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# Air-promoted selective hydrogenation of phenol to cyclohexanone at low temperature over Pd-based nanocatalysts

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Attaining high activity with high selectivity at low temperature is challenging in the selective hydrogenation of phenol to cyclohexanone due to its high activation energy ( $E_a$ , 55–70 kJ/mol). Here we report a simple and efficient strategy for phenol hydrogenation catalyzed by Pd in aqueous phase at 30 °C by introducing air to promote the catalysis. With the assistance of air, >99% conversion and >99% selectivity were achieved over Pd(111)/Al<sub>2</sub>O<sub>3</sub> with an overall turnover frequency (TOF) of 621 h<sup>-1</sup>, ~80 times greater than that of the state-of-art Pd catalyst at 30 °C. Mechanism studies revealed that phenol was activated to generate phenoxyl radicals. The radicals were yielded from the reaction between phenol and hydroxyl radicals in the presence of hydrogen, oxygen and protic solvent on Pd. The phenoxyl pathway resulted in a low apparent  $E_a$  (8.2 kJ/mol) and thus high activity. More importantly, this strategy of activating substrate by air can be adapted to other Pd based catalysts, offering a new thinking for the rational design of cyclohexanone production in industry.

selective hydrogenation, phenol, palladium, nanocatalysis, radical

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# **1** Introduction

Selective hydrogenation of phenol has attracted wide attention because it was considered as a promising route to produce cyclohexanone [1–7], an important industry intermediate in the synthesis of nylons and polyamide resins [8]. Compared with oxidation of cyclohexane [9,10] which is another industrial route to prepare cyclohexanone, selective hydrogenation of phenol can occur at relatively low temperature without excessive energy consumption and side reactions [1,2,11–17]. The hydrogenation of phenol to cyclohexanone can be conducted through either gas-phase or liquid-phase reactions. The gas-phase reactions usually have high selectivity (>95%) and turnover frequency (TOF) but low conversion (<80%), and only occur at elevated temperature (150 to 250 °C) [1,2,18–21]. On the other hand, the liquid-phase reactions can occur under mild temperature (<100 °C) with satisfying selectivity (>95%) and gratifying conversion (>90%), but usually with low TOF because of the lower reaction temperature in comparison with gas-phase hydrogenation [3,7,12–14,16,17,22]. Hence, achieving high TOF with high conversion and selectivity for phenol hydrogenation is desirable.

Generally, the reaction can be accelerated either through increasing reaction temperature or decreasing apparent activation energy ( $E_a$ ) according to Arrhenius equation [15,23].

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While increasing reaction temperature makes the reaction more energy consuming, the increased reaction temperature also accelerates the over-hydrogenation (herein cyclohexanone to cyclohexanol) and thus decreases the selectivity [1-3,7,14,24]. For this reason, it is highly desirable to develop a room-temperature catalytic process that offers both high catalytic activity and selectivity [25-27]. Nevertheless, due to high apparent  $E_a$  (55–70 kJ/mol) of selective hydrogenation from phenol to cyclohexanone [18,28,29], it is challenging to achieve high TOF at low temperature.

Herein, we report a facile and efficient method to reduce apparent  $E_a$  in phenol hydrogenation to cyclohexanone at 30 °C by simply introducing air. With the assistance of air and using Pd(111)/Al<sub>2</sub>O<sub>3</sub> as model catalyst, the apparent  $E_a$ was reduced from 68.3 to 8.2 kJ/mol. In an aqueous-phase reaction, 99% conversion of phenol was achieved with >99% selectivity to cyclohexanone within 7 h in a mixture of H<sub>2</sub> and air (1:1, in volume) at 30 °C. The overall TOF was greater than the highest value by a factor of 80 reported in liquid-phase hydrogenation at 30 °C [17,25,26] and also a little higher than that of gas-phase hydrogenation operated at 180 °C [2.20.21]. It is demonstrated that the reaction undergoes an alternative mechanism involving hydroxyl radicals (OH) and phenoxyl radicals (OPh). This study provides new insights into the catalytic hydrogenation of phenol to cyclohexanone for industrial applications.

## 2 Experimental

#### 2.1 Preparation of catalysts

The synthesis of Pd(111)/Al<sub>2</sub>O<sub>3</sub> catalysts (1 wt% Pd loading; Pd nanosheets on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was conducted via a modified method, using carbon monoxide as a reducing and shape-controlling agent [30]. In a typical experiment, 20 µL of 1 M H<sub>2</sub>PdCl<sub>4</sub> aqueous solution was added to 15 mL anhydrous dimethyformate (DMF). [Pd<sub>2</sub>(µ-CO)<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup> was formed after the solution was treated under 1-atm CO for 10 min.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (200 mg) was dispersed in 5 mL anhydrous DMF and slowly added into the above mixture while stirring. The final mixture was kept under 1-atm CO for more 5 min and the reaction was monitored by UV-Vis absorption spectroscopy (Figure S1, Supporting Information online). The solid was collected by centrifugation and washed with ethanol twice. Purified product was dried under vacuum at room temperature.

The Pd NP/Al<sub>2</sub>O<sub>3</sub> (1 wt% Pd loading; NP, nanoparticle) nanocatalyst was prepared by incipient wetness impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with an aqueous solution of H<sub>2</sub>PdCl<sub>4</sub> (20 µL, 1 M). The solvent was then gradually evaporated by heating the solution at 120 °C until dried. The sample was then calcined under air flow (30 mL/min) at 300 °C for 2 h and further reduced under H<sub>2</sub> flow (30 mL/min) at

#### 60 °C for another 2 h.

#### 2.2 Characterization

Transmission electron microscopy (TEM), including high-resolution transmission electron microscopy (HRTEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) studies were performed on a TECNAI F-30 high-resolution transmission electron microscopy (Philips, Netherlands) operating at 300 kV. The samples were prepared by dropping the ethanolic dispersion of samples onto 300-mesh carbon-coated copper grids and immediately evaporating the solvent.

The UV-Vis absorption spectra were taken on UV-2600 (Shimadzu, Japan). DMF was used as solvent during measuring H<sub>2</sub>PdCl<sub>4</sub> and  $[Pd_2(\mu$ -CO)<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup> cluster.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and freshly prepared Pd(111)/Al<sub>2</sub>O<sub>3</sub> were directly measured in the form of solid.

CO stripping was carried out on CHI660E (CH Instruments, USA).  $Pd(111)/Al_2O_3$ -modified working electrode was fabricated by depositing the ethanolic dispersion of freshly prepared catalyst onto a glassy carbon electrode followed by drying under an infrared radiation (IR) lamp. A saturated calomel electrode (SCE) and a platinum foil were used as the reference and counter electrode, respectively. The CO stripping voltammogram was recorded in 0.1 M H<sub>2</sub>SO<sub>4</sub> at a sweep rate of 2 mV/s without introducing any additional CO.

CO-titration was carried out on a Micromeritics Auto Chem II 2920 (USA) chemical adsorption instrument with TCD detector to determine the metal dispersion for TOF calculations. Before analysis, Pd(111)/Al<sub>2</sub>O<sub>3</sub> was exposed in air for 3 d to release CO completely, then 100 mg Pd(111)/Al<sub>2</sub>O<sub>3</sub> was treated under argon flow (30 mL/min) at 200 °C for 2 h. Then the catalyst was cooled down to 40 °C and pulse mode CO titration was performed. The metal dispersion of Pd(111)/Al<sub>2</sub>O<sub>3</sub> was calculated to be 0.46 by assuming that the surface stoichiometry of Pd/CO was 2.

#### 2.3 Catalytic experiments

All reactions were conducted in a 48-mL glass pressure vessel charged with: (1) 0.2 MPa H<sub>2</sub> (first bubbled with N<sub>2</sub> to remove any air, then purged with pure H<sub>2</sub> to remove N<sub>2</sub> and finally charged with totally 0.2 MPa H<sub>2</sub>); (2) 0.1 MPa H<sub>2</sub>+0.1 MPa air (not bubbled to remove air; directly charged with 0.1 MPa H<sub>2</sub>).

For phenol hydrogenation catalyzed by  $Pd(111)/Al_2O_3$ , the freshly-prepared catalyst of  $Pd(111)/Al_2O_3$  (0.1 µmol Pd) and phenol (200 µmol dispersed in 10 mL water) were added to the glass pressure vessel and kept stirring (1500 r/min) at 30 °C in a water bath. Then 0.2 MPa pure H<sub>2</sub> or 1:1 H<sub>2</sub>&air was applied into the vessel. The reaction was carried out for various time durations and diluted with ethanol for further

use in gas chromatography. The mixture was well dispersed using ultrasonic. The products were identified by gas chromatograph-mass spectrometer (GC-MS, QP2100 plus, Shimadzu, Japan). Gas chromatography analysis was carried out on FULI 9790 II (China) with a KB-5 capillary column (30 m×0.32 mm×0.33  $\mu$ m) using acetophenone as an internal standard. The GC was operated at 90 °C for 3 min and the temperature was raised to 220 °C at a speed of 10 °C/min. Nitrogen was used as carrier gas. Injection port and flame ion detector (FID) were kept at 250 °C.

For phenol hydrogenation catalyzed by commercial Pd NP/C and home-made Pd NP/Al<sub>2</sub>O<sub>3</sub>, the amount of Pd was 0.2  $\mu$ mol and the reactions were kept under the same condition as for Pd(111)/Al<sub>2</sub>O<sub>3</sub>.

For the hydrogenation of cyclohexanone catalyzed by  $Pd(111)/Al_2O_3$ , the fresh prepared catalyst of  $Pd(111)/Al_2O_3$  (2 µmol Pd) and cyclohexanone (200 µmol, dispersed in 10 mL water) were added to the glass pressure vessel. 0.2 MPa pure  $H_2$  was applied into the vessel. Then the vessel was kept stirring (1500 r/min) in a water bath at different temperatures for 3 h. The analyzed condition was the same with mentioned above.

TOF was defined as mole of consumed reactant of 1 mol surface Pd atom in 1 h in a defined time period. The initial TOF was calculated as the initial reaction rates when the conversion was below 10%.

The apparent  $E_a$  of phenol hydrogenation with or without deoxygenation was calculated. The calculations were based on data collected from experiments under assorted temperature ranged from 30 to 70 °C catalyzed by Pd(111)/Al<sub>2</sub>O<sub>3</sub>:

(1) For the determination of  $E_a$  in the absence of air, the fresh prepared Pd(111)/Al<sub>2</sub>O<sub>3</sub> catalyst (2 µmol Pd) and phenol (200 µmol) were dispersed in 10 mL water and then added into the vessel. The solution was bubbled with nitrogen to remove air. Then 0.2 MPa H<sub>2</sub> was added and kept at 30 °C in a water bath.

(2) For the determination of  $E_a$  in the presence of air, the freshly-prepared Pd(111)/Al<sub>2</sub>O<sub>3</sub> catalyst (0.1 µmol Pd) and phenol (200 µmol) were dispersed in 10 mL water and then added into the vessel. Then 0.1 MPa H<sub>2</sub> was added and kept at 30 °C in a water bath.

#### 2.4 Mechanism analysis

Spin trapping of OH radicals ( $\cdot$ OH) by 5,5-dimethyl-1-pyrroline-1-oxide (DMPO): 2 mL (0.05 M) DMPO aqueous solution and 1 mg Pd(111)/Al<sub>2</sub>O<sub>3</sub> were added into a 48-mL glass pressure vessel. The vessel was then charged with H<sub>2</sub> to 0.1 MPa in the presence of air and kept at 30 °C in a water bath for 5 min with stirring. The reaction mixture was filtered off and the filtrate was detected by electron spin resonance (ESR).

Spin trapping of OH radicals by terephthalic acid (TA):

0.1 mg Pd(111)/Al<sub>2</sub>O<sub>3</sub> and a 10-mL aqueous solution containing 0.5 mM TA and 2 mM NaOH were added into a 48-mL glass pressure vessel. The solution was bubbled with nitrogen to remove air if needed to deoxygenate. Then the vessel was charged with pure H<sub>2</sub> or 1:1 H<sub>2</sub>&air to 0.2 MPa and kept at 30 °C in a water bath for assorted time duration with stirring. The fluorescence emission spectra excited at 315 nm from the 2-hydroxyterephthalic acid were captured on a Hitachi F-7000 fluorescence spectrophotometer (Japan).

Detection of phenyl radicals (·Ph): 1 mg Pd(111)/Al<sub>2</sub>O<sub>3</sub> was dispersed in 1 mL water in a 48-mL glass pressure vessel. The vessel was purged with nitrogen to remove air then charged with pure H<sub>2</sub> to 0.2 MPa and kept in water bath at 30 °C. 20  $\mu$ L phenol and 100 mmol DMPO were dispersed in 1 mL water and then injected into the above vessel. After stirring for 5 min, H<sub>2</sub> was removed and the solution was bubbled with air. The reaction mixture was filtered off and the filtrate was detected by ESR.

ESR spectra were recorded on a Bruker EMX-10/12 microspectrometer (Germany) at 30 °C. The operation frequency and power were 9.43 GHz and 19.83 mW, respectively. Liquid samples were injected into capillary tubes which were placed into NMR tubes for measurements. The data fitting process was conducted on an EPR simulator (www.eprsimulator.org) whose code was written by Victor Chechik at the University of York. Different species (DMPO-OH, DMPO-Ph and DMPO-degrade) were involved in the fitting process.

### **3** Results and discussion

Our experiments showed that by simply introducing air into the reaction system, the conversion of phenol to cyclohexanone at 30 °C was dramatically increased using commercial Pd NP/C catalyst (Figure 1(a) and Figure S2). Furthermore, the enhancement on the initial reaction rate by air was confirmed when home-made Pd NP/Al<sub>2</sub>O<sub>3</sub> (Figure S3) was employed as catalyst under same condition, also shown in Figure 1(a). The initial reaction rates using Pd NP/C and Pd NP/Al<sub>2</sub>O<sub>3</sub> as catalyst were amplified by 6 and 50 times, respectively. This effect unveils a progressive and robust approach to high conversion of phenol hydrogenation at low temperature.

For further utilization and industrial application of this method, it is demanding to understand the role of air and the reaction mechanisms over Pd-based catalysts. However,  $Al_2O_3$  supported Pd NPs have a complex structure containing different ration of edge, corner, terrace and defect sites [31]. It is too complicated to figure out why air can boost the hydrogenation conversion when Pd NPs were used. Thus, an uncomplicated and surface-clean Pd catalyst (i.e. Pd(111) nanosheets supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was chosen for further studies. The synthesis process was monitored by UV-Vis



**Figure 1** (a) Comparison of initial reaction rates of phenol hydrogenation catalyzed by commercial Pd catalyst (Pd NP/C) and home-made Pd NP/Al<sub>2</sub>O<sub>3</sub> in the presence of 0.2 MPa H<sub>2</sub> or 0.1 MPa H<sub>2</sub>+0.1 MPa air; (b) HR-TEM image of as-prepared Pd(111)/Al<sub>2</sub>O<sub>3</sub>; (c) time profiles of the conversion and selectivity of phenol hydrogenation to cyclohexanone catalyzed by Pd(111)/Al<sub>2</sub>O<sub>3</sub> at 30 °C; (d) apparent  $E_a$  of phenol hydrogenation catalyzed by Pd(111)/Al<sub>2</sub>O<sub>3</sub> (color online).

spectra (Figure S1), and the structure and exposed facets of as-prepared Pd(111)/Al<sub>2</sub>O<sub>3</sub> was determined by TEM, CO stripping and IR (Figure 1(b), Figures S4–S6).

As we expected, the air promoting effect was also observed in phenol hydrogenation using the as-prepared Pd(111)/Al<sub>2</sub>O<sub>3</sub> catalysts. Conversion exceeding 99% was achieved with over 99% selectivity within 7 h in the presence of H<sub>2</sub> and air at 30 °C in aqueous solution (Figure 1(c)). Furthermore, the conversion was maintained above 90% with selectivity over 99% after 5 cycling tests (Figure S7). On the contrast, the reaction barely happened in the absence of air, with conversion lower than 5% under similar condition. Results have also shown that the overall TOF in the presence of air is 621 h<sup>-1</sup> which is greater than the best reported value, 7.5  $h^{-1}$  [17,25,26], by a factor of 80 at the same temperature. Moreover, with the assistance of air, the initial TOF can reach 1300  $h^{-1}$  at 30 °C in our case, which is a little higher than that of gas phase hydrogenation of phenol at 180 °C [2,20,21]. These results revealed that introducing air into the reaction system readily increased the activity of the Pd catalyst in the selective hydrogenation of phenol to cyclohexanone at low temperature. With the enhanced activity at low temperature, a high selectivity toward cyclohexanone (>95%) was achieved owing to the relatively low activity of over-hydrogenation of cyclohexanone into cyclohexanol (Figure S8).

It is reported that the proceeds of phenol hydrogenation occurred in a stepwise manner. Phenol was first partially hydrogenated to an enol and then rapidly isomerized to form cyclohexanone. Cyclohexanone would be further hydrogenated into cyclohexanol [4,17]. However, our experimental data and literature result indicated that direct hydrogenation of phenol was hindered by high apparent  $E_a$  at low temperature. After introducing air into reaction system, the  $E_a$  was curtailed from 68.3 to 8.2 kJ/mol (Figure 1(d)), indicating that phenol was efficiently activated after introducing air. The low  $E_a$  in our case suggested a different reaction mechanism in the presence of air.

To better understand the role of air in the catalyzed reaction, firstly we figured out whether oxygen accelerated the catalytic activity. Various amount of pure oxygen was injected to the reaction system for further investigation, as nitrogen is known as an inert gas. From Figure 2(a), we can certainly conclude that the conversion of the reaction is highly dependent on the amount of oxygen.

It has been reported that active oxygen species, such as hydroxyl radicals, can be formed on Pd-based catalyst in the presence of both H<sub>2</sub> and O<sub>2</sub> [32,33]. The existence of  $\cdot$ OH was testified by fluorescence spectroscopy using TA as capture agent [34]. The presence of  $\cdot$ OH was only observed when air was introduced to the system, suggesting that OH radicals were generated from oxygen reacting with hydrogen catalyzed by Pd (Figure 2(b)).

The existence of OH radicals indicated that the reaction underwent a new pathway involving free radicals. To further understand the new mechanism, ESR was carried out using DMPO as spin trapping agent to detect free radicals in the reaction system. The ESR spectra (Figure 3(a)) from the reaction without phenol showed hyperfine coupling constants where  $a_N=15$  G and  $a_{H\beta}=15$  G, which were identified as DMPO-OH radicals [35]. This observation further confirmed the existence of hydroxyl radicals, which is consistent with the result in Figure 2(b).

ESR spectra from the reaction with phenol shown in Figure 3(b), with hyperfine coupling constants where  $a_N$ =



Figure 2 (a) Conversion of phenol to cyclohexanone catalyzed by  $Pd(111)/Al_2O_3$  as a function of oxygen amount (within 38-mL gas space); (b) the existence of hydroxyl radicals was testified by fluorescence spectroscopy using TA as a spin trapping agent.  $Pd(111)/Al_2O_3$  was used as catalyst throughout reactions (color online).

16 G and  $a_{H\beta}$  =23 G, revealed the existence of DMPO-Ph [36.37]. The presence of phenyl radicals (Ph) can be explained that phenol reacts with OH radicals to generate phenoxyl radicals (OPh) [38] which isomerise into ketocyclohexadienyl radicals ('Ph) at ambient conditions (Figure 3(c)) [39–41]. What is more, Li et al. [42] predicted that phenol dissociation to phenoxyl and further hydrogenation to form cyclohexanone was the major reaction route on Pd(111) by DFT studying. According to Li's DFT results and our experiment data, we can summary that the generation of phenoxyl species over Pd(111) is promoted through phenol reacting with OH radicals, leading to high reaction rate at low temperature (Figure 4). This is consistant with the previous reported by Nelson et al. [25] that the generation of phenoxyl species is conducive to promote reaction.

Based on above results, we can conclude that the formation of hydroxyl radicals is crucial to boost the hydrogenation of phenol to cyclohexanone. Thus, it is demanding to identify any factor that can affect the formation of OH radicals on Pd-based catalysts from the reaction between  $H_2$  and  $O_2$ . Besides the oxygen amount, we have proved that protic solvents



**Figure 3** Experimental and simulated ESR spectra of DMPO adducts obtained in water solution (a) after introducing air and then (b) adding phenol into the reaction system; (c) mechanism of phenoxyl radical isomerism to ketocyclohexadienyl radicals (·Ph) (color online).



Figure 4 Proposed mechanism of phenol hydrogenation by introducing air over Pd-based nanocatalysts (color online).

are also elemental for the increase of reaction activity by carrying out the reactions at same conditions with protic solvent (water) or aprotic solvents (*n*-hexane and ethyl acetate) (Figure S9). We predicted that the existence of protons is essential to generate OH radicals. The proton effect is consistent with the mechanism proposed by Wilson *et al.* [43], of which protons boosted oxygen-hydrogen reaction on Pd-based catalysts at low temperature.

# 4 Conclusions

In conclusion, we have developed a green, energy-saving and efficient method for selective hydrogenation of phenol to cyclohexanone by simply introducing air, over Pd-based nanocatalysts in aqueous system at low temperature. The activity was greatly enhanced due to the reduction of  $E_a$  as a result of the formation of phenoxyl radicals, which come from phenol reacting with hydroxyl radicals in the presence of oxygen and protic solvent. These findings provide deep insights into phenol hydrogenation in an alternative pathway and show great potential for industrial applications.

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**Conflict of interest** The authors declare that they have no conflict of interest.

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