bond activation in aldehydes. This study offers an alternative method for synthesis of carboxylic acids through a green and sustainable approach, demonstrating its potentials for practical applications.

## DECLARATIONS

### Authors' contributions

Designed the experiments, conducted characterization, analyzed data, interpreted results, drew the pictures, and wrote the manuscript: Meng, X.; Yan, B.; Cao, F.; Qu, Y.

Synthesized samples: Meng, X.; Yan, B.

Contributed to helpful discussions and provided material support: Qi, Z.; Xie, M.; Ma, Y.

Directed and supervised the project and revised the manuscript: Cao, F.; Qu, Y.

### Availability of data and materials

The experimental data and associated test results are available in the [Supplementary Materials](#) of this article.

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### Conflicts of interest

Qi, Z. and Xie, X. are affiliated with Xi'an Yiwei Putai Environmental Protection Co., LTD. The other authors declared that there are no conflicts of interest.

### Ethical approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

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### Supplementary Materials

[Supplementary Materials](#)

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