

Pd nanoparticles supported on CeO₂ as efficient catalyst for hydrogen generation from formaldehyde solution at room temperature

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A facile and efficient method for facilitating hydrogen generation from formaldehyde aqueous solution was developed using Pd nanoparticles supported on CeO₂ (Pd/CeO₂) as the catalyst. The prepared Pd/CeO₂ catalyst exhibited 100% H₂ selectivity and excellent catalytic activity for formaldehyde dehydrogenation with the initial rate of 2089 ml min⁻¹ g_{Pd}⁻¹ at room temperature and atmospheric pressure without any extra additive. The prepared catalyst was stable and reusable, and its catalytic activity kept almost unchanged after it was reused for the fifth run. Therefore, it is considered that this Pd/CeO₂ based hydrogen generation system may serve as an alternative hydrogen supply candidate for practical application.

KEYWORDS

CeO₂, dehydrogenation, formaldehyde, Pd nanoparticles

1 | INTRODUCTION

With the constant growth of earth's population and the rising standards of living, the demand for energy is raising dramatically, which cause that fossil fuels are dwindling at alarming rates and environmental pollution is becoming increasingly serious. Therefore, it is imperative to search an alternative and sustainable energy sources for solving the energy crisis and environmental pollution problem. Hydrogen as a clean fuel has attracted considerable attention in recent years, [1a,1b,1c] and it has more distinct advantages than traditional fossil fuels, such as light-weight, high energy density (142 MJ kg⁻¹) and environmental benefits.^[2] However, searching for the effective hydrogen (H₂) storage/generation materials remains one of the most difficult challenges. Recently, hydrogen generation from various chemical materials such as borohydride,^[3a,3b] ammonia borane,^[4a,4b]

hydrazine,^[5a,5b] formic acid,^[6] and formaldehyde^[7] have received considerable attention.

Compared with other hydrogen production systems, hydrogen generation from formaldehyde has many significant advantages: it generated hydrogen with low costs at room temperature^[8]; the one hydrogen atom of H₂O molecule could be utilized^[9a, 9b]; no CO and CO₂ generated as by-product. Moreover, it is well known that formaldehyde is a pollutant and exists extensively in waste water, modern building materials and household products. Hydrogen generation from formaldehyde not only can be used to degrade formaldehyde pollutant, but also can be served as probe reaction to detect formaldehyde.^[10] Conventionally hydrogen was generated from formaldehyde in alkaline solutions at room temperature and atmospheric pressure, but the efficiency of hydrogen generation is very low. Bi *et al.*^[7,11a,11b,11c,11d,11e] and others groups^[12] have found that metallic nanoparticles (NPs), such

as Cu, Ag, Pd and Au, can catalyze this reaction. However, the activity and thermal stability are still low. For example, the rate of hydrogen production is $140 \text{ ml min}^{-1} \text{ g}_{\text{catalyst}}^{-1}$ at 60°C with nano-Cu particles as catalyst. With the Pd nanotubes as catalyst, the rate of hydrogen production is $167.6 \text{ ml min}^{-1} \text{ g}_{\text{catalyst}}^{-1}$ at 25°C . Metallic NPs catalysts inevitably tend to agglomerate into large particles, which may greatly decrease the catalytic performances of the catalysts, and therefore, they have relatively short lifetime. The development of efficient and stable catalysts is still an important challenge for the dehydrogenation from formaldehyde under moderate conditions.

Using suitable supports to load the metal NPs is the most common method to prevent agglomeration of metal NPs and improve the activity and stability of the catalysts. Up to now, metal oxides,^[10,13] polymers,^[14] carbonaceous materials,^[15a,15b,15c] metal–organic frameworks^[16a,16b,16c,16d] have been widely used to stabilize metal NPs. Bi and his coworker found that metal NPs support on Al_2O_3 ,^[5] TiO_2 ,^[9] SrTiO_3 ^[10] exhibit higher catalytic activity than metal NPs solely. Recently, there has been growing interest in ceria as a support for metal NPs due to its high chemical stability.^[11] Compared with the various supporting materials, cerium oxide (CeO_2) has many advantages: cerium (Ce) is one of the most abundant elements, which is much more than copper or tin; CeO_2 has the broadest spectrum of applicability; the growth process of CeO_2 NPs can be easily controlled; the cyclic usability and stability of CeO_2 against chemical corrosion are very good.^[28a, 28b] And most importantly, ceria could improve the catalytic performance of transition metals through strong metal-support interaction, in particular, of the late-transition metal NPs.^[29a, 29b] Ceria supported catalysts have been used in many chemical reactions such as automotive pollution conversion,^[30a, 30b] water gas shift reaction,^[31a, 31b, 31c] CO oxidation and selective oxidation,^[32a, 32b, 32c] methane combustion,^[33a, 33b] soot oxidation,^[34a, 34b] reforming,^[35a, 35b, 35c, 35d, 35e, 35f, 35g, 35h] formic acid oxidation,^[12] hydrogen generation from ammonia borane^[13, 22b, 29a] and so on. Especially, the presence of oxygen vacancy in CeO_2 result in strong interaction between Pd and CeO_2 , which may facilitated the electron transfer from Pd to CeO_2 support. Therefore the Pd in Pd/ CeO_2 possesses higher binding energy.^[36a, 36b] Pd/ CeO_2 exhibited good catalytical activity for various reactions, such as oxidation

reaction,^[36a, 36b, 37a, 37b] steam reforming,^[14] amination of alcohols,^[15] water–gas-shift reaction^[16] and so on.

Although ceria has found broad applications in the field of catalysis, its performance in catalyzing hydrogen generation from formaldehyde has not been explored.

In this work, Pd nanoparticles were supported on the surfaces of CeO_2 by the impregnation reduction process, and it was used as a catalyst for catalytic dehydrogenation from formaldehyde for the first time (Scheme 1). Pd/ CeO_2 catalyst was characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, N_2 adsorption and X-ray photoelectron spectroscopy techniques. All the results reveal that Pd NPs were uniformly dispersed on the surface of CeO_2 . The supported Pd/ CeO_2 catalysts exhibited remarkable catalytic activities. The initial rate of hydrogen generation can reach $2089 \text{ mL min}^{-1} \text{ g}_{\text{Pd}}^{-1}$ at room temperature and atmospheric pressure. The results also showed that the Pd/ CeO_2 catalyst was reusable and its catalytic activity kept almost unchanged after it was reused for the fifth run.

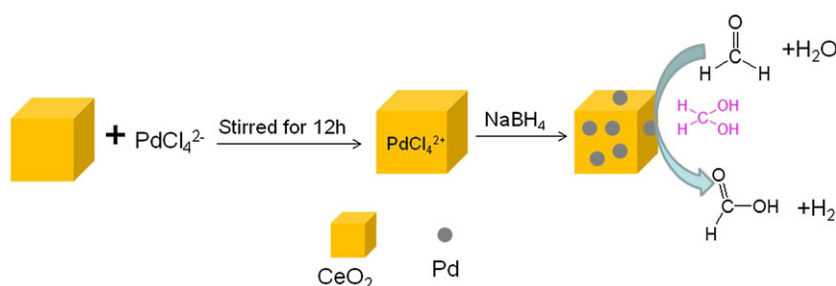
2 | EXPERIMENTAL

2.1 | Chemicals

Palladium (II) chloride (PdCl_2), sodium borohydride (NaBH_4 , 96%), cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), urea ($\text{CH}_4\text{N}_2\text{O}$, 99%) were purchased from Aladdin Reagent Limited Company (China). Hydrochloric acid (HCl , 37%) was obtained from Boaixin Chemical Reagents Company (Baoding, China) and used as received. Formaldehyde (AR, 37 wt. % in H_2O) was purchased from Shanghai Macklin Biochemical Co, Ltd (Shanghai, China).

2.2 | Characterization

Transmission electron microscopy (TEM) studies were conducted on a JEOL model JEM-2011(HR) instrument. X-ray photoelectron spectroscopy (XPS) was performed with a PHI 1600 spectroscope. The size and morphology of the Pd NPs were observed by transmission electron microscopy (TEM) using a JEOL model JEM-2011(HR) at 200 kV. The X-ray diffraction (XRD) patterns of the samples were recorded with a TD-3700 X-ray diffractometer (Dandong, China).



SCHEME 1 Schematic representation of the synthesis process of Pd/ CeO_2 and the hydrogen generation from formaldehyde

The analysis of CO₂, H₂ and CO was performed on SP-2000 (China) gas chromatograph (GC) with thermal conductivity detector (TCD) and flame ionic detector (FID)-Methanator. The high-performance liquid chromatography (HPLC) system was an LC-20A (Shimadzu, Japan), which consists of a SPD-20A UV/vis detector, two LC-20AT pumps, and LC-solution software. The column used was a Promosil C18 column (250 × 4.6 mm id, 5.0 m) from Bonna Agela Technologies (Tianjin, China). The mobile phase was a mixture of acetonitrile/water (60:40 v/v) at a flow rate of 1.0 ml/min. The UV monitoring wavelengths were chosen at 198 nm. The surface area, total pore volume and pore size distribution of the samples were measured by nitrogen adsorption using a APPV-Sorb 2800P Surface Area and Porosity Analyzer, the degassing of the samples was performed at 120 °C for 2 h.

2.3 | Synthesis of ceria (CeO₂)

Ceria (CeO₂) was synthesized according to the reported procedure.^[17] Briefly, Ce(NO₃)₂·6H₂O (1.303 g, 3 mmol) and urea (5.404 g, 90 mmol) were dissolved in 15 ml of deionized water. Then the solution was treated with microwave at 90 °C for 1 h in a three-neck flask. After centrifugation and washing with water, the obtained white solid was dried at 80 °C in vacuum for 24 h. Finally, the CeO₂ was obtained by calcination at 300 °C for 5 h.

2.4 | Synthesis of Pd/ CeO₂ catalyst

For preparation of Pd/CeO₂, 50 mg of CeO₂ was dispersed in 20 ml deionized water, then 6.187 ml of 1 mg ml⁻¹ H₂PdCl₄ solution (0.025 mmol) was added. The mixture was vigorously stirred at room temperature for 12 h. The above obtained solution was reduced by NaBH₄ solution (10 mg NaBH₄ + 10 ml H₂O) at room temperature for 2 h with vigorous stirring. After filtration and washing with deionized water, the obtained Pd/ CeO₂ (The mass content of total metals was 5%) was dried at 70 °C in vacuum overnight.

2.5 | Activity test

The hydrogen production from formaldehyde solution was carried out in a 600 ml sealed flask, which was placed in a water bath with magnetic stirrer at a preset temperature (25-50 °C) under ambient atmosphere. First, the as-prepared catalyst (15 mg) was dispersed in HCHO and NaOH aqueous solution (100 ml). The mixture solution was placed in a water bath at a preset temperature with stirring vigorously. The amounts of hydrogen produced were measured every 5 min by a gas chromatograph equipped with TCD detector using argon as carrier gas.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of catalyst

The morphology of Pd/CeO₂ was characterized by transmission electron microscopy (Figure 1). As shown in the Figure 1, rodlike CeO₂ is formed and Pd NPs were homogeneously dispersed on the surface of the CeO₂ nanoparticles. As shown in Figure 2, it is very difficult to identify crystallites of Pd. It looks like Pd lattice is covered by CeO₂ lattice. But we can identify the position of Pd according to the lattice spacing. The lattice spacing of Pd (111) and (200) is 0.22 nm and 0.25 nm, respectively. The high-resolution TEM (HRTEM) of Pd/CeO₂ (Figure 1c) shows that the lattice spacing of CeO₂ is 0.26 nm, 0.29 nm and 0.30 nm, which can be assigned to the (200) plane and (111) plane of CeO₂, respectively, which is lower than that of CeO₂ solely (Table 1). The result proves that Pd species are incorporated into the CeO₂ lattice.

As shown in Figure 2, the rodlike CeO₂ possess mesoporous structure. The Brunauer–Emmett–Teller (BET) surface area and the total pore volume of CeO₂ were 128 m² g⁻¹ and 0.12 cm³ g⁻¹, respectively. The BET surface area of the prepared CeO₂ is much larger than that of CeO₂ reported in the literature (83.1 m² g⁻¹).^[37a] The large surface area may provide more sites for loading metal Pd NPs, and the resulting Pd/CeO₂ can provide more active centers for catalyzing the dehydrogenation reaction. As shown in Figure 2, the BET surface area of Pd/CeO₂ (60 m² g⁻¹) is lower than that of the prepared CeO₂ (128 m² g⁻¹), which indicates that the Pd NPs located on the external surface CeO₂.

The crystallographic structure of the as-prepared Pd/CeO₂ was researched by XRD. As shown in Figure 3a, the diffraction peaks of Pd/CeO₂ at 2θ 28.58°, 33.02°, 47.76°, 56.86°, were corresponded to (111), (200), (220) and (311) planes of CeO₂ crystals, respectively. The CeO₂ in Pd/CeO₂ is a face-centered cubic (fcc) crystal structure (PDF No.75–0390, a = b = c = 0.5411 nm). It is noteworthy that no significant diffraction peak of palladium phase can be seen in the Figure 3a, which can be ascribed to the well dispersed metal nanoparticles, low loading of Pd NPs. Other reasons for that might be that palladium species has been incorporated into the CeO₂ lattice to form a solid solution (which is denoted as Pd–O–Ce)^[38a, 38b] or covered by CeO₂ lattice or Pd nanoparticles existed in an amorphous state on the support.

In order to study the surface constitution, the Pd/CeO₂ was further characterized by X-ray photoelectron spectroscopy (Figure 4). Ce, O, C and Pd signal were observed on the surface of the sample, which demonstrates that metal of Pd was successfully supported on the surface of CeO₂. The 3d_{5/2} and 3d_{3/2} peak of Pd⁰ appear at 335.42 eV and 340.62 eV, respectively.^[18] Two peaks located around

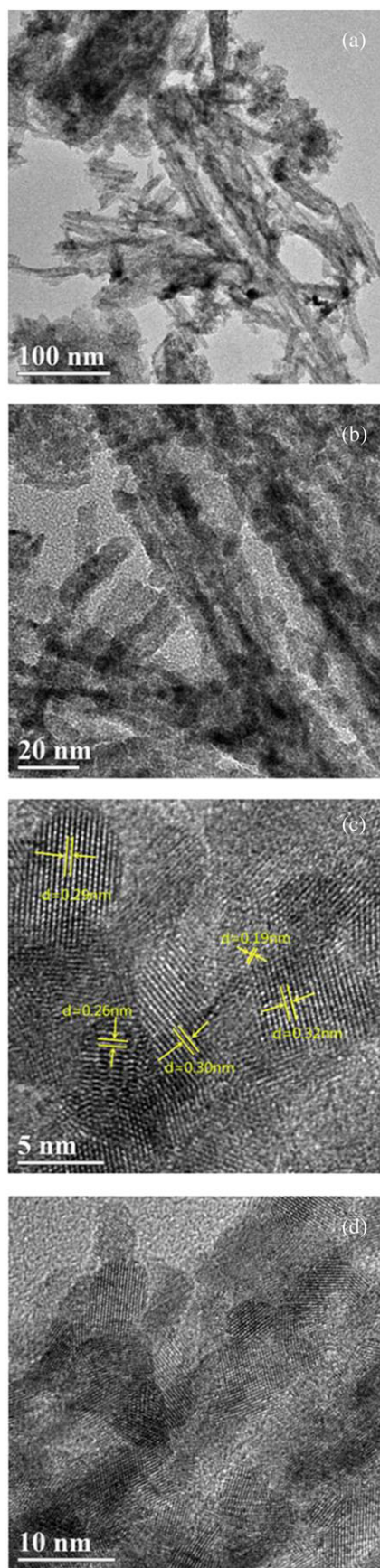


FIGURE 1 TEM images (a and b) and HRTEM images (c and d) of 5 wt% Pd/CeO₂

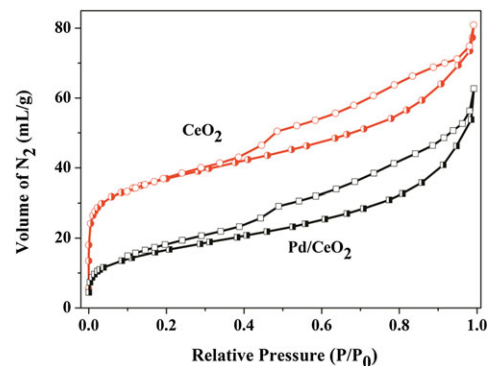


FIGURE 2 N₂ adsorption–desorption isotherms of CeO₂ and Pd/CeO₂

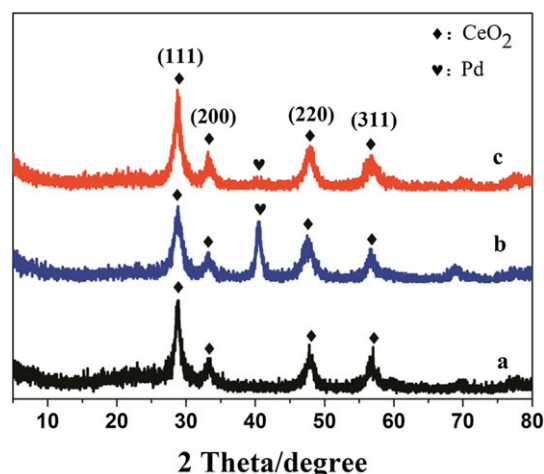
336.42 eV and 341.42 eV are a characteristic of the electron binding energy of Pd²⁺ in the 3d_{5/2} and 3d_{3/2} level.^[39a, 39b] Two peaks located around 337.77 eV and 343.02 eV are assigned to Pd²⁺ in Pd–O–Ce solid solution. The existence of Pd²⁺ in the catalyst come from the oxidation of metallic Pd by air^[40a, 40b] and the palladium particles in the catalysts are oxidized because of the formation of Pd–O–Ce bonding.^[19] To identify which Pd species is active catalytic one for the hydrogen generation from HCHO, the composition and catalytic activity of Pd/CeO₂ exposed in air for two months were investigated. The XPS of Pd/CeO₂ exposed in air for two months is shown in Figure S1. From which we can see that the amount of PdO increased significantly compared with the fresh prepared Pd/CeO₂. The catalytic activity of Pd/CeO₂ exposed in air for two months was investigated and the results are shown in Figure S2. From which we can see that the activity of Pd/CeO₂ exposed in air for two months decreased greatly. It is safely to say that metallic Pd is the active species for the hydrogen generation reaction.

3.2 | Effect of Pd loading amounts

Figure 5 shows the effect of Pd loading amounts on the hydrogen production from HCHO solution. The loading amounts of Pd on CeO₂ highly influence the hydrogen production rate. When the loading amounts of Pd increased from 2 wt% to 5 wt%, the average rate of hydrogen production increased. Further increasing the amounts of Pd to 15 wt%, the average rate of hydrogen production decreased. The results may be ascribed to that the high loading amount of Pd lead to the aggregation of Pd nanoparticles, As shown in Figure 3, the diffraction peaks of Pd at $2\theta = 40.04^\circ$ can be assigned to (111) planes of Pd. However, no significant diffraction peak characteristic of Pd species is detected from the XRD pattern of 5 wt% Pd/CeO₂ (Figure 3a), which can be ascribed to the well dispersed metal nanoparticles and low metal loading. For 15 wt% Pd/CeO₂ (Figure 3b), the diffraction peak of Pd at $2\theta = 40.04^\circ$ is detected and the particle size of Pd is apparently bigger than that of 5 wt% Pd/CeO₂.

TABLE 1 Lattice parameter of CeO₂ and Pd/CeO₂

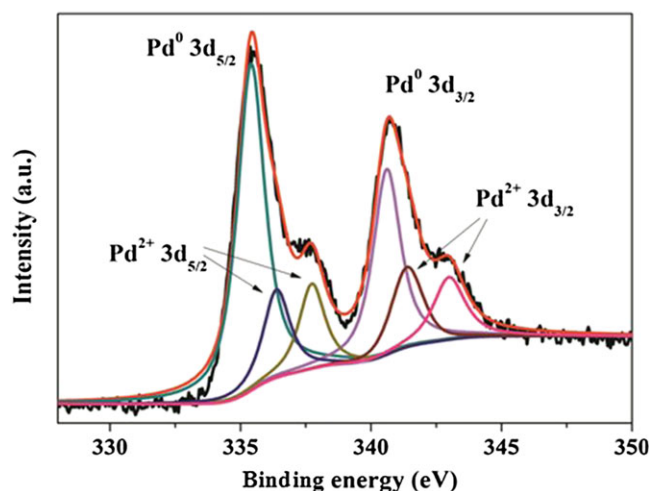
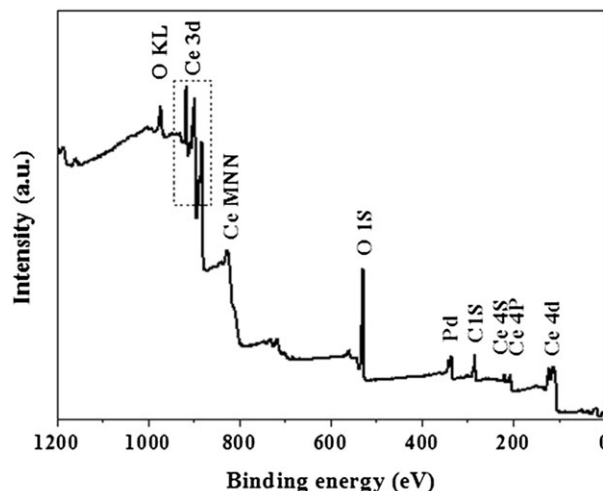
Samples	Exposed crystallographic plane	Lattice spacing [ref.]
CeO ₂	110	0.19 nm ^{36a}
CeO ₂	111	0.31 nm ^{24a, 36a}
CeO ₂	200	0.27 nm ^{37a}
5% Pd/CeO ₂	CeO ₂ (200)	0.26 nm
5% Pd/CeO ₂	CeO ₂ (111)	0.30 nm
5% Pd/CeO ₂	CeO ₂ (111)	0.29 nm

**FIGURE 3** XRD pattern of the Pd/CeO₂. a. 5% Pd/CeO₂; b. 15% Pd/CeO₂; c. Recycled 5% Pd/CeO₂

The aggregation of Pd nanoparticles is not favorable for the catalytic activity. In order to enhance the hydrogen generation rate, 5 wt% Pd/CeO₂ (the mass content of Pd in Pd/CeO₂ was 5%, the molar ratio of palladium to formaldehyde is 0.00013) was selected as catalysts for the hydrogen generation reaction from alkaline formaldehyde solution.

3.3 | Effect of HCHO concentration

The influence of HCHO concentrations on hydrogen generation was studied, and the result was shown in Figure 6. It can be seen that the average rate of hydrogen generation increased with increasing the HCHO concentration from 0 to 0.54 mol L⁻¹. When the HCHO concentration was 0.54 mol L⁻¹, the average rate of hydrogen generation was the highest (2089 ml min⁻¹ g_(Pd)⁻¹). However, further increase the concentration of formaldehyde, the rate of hydrogen generation slow down. The results indicated that concentration of formaldehyde has remarkable effects on the hydrogen generation from HCHO solution. Therefore, in order to achieve higher hydrogen generation rate, 0.54 mol L⁻¹ was chosen as the optimal HCHO concentration.

**FIGURE 4** XPS pattern of the Pd/CeO₂

3.4 | Effect of NaOH concentration

The effect of NaOH concentration on the hydrogen generation rate was also investigated. As can be seen in Figure 7, no hydrogen can be detected in the absence of NaOH. When a small amount of NaOH was added into the reaction system, hydrogen generated immediately. The result indicates that NaOH play an important role in the reaction. As NaOH concentration increased from 0.5 to 1 mol L⁻¹, the average rate of hydrogen generation increased. Further increasing NaOH

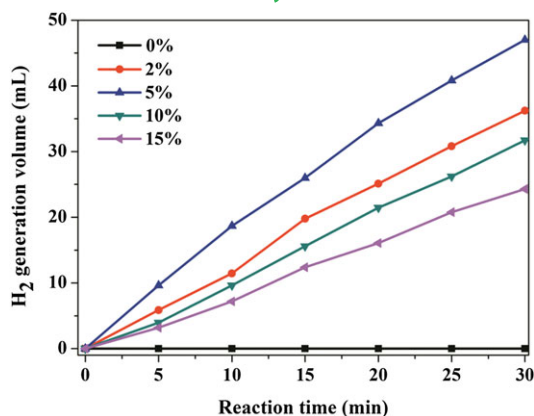


FIGURE 5 Effect of Pd loading amount on the rate of hydrogen generation. Reaction condition: $T = 30\text{ }^{\circ}\text{C}$; NaOH concentration = 1 mol L^{-1} ; HCHO concentration = 0.54 mol L^{-1} ; amount of catalyst = 15 mg

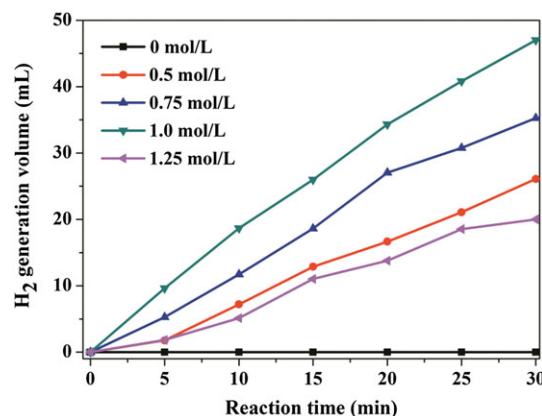


FIGURE 7 Effect of NaOH concentration on the rate of hydrogen generation. Reaction condition: $T = 30\text{ }^{\circ}\text{C}$; HCHO concentration = 0.54 mol L^{-1} ; amount of catalyst = 15 mg

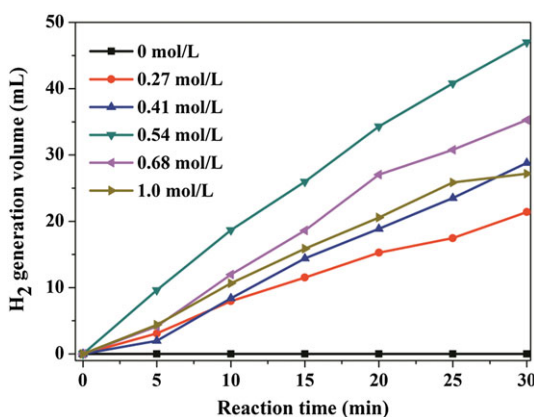


FIGURE 6 Effect of HCHO concentration on the rate of hydrogen generation. Reaction condition: $T = 30\text{ }^{\circ}\text{C}$; NaOH concentration = 1 mol L^{-1} ; amount of catalyst = 15 mg

concentrations to 1.25 mol L^{-1} , the rate of hydrogen production decreased obviously. This may be due to the competition with the Cannizzaro reaction. In Cannizzaro reaction, the formaldehyde was transformed into corresponding methanol and formic acid in high concentration of alkaline.^[25a] No hydrogen was detected when methanol or formic acid was used as the reactant. The composition of the evolved gas from formaldehyde solution was also measured by GC. The chromatograms are shown in Figure S3 and Figure S4, respectively. From which we can see that the composition of the evolved gas from formaldehyde decomposition over Pd/CeO₂ include H₂, O₂ and N₂. The O₂ and N₂ both come from the air. Moreover, no CO and CO₂ can be detected in the evolved gas, which indicated that no CO and CO₂ formed in the formaldehyde hydrolysis reaction. The HPLC chromatogram of the reaction solution of formaldehyde decomposition is shown in Figure S5. From which we can see that sodium formate exist in the liquid phase, which is formed from formaldehyde decomposition in alkali media.

3.5 | Effect of reaction temperature

The influence of reaction temperature on the hydrogen production from HCHO has been investigated. As shown in Figure 8a, the rate of hydrogen generation increased rapidly from $1726\text{ to }3832\text{ ml min}^{-1}\text{g}_{\text{Pd}}^{-1}$ when the temperature increased from 25 to $50\text{ }^{\circ}\text{C}$, which demonstrated that high temperature is favorable to hydrogen generation from HCHO. Because the amount of hydrogen generation was linearly increased with reaction time in the range of $25\text{--}50\text{ }^{\circ}\text{C}$, the hydrogen generation reaction could be considered as zero order reaction. So, the reaction rate equation can be written as follows:

$$k = A \exp(-E_a/RT) \quad (1)$$

where k is the rate constant; A is the frequency factor; E_a is the activation energy; R is the gas constant, and T is the absolute temperature. The Arrhenius plot of $\ln k$ vs. $1/T$ for the catalyst was plotted in Figure 8b. The activation energy was calculated to be 22.13 kJ mol^{-1} , which was much lower than the reported value (39.87 kJ mol^{-1} and 65 kJ mol^{-1}).^[24a, 24b]

4 | STABILITY OF Pd/CeO₂ CATALYST

The stability of catalyst was investigated. As shown in Figure 9, the rate of H₂ generation kept constant after five runs, which demonstrated that the Pd/CeO₂ exhibited an excellent catalytic activity and stability. The XRD of the recyclable catalyst was tested (Figure 3c) and the diffraction peaks remained unchanged compared with the fresh Pd/CeO₂ (Figure 3a).

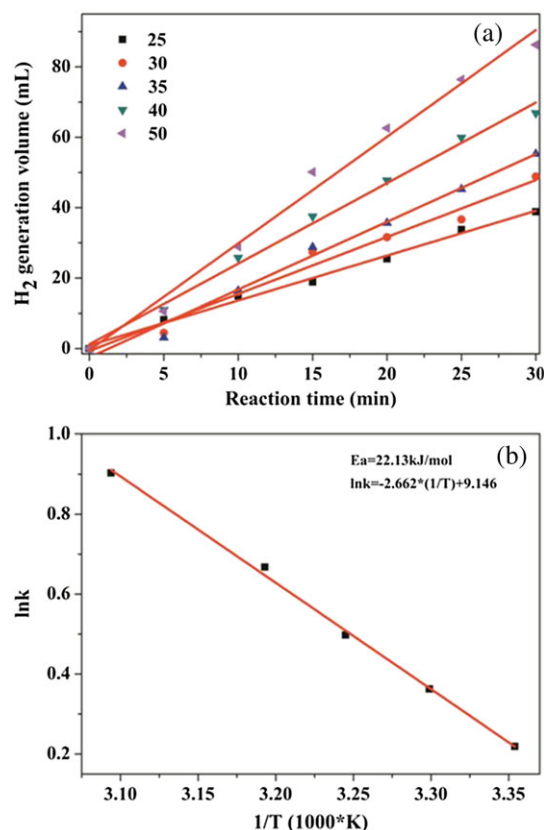


FIGURE 8 Effect of reaction temperature on hydrogen generation from HCHO (a) and Arrhenius plot ($\ln(\text{TOF})$ vs. $1/T$) (b). Reaction condition: NaOH concentration = 1 mol L^{-1} ; HCHO concentration = 0.54 mol L^{-1} ; amount of catalyst = 15 mg

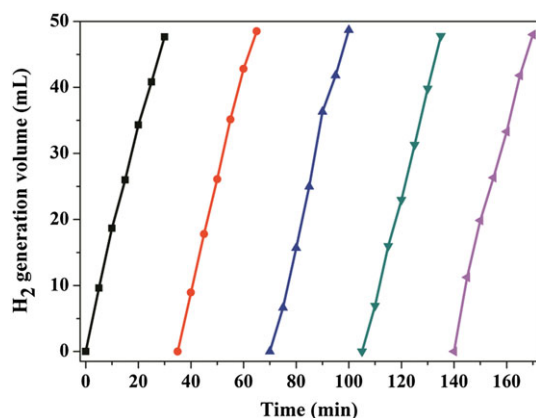


FIGURE 9 Stability of catalyst. Reaction condition: $T = 30 \text{ °C}$; NaOH concentration = 1 mol L^{-1} ; HCHO concentration = 0.54 mol L^{-1} ; amount of catalyst = 15 mg

5 | CONCLUSIONS

In this work, we developed a facile and efficient method for facilitating hydrogen generation from alkaline formaldehyde aqueous solution at room temperature using Pd/CeO₂ as the catalyst. The catalyst exhibited excellent catalytic activity with the hydrogen generation rate of $2089 \text{ ml min}^{-1} \text{ g}_{\text{(Pd)}}^{-1}$

without any extra additive. Owing to the low costs and high efficiency of the catalyst, it may greatly encourage the practical application of formaldehyde as a hydrogen storage material.

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