# Catalysis Science & Technology

# PAPER

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Cite this: DOI: 10.1039/d0cy01704c

Received 31st August 2020, Accepted 9th October 2020

DOI: 10.1039/d0cy01704c

rsc.li/catalysis

## Introduction

With the world's progress in industrialization, organic contaminants from a huge amount of industrial effluents have caused greater concerns over the growing risk of environmental pollution.1,2 Among various organic contaminants, p-nitrophenol (PNP), which has been widely used in the manufacturing industry, is considered as a priority pollutant due to its carcinogenic character, high toxicity, and overall recalcitrance to microbial degradation.<sup>3,4</sup> Consequently, exploring a highly efficient technique to eliminate PNP from wastewater is becoming an essential environmental concern.5 Importantly, by introducing catalytic hydrogenation reactions, PNP can be converted into more valuable p-aminophenol (PAmP), which is a key intermediate in pharmaceuticals, agrochemicals, dyes and pigments.6,7 To this end, extra hydrogen resources such as sodium borohydride (NaBH<sub>4</sub>) or

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# Adsorption driven formate reforming into hydride and tandem hydrogenation of nitrophenol to amine over PdO<sub>x</sub> catalysts†

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Due to their high toxicity and non-biodegradability, efficient reduction of nitroarenes to amines is of great practical importance, yet it still remains a significant challenge. Herein, we report PdO/PdO<sub>2</sub> nanoparticles uniformly supported on titanate nanotubes (PdO<sub>x</sub>/TiNTs) for catalyzing the tandem dehydrogenation of sodium formate (SF) and hydrogenation of *p*-nitrophenol (PNP) to *p*-aminophenol (PAmP) under mild conditions. Notably, SF adsorption is mainly driven by the hydrogen bonding interactions between the H atom in SF and surface Pd sites, which factually makes the interface of PdO<sub>x</sub>/TiNT-SF an effective platform for C-H activation. Meanwhile, it is also found that the efficiency of the hydrogenation reaction depends on the reduction rate of the nitro group to nitroso group, and the O atoms adjacent to Pd are considered as the essential sites that facilitate this process. On the basis of the above two effects, the PdO<sub>x</sub>/TiNT catalyst shows unprecedented catalytic activity (turnover frequency, TOF, is 45.6 h<sup>-1</sup>) and good selectivity (~100%) during PNP reduction at room temperature. This work deepens our understanding on tandem catalytic (de)hydrogenation systems, and will benefit the design of heterogeneous catalysts for the production of industrially important chemicals.

hydrazine hydrate ( $N_2H_4$ · $H_2O$ ) are usually required as reducing agents to remove oxygen atoms from nitro groups and ultimately give rise to aniline products.<sup>8-11</sup>

In recent years, a variety of heterogeneous catalytic systems based on noble metals (e.g. Pd, Pt, Au and Ag) have been developed for the effective catalytic reduction of PNP to PAmP.<sup>12-16</sup> Lai and co-workers used dispersedly anchored Au on chitosan functionalized activated coke to improve the stability of catalysts in the reduction process.<sup>17</sup> Jiang et al. reported Pd nanoparticle-decorated hierarchically porous TiO<sub>2</sub> scaffolds with strong synergistic interactions for the reduction of highly concentrated PNP wastewater. In addition, construction of bimetallic structures is also a reliable alternative to establish efficient catalytic systems.<sup>18</sup> In this case, Xiao et al. showed that the catalytic reaction pathway can be altered by controlling the alloying segment of Cu into Au nanoparticles, which allows nitroaromatics to be transformed directly into anilines in a highly selective manner.<sup>19</sup> Similarly, Song and co-workers revealed remarkable Pt-Au synergistic catalytic effects on PtAu-nanoflowers/rGO with improved catalytic performances for the reduction reaction.<sup>20</sup> So far, most of the research is limited to the design and preparation of novel catalysts to enhance the catalytic activity, selectivity, and stability during PNP hydrogenation reactions, while very few reports focus on the optimization of the kinetic process and elucidation of the catalytic mechanism.



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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available. See DOI: 10.1039/ d0cy01704c

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As a water-soluble salt with moderate theoretical H<sub>2</sub> weight efficiency, sodium formate (SF) represents a potentially interesting reducing agent.<sup>21–24</sup> Recently, we reported that hollow PdO supported on titanate nanotubes (TiNTs) is a highly active and stable catalyst for the dehydrogenation of SF solution into molecular hydrogen at room temperature. It is found that the presence of both Pd centers and their terminated oxygen atoms strongly enhances the reactivity of PdO toward the C-H bond as well as water activation.<sup>25</sup> Herein, PdO<sub>x</sub>/TiNTs are coupled with SF to reduce PNP into PAmP in an aqueous phase, thus representing an exemplary system for the investigation of nitro  $(-NO_2)$  group reduction kinetics. The operando Raman study and GC-MS results suggest that the adsorption of SF onto the catalyst surface would drive hydride in SF to the Pd sites and subsequently construct the novel Pd···H···C complex. It is demonstrated that the rate-limiting step is the reduction of the nitro group to nitroso group, and the nitrogen atoms in nitro-compound species can be captured by a high density of surface terminated O atoms, resulting in the direct reduction of PNP to intermediate species. Therefore, this unique PdOx/TiNT catalyst shows ~100% selectivity and a fast reaction rate (turnover frequency, TOF, is up to 45.6  $h^{-1}$ ) for PNP reduction to PAmP under ambient conditions, which is one order of magnitude higher than analogous catalytic systems (Scheme 1). In addition, this reaction is also similar to our previously reported catalytic hydrogen production from SF solution using PdO/TiNT catalysts, where only palladium or palladium oxide is active for the reduction of organic dyes in the presence of SF.<sup>25</sup> This work not only provides insights into the mechanism of tandem catalytic dehydrogenation and hydrogenation systems, but also paves a way to improve the catalytic performance of supported catalysts for the production of industrially important chemicals.

## **Experimental**

### Materials synthesis

**Materials.** Materials: P-25  $TiO_2$  (Sigma-Aldrich), sodium hydroxide, hydrochloric acid, nitric acid, ethyl acetate,



anhydrous ethanol (>99%), palladium( $\pi$ ) nitrate (Pd(NO<sub>3</sub>)<sub>2</sub>), sodium formate (HCOONa), *p*-nitrophenol (PNP), *p*-nitrosophenol (PNSP), *p*-aminophenol (PAmP), *p*-nitrobenzyl alcohol, *p*-nitrobenzoic acid and distilled water were supplied from local sources. All the reagents were used without further purification.

Protonated titania nanotubes were prepared the same as in our previous method.<sup>25</sup> Typically,  $TiO_2$  nanoparticles (25 nm) were first placed into a beaker (50 mL). Using a syringe, 10 M sodium hydroxide solution (60 mL) was added. The mixture was left stirring for 12 h in the dark. The resultant white slurry was transferred to a Teflon vessel which was then placed into a sealed autoclave and put in an oven at 150 °C for 72 h. After cooling to room temperature, the precipitated powder was filtered and washed with 0.1 M aqueous HCl solutions and Milli-Q water, until the filtrate reached pH = 7. This resulting sample was protonated titania nanotubes and denoted as TiNTs.

To *in situ* load PdNPs onto TiNTs, a given amount of  $Pd(NO_3)_2 \cdot 2H_2O$  (palladium(II) nitrate dihydrate) was dissolved in 50 mL dilute nitric acid solution to form a yellow transparent solution. 1 mg TiNTs were added into 100 mL deionized water and ultrasonicated for 10 min to ensure that they were evenly dispersed in water. Then the yellow palladium precursor solution was dropped into the aforementioned TiNTs dropwise under stirring. The mixture was kept stirring overnight, then the stirrer was switched off and the mixture was set aside for a certain time till the solid–liquid separation. After abandoning the supernatant, the precipitant was accumulated and washed several times with water and ethanol. Finally, the precipitate was dried overnight in a vacuum box at 80 °C. The PdNPs/TiNTs were calcined at 300 °C for 3 h in an O<sub>2</sub> or N<sub>2</sub> atmosphere to obtain the final catalysts.

### Characterization

TEM images were recorded on a JEOL JEM-1230 operated at 100 kV. HR-TEM and HAADF-STEM combined with EDS measurements were performed on an FEI TITAN Cs-corrected ChemiSTEM equipped with an energy dispersive X-ray (EDX) spectroscope, operating at 200 kV.

X-ray photoelectron spectroscopy (XPS) analysis was conducted using a Thermo Scientific ESCA Lab250 spectrometer, which consists of monochromatic Al K $\alpha$  as the X-ray source, a hemispherical analyzer and a sample stage with multiaxial adjustability to obtain the composition on the surface of the samples. All the binding energies were calibrated by the C1s peak of the surface adventitious carbon at 284.6 eV.

To confirm the terminal products of this reaction, gas chromatography-mass spectrometry (GC-MS) was used. The reacted solution was centrifuged at 5000 rpm for 5 min to separate the supernatant and the catalyst solid. Then the solution was freeze dried to dislodge the water from the intermediate products or the end-products. Extra ethyl acetate (EA) was added into the dry products, and then the organic compounds were dissolved in the EA; some inorganic salts like NaHCO<sub>3</sub> or the unreacted HCOONa were discarded.

In situ Raman spectra were recorded on a Tri Vista Raman spectrometer. The Raman scattering was induced by irradiating aqueous solutions of SF and PNP in the presence of solid catalysts with the second harmonic radiation at 633 nm of a Nd: YAG laser. A back scattering geometry was used to excite sample and collect the Raman scattered light by reflective optics. The data was recorded with a collection (integration) time of 100 s and a spectral resolution of 2 cm<sup>-1</sup> in the range of 750–1650 cm<sup>-1</sup>.

Attenuated total reflectance (ATR-FTIR) was used to confirm the real time reaction process. The range of wavenumbers was set from 400 to 4000 cm<sup>-1</sup>. 1–2 drops of 0.01 M PNP solution were dropped into the center of the crystal stage, and then a small amount of catalysts was added. The spectral changes during the reaction were measured at regular intervals. Considering the difficulty in determining the amount of catalyst, this method could just reflect the catalytic activity in the qualitative aspect.

### Catalytic activity

The catalytic reduction of PNP to PAmP was carried out as follows: first, 1 M SF and 0.1 mM PNP were selected to determine the activity of the catalysts. Second, in separate standard quartz cuvettes, 2 mL probe solution was added, followed by adding 1 mg catalysts without stirring. After the solid catalysts sank into the bottom of the cuvette in several seconds, the upper solution was recorded by using a UV-2550 spectrometer (Shimadzu Inc.). The parameters were set as follows: spectral scanning range from 200 to 500 nm, and cyclic scan of 60 cycles with an interval of 60 s.

For the recycling experiment, 10 mg catalysts were added into 20 mL PNP/SF reaction solution in a 50 mL beaker; after 30 min of reaction, the solution was centrifuged, and the upper solution was detected using the UV-vis spectrometer to confirm the reduction degree and the solid catalyst was collected for the next cycle.

Analysis of gases in the reaction system was carried out with 1 mg of catalysts suspended in a 10 mL solution containing 1 M SF and 0.01 M PNP in a 55 mL Pyrex test tube under stirring (400  $\pm$  10 rpm). A water bath was used to maintain the reaction temperature at room temperature (25  $\pm$  0.5 °C). Nitrogen gas was used to eliminate the oxygen in the test tubes, and the tubes were finally sealed with silica gel stoppers. Gas volumes of 400  $\mu$ L were extracted from the test tubes using a microliter syringe at regular intervals, and GC-TCD was employed for evaluating the gas evolution amount, including H<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and CO. Triplicate reactions were studied from which statistical analysis of the reactivity could be extracted.

The TOF reported here is an apparent TOF value based on the surface number of Pd atoms in the catalyst, which is calculated by the following equation: TOF =  $(n_{\rm H_2}/n_{\rm Pd} \times t) \times$ (d/1.3), where  $n_{\rm H_2}$  and  $n_{\rm Pd}$  represent the molar amounts of evolved H<sub>2</sub> within *t* h and Pd catalyst, respectively, and *d* is the average diameter of PdNPs; 1.3/*d* is the empirical surface atom dispersion degree for nanoscale particles. The TOF values in references are also in similar calculations.

## Results and discussion

### Catalyst characterization

PdO<sub>r</sub>/TiNT and Pd/TiNT catalysts with a Pd loading amount of 1.0 wt% were synthesized by the incipient wetness impregnation (IWI) method followed by calcination under an O<sub>2</sub> or N<sub>2</sub> atmosphere, respectively (ESI<sup>†</sup>). Highly dispersed PdNPs on the surface of nanotubes are observed in the transmission electron microscopy (TEM) images of PdO<sub>x</sub>/TiNTs (Fig. 1a) and Pd/TiNTs (Fig. S1<sup>†</sup>). The results show that these two specimens have similar particle sizes, viz. the average sizes for PdO and Pd are 4.93 and 4.62 nm, respectively. The highresolution TEM (HRTEM) image (inset of Fig. S1<sup>†</sup>) of Pd/TiNTs presents a typical Pd(111) facet, while the image of PdO<sub>x</sub>/TiNTs (inset of Fig. 1a) reveals a lattice spacing of about 0.275 nm for PdO<sub>r</sub>/TiNTs, corresponding to the (101) plane of PdO. Energydispersive X-ray spectroscopy (EDS) analysis confirms that Pd, Ti, and O elements are uniformly distributed (Fig. 1b). The powder X-ray diffraction (XRD) patterns of the as-prepared catalysts display diffraction peaks located at  $2\theta = 11.3^{\circ}$ , 24.4°, 29.3°, and 48.4°, which could be attributed to the characteristic peaks of layered protonated titanates (PDF# 47-0561). Due to the relatively low loading amount and high dispersity, only small characteristic XRD peaks for Pd(111), PdO(101) and PdO<sub>2</sub>(211) are identified,<sup>26</sup> which is consistent with the TEM results (Fig. 1c).

A detailed investigation of the electronic states of the surface metal species is carried out by X-ray photoelectron spectroscopy (XPS) analysis (Fig. 1d and S2†). To determine the oxidation states of palladium, the main peak of the  $Pd3d_{5/2}$ 



Fig. 1 (a) TEM image of  $PdO_x/TiNTs$  (inset shows the HRTEM image); (b) STEM image of  $PdO_x/TiNTs$  and EDS maps of O, Pd, and Ti, respectively; (c) XRD patterns of 1.0 wt% Pd/TiNTs calcined under N<sub>2</sub> or O<sub>2</sub>; (d) high resolution Pd3d XPS spectra of 1.0 wt% Pd/TiNTs calcined under N<sub>2</sub> or O<sub>2</sub>.

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core-level spectra is fitted with two components at 335.11 and 336.04 eV corresponding to Pd<sup>0</sup> and surface Pd<sup>2+</sup> species, respectively (Fig. 1d). A large fraction of palladium is present in the Pd<sup>0</sup> metallic state in the Pd/TiNT samples. Additionally, the absence of any shake-up satellite feature in the spectra at binding energies above 338.0 eV further indicates the lower palladium oxidation state. The PdOx/TiNT catalyst shows that the position of the palladium main peak shifts slightly toward a higher binding energy, which is strongly related to the modification of the electron density on Pd species after calcination under different atmospheres. Moreover, it appears that the fraction of Pd<sup>2+</sup> on the surface, as estimated from the ratio of PdO/(Pd + Ti + O) peaks tends to increase within  $PdO_x/$ TiNTs. More critically, a new peak at around 340.3 eV is observed, indicating that the oxidation state of a fraction of Pd species becomes +4 after calcination in an O2 atmosphere.<sup>27-29</sup> However, only negligible shifts of O1s as well as Ti2p are observed in the PdOx/TiNT and Pd/TiNT samples (Fig. S3<sup>†</sup>), suggesting that the incorporated nanoparticles do not cause obvious modification in the TiNT structure.

The reduction of PNP is chosen as an ideal probe reaction to assess the catalytic activity of as-prepared PdO<sub>x</sub>/TiNTs. The UV-vis spectra of standard PNP solutions with or without SF are presented in Fig. S4.† Two control experiments indicate that PNP will not be reduced in the absence of SF, yet PNP shows better adsorbability on the PdO<sub>x</sub>/TiNT surface than on pristine TiNTs (Fig. S5<sup>†</sup>). The PNP reduction reaction over PdO<sub>x</sub>/TiNTs and Pd/TiNTs obeys the quasi-first-order kinetics, and the fitting linear dependency with slopes of 0.15 and 0.07 corresponding to PdO<sub>x</sub>/TiNTs and Pd/TiNTs respectively is obtained from logarithmic plots of  $c_0/c vs.$  reaction time, indicating that surface oxygen species most likely participate in this reaction (Fig. 2). Two effects result in the different catalytic activities of PdOx/TiNTs and Pd/TiNTs. First, oxidized palladium performs far superior to metallic Pdbased counterpart catalysts in the activation of the C-H bond in SF, as discussed in a previous report.<sup>25</sup> Second, the oxygen atoms in the vicinity of Pd supply more appropriate sites for the capture of nitrogen atoms in nitro-compound species benefited by the high density of surface terminated O atoms and the conjugation effect of the nitro group in the *para*-position of nitrophenol. The reaction efficiency of  $PdO_x/$ TiNTs is nearly one order of magnitude higher than those of other analogous PNP catalytic reduction reactions. We also compared the activity and selectivity among different catalytic systems with similar reaction conditions, as listed in Table S1.† To assess the reusability and stability of PdO<sub>x</sub>/TiNTs, 10 consecutive utilization cycles are performed. Similar conversion and selectivity are determined as compared with the fresh catalyst, indicating the excellent reusability of the PdO<sub>x</sub>/TiNT catalyst (Fig. S6<sup>†</sup>).

To further confirm the degradation process of PNP over the  $PdO_x/TiNT$  catalyst in the presence of SF, *in situ* Raman spectroscopy is conducted. As shown in Fig. 3a, the characteristic vibration peaks of PNP groups are observed at 1113, 1170, 1284, 1350, and 1595 cm<sup>-1</sup>. The former peaks at



Fig. 2 Concentration changes of PNP and kinetic curves at 400 nm: (a) PdO<sub>x</sub>/TiNTs and (b) Pd/TiNTs. Reaction conditions: PNP solution (10  $\mu$ M) + HCOONa (1 M) (insets are the images of the visual color change as a function of reaction time).

1113 and 1170 cm<sup>-1</sup> can be attributed to the C-H in-plane bending vibration of the benzene ring, while the bands at 1284 and 1350 cm<sup>-1</sup> are assigned to the stretching vibration of  $-NO_2$  groups.<sup>30</sup> Additionally, the SF stretching vibration of C=O also centers at around 1350 cm<sup>-1</sup>, which is interfered by the characteristic peak of PNP. The intensity of PNP vibrational peaks decreases steadily as a function of monitoring time, and the final disappearance indicates its successful reduction.



**Fig. 3** Real time Raman vibration spectrum change: (a) SF/PNP solution reacted with  $PdO_x/TiNTs$ , (b) SF solution with or without  $PdO_x/TiNTs$ , and bare  $PdO_x/TiNTs$  (black line). Notes: stretching vibration:  $v_r$ , asymmetric stretching vibration:  $v_{sr}$  bending vibration:  $\beta$ , flexion:  $\delta$ . (c) GC-TCD detected the change of gas composition in the system of PNP/SF. (d) Real-time ATR-FTIR vibration of CO<sub>2</sub> in solution. 0.01 M PNP + 1 M SF + PdO\_x/TiNTs, 25 °C.

Notably, neither the relative intensity nor the peak position of all the PNP vibration modes changes when the PdO<sub>x</sub>-TiNT catalyst is initially introduced into the system involving both PNP and SF, which is in sharp contrast to the influence of the PdOx-TiNT catalyst on the vibration modes of bare SF. As shown in Fig. 3b, the bare SF solution (blue line) shows four characteristic peaks at 1212, 1297, 1348 and 1378 cm<sup>-1</sup>, assigned respectively to the  $\beta$ (C-H)<sub>in-plane</sub>,  $\beta$ (C-H)<sub>out-plane</sub>, v(C=O), and v(C-H) vibrations. The stretching vibration is the main mode for SF, and the C-H vibration intensity is apparently much stronger than that of C=O.<sup>31,32</sup> However, once SF and PdOx/TiNTs co-exist, two bending vibrations of C-H bonds vanish (red line). Furthermore, the intensities of stretching vibration of C-H and C=O are also exchanged while no relative shift is observed. In analogy to the size-dependent behavior of the adsorption modes of formate species on PVP-Ru nanoparticles, the v(C=O)around 1348 cm<sup>-1</sup> most likely belongs to the asymmetric mode of O-C-O stretching in a monodentate mode and no bidentate formate species is observed.<sup>33</sup> The obvious decrease in the intensity of v(C-H) vibration coupled with the absence of bands characteristic of  $\beta$ (C-H) upon introduction of the PdO<sub>x</sub>/TiNTs suggests that the coordination environment of SF over the PdO<sub>x</sub>/TiNT surface has been changed. As Pd possesses favorable hydrogen affinity, it is reasonable to propose that the H atom from SF would combine with Pd to form a Pd…H…C complex on the catalyst surface, which restricts and thus decreases the vibration of the C-H bond. In addition, the enhanced v(C=O) vibration mode can be interpreted in terms of a delicate balance between the force of the C-H bond to the metal and the back force to the C=O bond. This transformation factually makes the interface of PdO<sub>x</sub>/TiNTs and SF an effective platform for activating the H atom and subsequently driving it away from the SF molecule, suggesting great potential applications for subsequent -NO<sub>2</sub> reduction and/or H<sub>2</sub> generation.

The composition of the evolved gas is examined in real time by GC-TCD (Fig. 3c). It is observed that the amount of evolved carbon dioxide (CO<sub>2</sub>) increases gradually in the initial 2 hour reaction, and the reaction solution also turns colorless. Further prolonging the reaction time leads to a slight increase of the CO<sub>2</sub> amount, with a maximum amount of around 80 µmol during the entire reaction. Because partial CO<sub>2</sub> is dissolved in the reaction solution, the free CO<sub>2</sub> gas detected by GC-TCD cannot reach the theoretical content (~100 µmol). However, an opposite reaction trend is observed in the yield of H<sub>2</sub> gas: almost no H<sub>2</sub> is produced in the first 2 h of reaction, whereas the H<sub>2</sub> evolution sharply increases after this critical range of reaction time. This result indicates that, at the PNP fading stage, only CO<sub>2</sub> gas is generated in the reaction system.

ATR-IR and GC-MS are conducted to explore the reduction pathway of PNP. As shown in Fig. 3d, in the absence of catalysts, no vibration is observed within  $2250-2450 \text{ cm}^{-1}$  (the CO<sub>2</sub> vibration peaks appear at around 2330 and 2360 cm<sup>-1</sup>).<sup>34</sup> After the PdO<sub>x</sub>/TiNT catalyst is introduced into the catalytic system,

the vibration intensity of the CO<sub>2</sub> doublet peaks increases immediately and then decreases until vanishing. The variation tendency can also be observed more intuitively in the inset figure, which shows the U-like shape evolution of CO<sub>2</sub> absorption intensity at 2360 cm<sup>-1</sup>. Such a trend demonstrates that CO<sub>2</sub> is more likely to generate around the surface of the PdO<sub>x</sub>/TiNT catalyst, and desorbs from the solution. Furthermore, GC-MS is used to confirm the intermediates and final products of the reaction solution. From Fig. S7,† it can be seen that before the reaction, only PNP is detected at 18.3 min (black line). Upon 5 min of the reaction, the intensity of PNP obviously decreases, whereas one additional characteristic peak of PAmP appears at 14.9 min. The substances in both positions are further confirmed subsequently using a connected MS detector (Fig. S8<sup>†</sup>). In addition, the reaction for a longer period (30 min) gives the same and exclusive product of reduced PNP. Therefore, based on the GC-MS results, we reasonably suggest that PAmP is the final product after the whole reduction reaction. Moreover, this reaction system can be also applied to other organic contaminants, e.g. nitrobenzene derivative p-nitrobenzyl alcohol, and the results are shown in Fig. S9-S11.†

The C-H bond in SF can be activated and cleaved to produce active hydride (\*H) species on the PdOx/TiNT surface, as indicated by the Raman results. Meanwhile, the formate residue after dehydrogenation can also be hydrolyzed to form bicarbonate (HCO<sub>3</sub><sup>-</sup>). According to the Henderson-Hasselbalch equation (pH = pKa + log([base]/[acid])) and the conjugate acidbase equilibrium theory, it is estimated from Table S2<sup>†</sup> that both SF and NaHCO<sub>3</sub> are alkaline and NaHCO<sub>3</sub> has a relatively stronger alkalinity. PNP is alkalescent (acid dissociation constant pKa = 7.15) and PAmP is a weak acid (pKa = 5.48), thus in principle, the catalytic products PAmP and NaHCO<sub>3</sub> will continue to complete the so-called acid and alkali neutralization reaction in aqueous solution. Consequently, the carbonate was easily decomposed into water and CO<sub>2</sub>, which explains the origin of CO<sub>2</sub> detected in GC-TCD and ATR-IR. After all the PNP molecules were transformed into PAmP, the redundant \*H species generated by SF activation will combine with each other to produce H<sub>2</sub> gas.

More importantly, the fact that no aqueous by-products or intermediates are detected by GC-MS shows the high catalytic selectivity of PdO<sub>x</sub>/TiNTs. Within the catalytic process from PNP to PAmP, nitroso, imine and hydroxylamine are considered as the possible intermediate products. However, both imine and hydroxylamine are unstable and facile to reduce or oxidize, and one of the nitroso intermediate products *p*-nitrosophenol (PNSP) with relative better stability is selected and used for a series of designed experiments to determine the rate-limiting step (Fig. 4). It should be noted that PNP and PNSP cannot be distinguished from the peak position as both of them exhibit the major peaks at 400 nm in the UV-vis spectra (blue and pink lines in Fig. S4<sup>†</sup>). Therefore, the kinetics of concentration change is carried out. By comparing the kinetic curves in Fig. 4 and 2,  $k_{PNSP}$  is more than three times higher than  $k_{PNP}$  during the reduction process, and  $k_{\text{PNP/PNSP}}$  is in between them. These results



Fig. 4 Concentration changes of control experiments: (a) PNP/PNSP and (b) PNSP with corresponding kinetic curves monitored at 400 nm. Reaction conditions: PNP and/or PNSP solution (10  $\mu$ M) + HCOONa (1 M) + PdO<sub>x</sub>/TiNTs.

mean that imine is reduced to hydroxylamine and amine rapidly, while reduction of nitro to nitroso is relatively difficult, which is consistent with the GC-MS results. Consequently, the rate-limiting step is most likely the reduction process of nitro to nitroso.

The whole reaction is shown in Fig. S12:† SF molecules are adsorbed on PdO<sub>x</sub>/TiNTs through the formation of a H-Pd intermediate, and the C-H bond is cleaved to form HCO3- and \*H species. PNP molecules are also adsorbed simultaneously. Since the -NO2 group in PNP is characteristic of its electron affinity, the N atom is prone to be adsorbed on the terminated O atoms in  $PdO_x$  due to the conjugation effect.<sup>28,35</sup> Thus, the -NO<sub>2</sub> group is easily reduced into -NH<sub>2</sub> by free \*H species without the production of H<sub>2</sub> unless the reduction process is completely finished. Because the -NH<sub>2</sub> group in PAmP shows electron donating ability, PAmP molecules are readily desorbed from the catalyst surface, leading to the high catalytic selectivity.36 Meanwhile, as a by-product, NaHCO3 will continue to react with PAmP to produce CO<sub>2</sub> and sodium salt. Therefore, the present work provides a new tandem catalytic system that couples hydrogen production with organic contaminant degradation in a "one-pot" reaction vessel.

## Conclusions

In summary,  $PdO_x/TiNTs$  are prepared by the IWI method and subsequent annealing in an oxygen atmosphere, and show high selectivity and catalytic activity for the tandem dehydrogenation of SF and hydrogenation of PNP to PAmP under mild conditions. Notably, SF adsorption is mainly driven by the hydrogen bonding interactions between the H atom in SF and surface Pd sites, which factually makes the interface of  $PdO_x/TiNTs$  and SF an effective platform for C–H activation. The efficiency of the hydrogenation reaction depends on the reduction rate of the nitro group to nitroso group, and the terminated O atoms in the  $PdO_x$  species are considered as the essential active sites to this specific reaction. These two effects result in the unprecedented catalytic activity and excellent selectivity (~100%) over the  $PdO_x/TiNT$  catalyst during PNP reduction to PAmP at room temperature. The present work deepens our understanding on tandem catalytic dehydrogenation and hydrogenation systems, and will benefit the design of heterogeneous catalysts for the production of industrially important chemicals.

## Conflicts of interest

The authors declare that they have no conflict of interest.

## Acknowledgements

We are grateful for financial support from the National Science Foundation of China (21872123) and the Zhejiang Provincial Natural Science Foundation of China (LY18B030007).

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