



Palladium nanoclusters decorated partially decomposed porous ZIF-67 polyhedron with ultrahigh catalytic activity and stability on hydrogen generation

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ABSTRACT

Metal-organic frameworks have attracted extensively attentions due to their unique structural properties such as high porosity, good crystallinity, and three-dimensional networking. However, to the best of our knowledge, there is no report concerning the application of partially decomposed metal-organic frameworks based catalyst for sodium borohydride hydrolysis for H₂ generation. Herein, the partially decomposed cobalt-based zeolitic imidazolate frameworks supported Pd nanoclusters are fabricated by evaporation solvent assisted method followed by subsequent annealing under H₂ atmosphere. Our results show that catalytic performance of the designed catalyst can be largely improved by optimizing the Pd loading and the annealing temperatures. The optimized catalyst exhibits a high catalytic activity towards hydrolysis of alkalized sodium borohydride with a specific H₂ generation rate of 20.6 l min⁻¹ mg_{Pd}⁻¹ and turnover frequency of 495.0 mol min⁻¹ mol_{Pd}⁻¹ at 25 °C, which is the highest reported so far among the similar catalysts. Moreover, the resulted catalyst also demonstrates a high level of stability. Based on structural characterization and experimental optimization, the extraordinary performance of the fabricated catalyst is mainly contributed to the synergetic effect of highly dispersed Pd nanoclusters with partially decomposed cobalt-based zeolitic imidazolate frameworks.

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1. Introduction

Hydrogen is considered as one of the most promising sustainable energy sources due to the high chemical energy density [1–3]. However, the conventional hydrogen storages methods such as gas compression or liquefaction cannot meet the high-energy demand of automobile industry due to the relatively low storage density [4]. Accordingly, many works have been done to find high energy density hydrogen storage methods [5–8]. Sodium borohydride (NaBH₄) is studied extensively due to the high theoretical hydrogen storage capacity (10.8%), easy-to-process and environmental

friendly, which makes it a good candidate for portable hydrogen generator [9–11]. Over past decades, the noble metal based catalysts were reported with a particularly high efficiency in terms of rapid hydrogen generation from NaBH₄ solution, such as Pt/CeO₂–Co₇Ni₂O_x [12], Pt/3D SiC [13], Pt/Co₃O₄ [14], Pt/LiCoO₂ [15], Rh/Ni BNPs [16], Co_{0.8}–Ag_{0.2}–B [17], Ni/Au/Co [18], Ni_{0.9}Pt_{0.1}/Ce₂O₃ [19], Ru@SiO₂ [20], and Ag/SiO₂–CoFe₂O₄ [21]. However, owing to the high cost of noble metals and self-agglomeration, transition metal based catalysts would be a desirable alternative [22–24]. Recently, many non-noble transition metal catalysts have been investigated in this regards but most of the results are unsatisfactory due to the low activity and poor reusability [25,26]. Another alternative approach is to improve the catalyst support to improve catalyst dispersion and decrease the catalyst loading [27,28]. As a result, the price of the noble metals will not be an issue. In this regards, metal-organic frameworks (MOFs) supported noble metal catalysts have attracted broadly attention due to their high surface areas, tunable porosities and thermal stability [29]. It has been well

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accepted that the confined pores and cavities of MOFs define the anchored metal particles sizes and distribution, which in turn not only improve the catalytic activity, but also inhibit particle migration and aggregation, consequently enhance the catalyst stability in the hydrolysis process [30,31]. So far, a series of metal particles/MOFs catalysts have been developed for hydrolytic H_2 generation, e.g., Pd@MIL-101 [32], PdNi@MIL-101 [33], AgPd@UIO-66-NH₂ [34], RhNi@ZIF-8 [35], Pt@MIL-101 [36], Ru@MIL-53 [37], Ru@MIL-96 [38], and so on. But the TOF values of most catalysts for NaBH₄ hydrolysis are between 80 and 270 min⁻¹. In general, most of the MOFs used as supports have very low conductivity thereof hindering charge transfer process during the hydrolysis, thereby significantly reducing the catalytic activity. Furthermore, the current knowledge on the reaction mechanism of MOF supported noble metal catalyst for NaBH₄ hydrolysis remains rather limited and unclear.

Herein, we designed and synthesized partially decomposed cobalt-based zeolitic imidazolate frameworks supported Pd catalyst (Pd/PD-ZIF-67) for NaBH₄ hydrolysis that exhibits high level of structural stability, good conductivity and well-dispersed active sites. Accordingly, the optimized Pd/PD-ZIF-67 catalyst shown the highest catalytic activity so far reported among the metal/MOF catalyst for H_2 generation with a TOF value of 495.0 mol min⁻¹ mol Pd⁻¹ toward hydrolysis of NaBH₄ at 25 °C. Additionally, the Pd/PD-ZIF-67 catalyst also displayed remarkable stability on the NaBH₄ hydrolysis for H_2 generation with a minimum decay of catalytic activity around 10% after five consecutive cycles. The superior catalytic performance could be ascribed to the partial oxidation of Co induced fast electron transfer property and high level of hydrophilicity that synergistically combined with the highly dispersed Pd nanoclusters thereof enhances the catalytic activity. Accordingly, we are proposed a possible catalytic mechanism.

2. Experimental

2.1. Synthesis of Pd/PD-ZIF-67

All chemical reagents are analytical grade and used without further purification. ZIF-67 was prepared by a solution precipitation method (Fig. S1) [39]. The hybrid material of Pd/PD-ZIF-67 was achieved by the following two steps. Initially, 50 mg of as-synthesized ZIF-67 was ultrasonically dispersed into 10 mL of acetone for 20 min. After that, a certain amount of Pd(NO₃)₂ aqueous solution (10 mg mL⁻¹) was added into the above solution under vigorous stirring at room temperature. After continuous stirring for another overnight, the acetone was evaporated and the remaining solids were collected. Then, the collected solid was finely ground to a fine powder before being put into in a tube furnace. The heating temperatures slowly rise to the target temperatures (150 °C–350 °C) at a fixed heating rate of 2 °C min⁻¹ in H_2 atmosphere for 2 h. After cooling to ambient temperature, the resulted Pd/PD-ZIF-67 hybrid materials were obtained for subsequent use.

2.2. Catalyst characterizations

The morphologies and microstructures of the catalysts were characterized by scanning electron microscope (SEM, FEI Quanta 200 FEG) and transmission electron microscope (TEM, JEM-2100F). The crystal structures of different catalysts were analyzed by X-ray powder diffraction (XRD, Rigaku D/Max 2500 V/PC) with a sweep speed for 5.0° min⁻¹. The X-ray photoelectron spectrometer (XPS, JPS-9010 Mg K α) was used to analyze of the chemical states of different elements in the hybrid materials. The actual metal loading

of different metals in the composite were detected by inductive coupled plasma emission spectrometer (ICP, IRIS IntrepidII XSP). The conductivity of the synthesized materials were measured by a four-probe system (RTS-2A).

2.3. Catalytic measurements

The synthesized catalysts of catalytic performance, reusability and activation energy were studied as following. Initially, 50 mL of 150 mM NaBH₄ (contained 0.4 wt% NaOH) was injected into a round-bottomed flask (100 mL) and continuously stirred for 0.5 h at 25 °C in water bath heater. After that, 10 mg catalyst was added into the above solution. The produced H_2 was calculated by a drainage method, in which the overflowed water was collected and weighted by a balance. The instantly changed qualities of water were recorded by a computer which had connected with the used balance. The reusability procedures of the catalyst were described as following. The above hydrolyzed solution of NaBH₄ was stirred for another 1 h for the completed reaction in the first-cycle, and then the catalytic procedure of NaBH₄ hydrolysis was repeated and detected the H_2 generation again using the same amount of NaBH₄. The activation energy of the designed catalyst was evaluated by research at different temperatures in the same device including 25 °C, 30 °C, 35 °C, 40 °C and 45 °C.

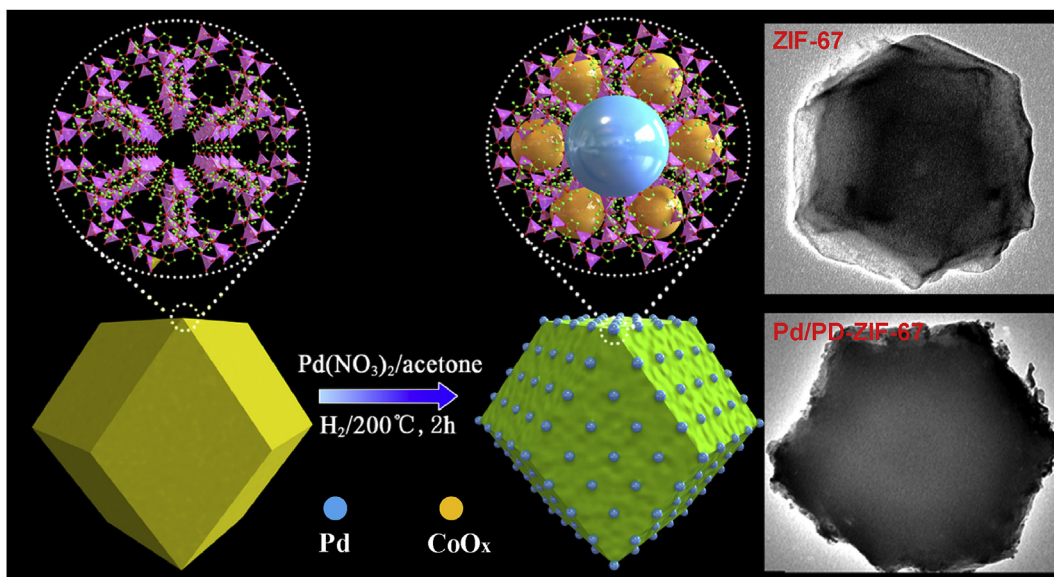
3. Results and discussion

3.1. Synthesis and characterizations of Pd/PD-ZIF-67

As a zeolitic imidazole framework (ZIF), the ZIF-67 was selected because it can be rapidly synthesized with commercial available reagents, thermally stable and highly porosity [40]. The Pd/PD-ZIF-67 nanocomposites are prepared by dispersing the ZIF-67 particles in the acetone solution of Pd(NO₃)₂ followed by slow evaporation of the solvent. The resulting mixture was subsequently calcined in the H_2 atmosphere for 2 h. The schematics are shown in Scheme 1. The optimal performance of the catalyst was obtained 1.62 wt% Pd loading at the reduction temperature of 200 °C.

The crystal structures of the synthesized Pd/PD-ZIF-67 materials at different temperatures along with ZIF-67 are characterized by X-ray diffraction (XRD) patterns. As shown in Fig. 1a, the Pd/PD-ZIF-67 (200 °C) exhibits several additional peaks compared to the that of pure ZIF-67 [41]. Whereas the peaks at 19.0, 31.2, 36.8, 38.6, 44.7, 55.6, 59.3 and 65.1° can be ascribed to the cubic structures of Co₃O₄ (JCPDS: 43-1003) [42], while the peaks at 42.3, 61.5, 73.7 and 77.3° are due to the cubic structures of CoO (JCPDS: 43-1004). The peaks at 40.1, 46.7, 68.4 and 82.3° are attributed to the cubic crystal of (111), (200), (220) and (311) facets of Pd (JCPDS: 46-1043) [43,44]. Other than these features, the rest of the peaks are perfectly overlapped with these of ZIF-67. However, when the reduction temperatures are equal to or higher than 250 °C, the diffraction peaks of ZIF-67 in the hybrid materials are all disappeared and all the Co-species were transformed into CoO_x (Fig. S1), meaning the Pd/PD-ZIF-67 can be decomposed at the annealing temperature higher than 200 °C (Fig. S2). The morphologies of Pd/PD-ZIF-67 start to collapse from 200 °C indicating that the partial decomposition becomes visible after 200 °C.

The microstructures of ZIF-67 and the corresponding Pd/PD-ZIF-67 were investigated by scanning electron microscope (SEM) and transmission electron microscopy (TEM). As shown in Fig. 1b and c, the SEM images of the ZIF-67 exhibits clear edges and well-defined structures. After Pd deposition, the new catalyst Pd/PD-ZIF-67 still kept the rhombic dodecahedron crystal morphology of ZIF-67, but the surface became relatively rough compared to that of ZIF-67 (Fig. 1d and e). The TEM image shows well-dispersed Pd



Scheme 1. Schematic synthesis of Pd nanoclusters on PD-ZIF-67 support by a facile evaporation method combined with a subsequent H₂-assisted reduction treatment.

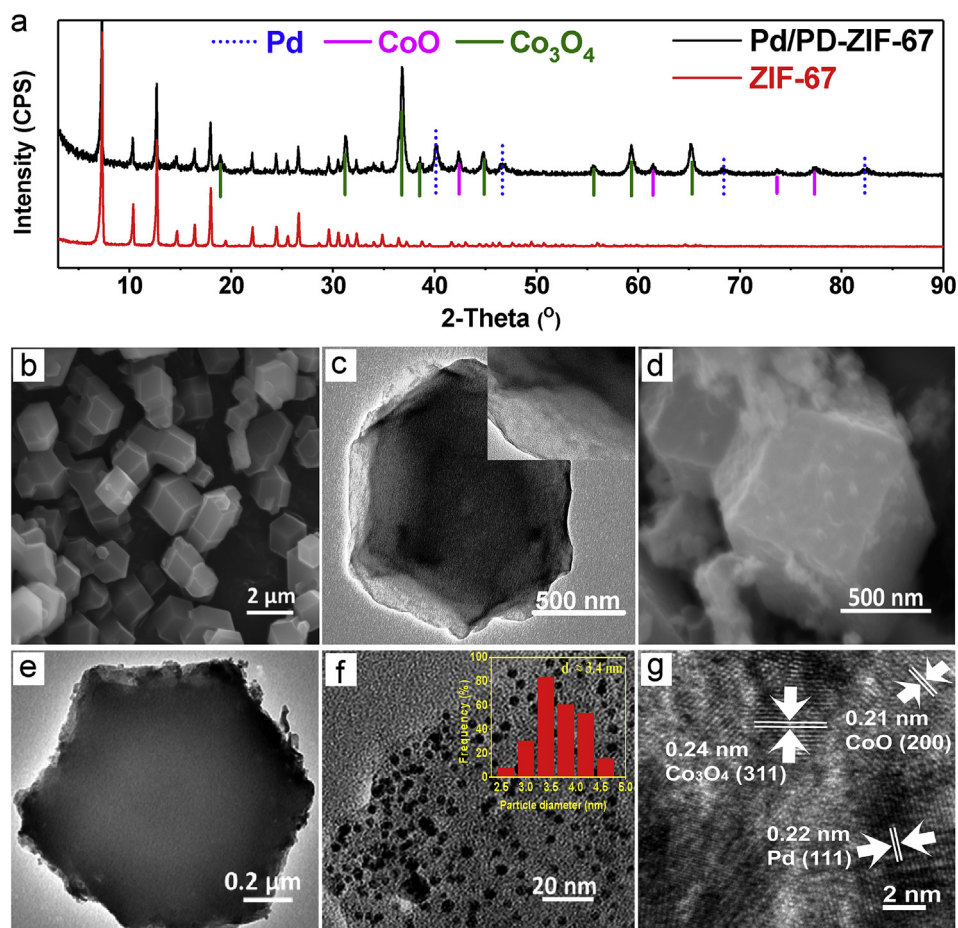


Fig. 1. (a) XRD patterns of synthesized ZIF-67 and Pd/PD-ZIF-67. (b) SEM image and (c) TEM image of ZIF-67. (d) SEM image of Pd/PD-ZIF-67. (e, f) TEM images of Pd/PD-ZIF-67 with different magnifications. (g) High-resolution TEM image of Pd/PD-ZIF-67.

nanoclusters with the size distribution between 2.4 and 4.8 nm, and the average particle size is 3.4 nm (Fig. 1f). The Pd nanoclusters start to agglomerate when the annealing temperature under H₂ is increased to 300 °C and a clear agglomeration can be visualized by

TEM (Fig. S3). The three different lattice d-spacings with the value of 0.24, 0.21 and 0.22 nm correspond to the Co₃O₄ (311), CoO (200) and Pd (111) respectively, which clearly indicates the coexistence of these three components in the Pd/PD-ZIF-67 treated at 200 °C for

2 h (Fig. 1g). The mapping of energy dispersive spectroscopy (EDS) reveals the uniform distributions of the Co, Pd, O, N and C species on the Pd/PD-ZIF-67 surface (Fig. S4). Moreover, the actual loadings of Pd species in hybrid materials (200 °C) are determined by ICP and the results are consistent with the experimental values (Table S1).

The elemental compositions and chemical states of the Pd/PD-ZIF-67 (200 °C) are also determined by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum revealed the Pd, Co, N, O and C elements in Pd/PD-ZIF-67 composite as shown in Fig. S5 and the high resolution C 1s XPS spectrum is convoluted into C=C (284.0 eV), C–C (284.8 eV) and C–O (286.0 eV), respectively [39]. The high-resolution Pd 3d spectrum is analyzed by fitting into six asymmetric peaks (Fig. 2a), whereas the peaks are assigned according to the literature on Pd 3d_{5/2}. The Pd 3d_{5/2} three doublets at 335.2, 336.8 and 338.6 eV are corresponding to metallic Pd, adsorbed Pd²⁺ and PdO, respectively [45]. The relative contents of the metallic Pd, adsorbed Pd²⁺ and PdO are 20.9%, 16.4% and 62.7% in the total Pd, respectively. Fig. 2b shows the high-resolution Co 2p spectrum, where the characteristic peaks of metallic Co⁰ locate at 778.8 eV (2p_{3/2}), while the binding energies at 780.3 eV (2p_{3/2}) and 795.7 eV (2p_{1/2}) and their corresponding satellites are due to Co³⁺/Co²⁺ [46]. The two peaks corresponding to N 1s appear at 398.6 and 400.1 eV (Fig. 2c), which are ascribed to pyridinic-N and pyrrolic-N [47], respectively.

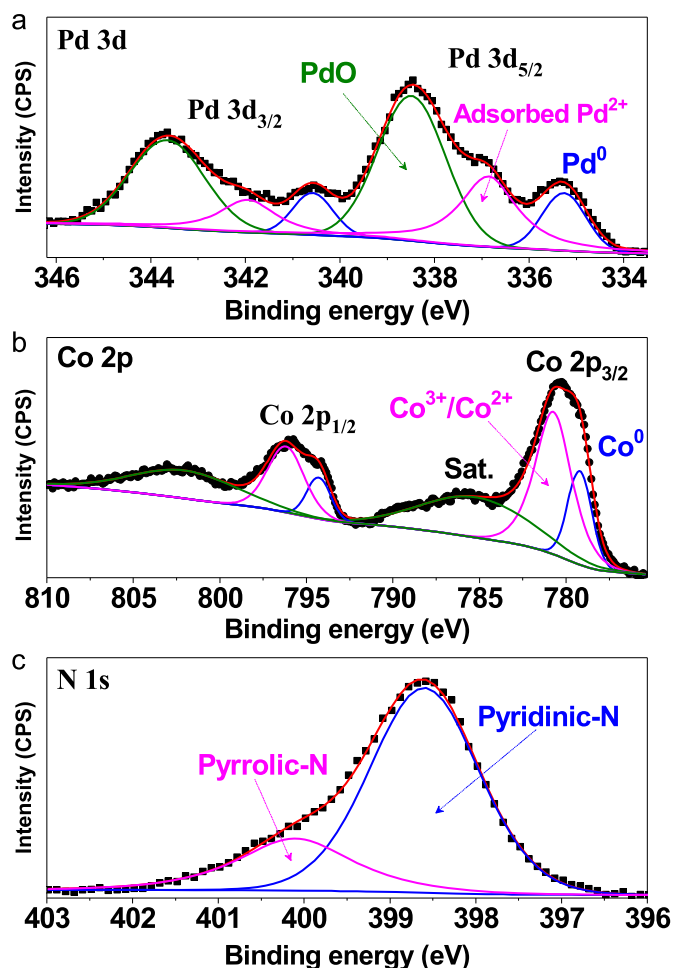


Fig. 2. High-resolution XPS spectra and corresponding peak convolutions of (a) Pd 3d, (b) Co 2p and (c) N 1s from Pd/PD-ZIF-67 material (H₂, 200 °C, 1.62 wt% Pd).

3.2. Catalytic hydrolysis analysis

A series of Pd/PD-ZIF-67 catalysts with various compositions have been applied to hydrolytic dehydrogenation of NaBH₄ at ambient temperature under the alkaline condition in which the concentration of NaBH₄ is 150 mM and mass fraction of NaOH is 0.4 wt%. The schematic illustration of the setup is shown in Fig. S6 for better understanding the experimental process. Initially, we performed quick screening experiments according to the anticipated Pd loadings which could be somewhere around 1 to 2 wt%, therefore Pd loading of 1.62 wt% was used to optimize the effect temperature on the catalytic activities of Pd/PD-ZIF-67. The catalytic performance of the Pd/PD-ZIF-67 varies with the changing reduction temperatures from 150 °C to 350 °C (Fig. 3a and b). When the reduction temperature reaches 200 °C, the specific H₂ generation rate and TOF reach the maximum value of 20.6 L min⁻¹ mg_{Pd}⁻¹ and 495.0 mol min⁻¹ mol_{Pd}⁻¹, respectively. The changes in catalytic performance of Pd/PD-ZIF-67 at various temperatures could be due to following two reasons. First of all, under the lower temperature (<200 °C), the catalyst conductivity is very low due to the lack of CoO_x species in the system (Fig. S1). Notably, the conductivity of Pd/PD-ZIF-67 (200 °C) is around 0.058 S cm⁻¹ by a four-probe measurement, which is significantly higher than that of pure ZIF-67 (0.025 S cm⁻¹). As a result, the catalytic activity is low. On the other hand, the structure of the catalyst is destroyed and Pd is agglomerated at the higher temperature (>200 °C) (Fig. S1–S3). Hence, the optimal performance at 200 °C is the result of the direct interaction of above two main factors namely conductivity and structural integrity.

Furthermore, the effects of various Pd loadings on the Pd/PD-ZIF-67 on the hydrolysis of alkalized NaBH₄ at optimal annealing temperature of 200 °C are further investigated. The results revealed that the specific H₂ generation rate (Fig. 3c) and TOF value (Fig. 3d) show parabolic behaviors where the maximum values of H₂ generation rate and TOF are obtained with 1.62 wt% Pd loading. The catalytic activities of various Pd loadings heavily altered by the agglomeration of Pd nanoclusters when sufficient active sites present on the support (Fig. S7). The optimal catalytic performance is not only significantly higher than these of the PD-ZIF-67, original ZIF-67 and commercial Pd/C catalysts (Fig. S8) but also is the best performance reported so far among the similar catalysts (Table S2).

The activation energy of the NaBH₄ hydrolysis in alkaline solution of the best performing Pd/PD-ZIF-67 is calculated using Arrhenius equation ($k = A \cdot e^{-E_a/RT}$) in 150 mM NaBH₄ + 0.4 wt% NaOH solution and the reaction temperatures are varied from 25 °C to 45 °C as shown in Fig. 4a [48]. Where the k (L min⁻¹ g⁻¹) is the specific H₂ evolution rate, E_a is the activation energy (kJ mol⁻¹), R is the gas constant (8.314 J mol⁻¹ K⁻¹) and T is the applied solution temperature (K). The plot of the ln k (rate constant) versus the inverse of the temperature as shown in Fig. 4b reveals straight line. The value of E_a is calculated according to the slope of the line, which is equal to E_a/R . The E_a of the best performing catalyst is estimated to be 58.5 kJ mol⁻¹.

The stability of the optimized Pd/PD-ZIF-67 catalyst is evaluated by continuous recycle the experiment of NaBH₄ hydrolysis. The catalyst was cleaned and a fresh solution was used in each reaction cycle. The H₂ generation rates were decreased slightly after five cycles around 10% as shown in Fig. 4c and d. Interestingly, H₂ generation rate increases slightly at the third cycle compare to the first two cycles, which can be ascribed to the increase of the metallic Pd content from 20.9% to 59.2% as shown in XPS (Fig. S9) resulted from NaBH₄ reduction. On the other hand, the content of metallic Co is slightly increased (Fig. S10) due to the Pd–H assisted BH₄⁻ reduction [49,50], and the metallic Co could also involve the

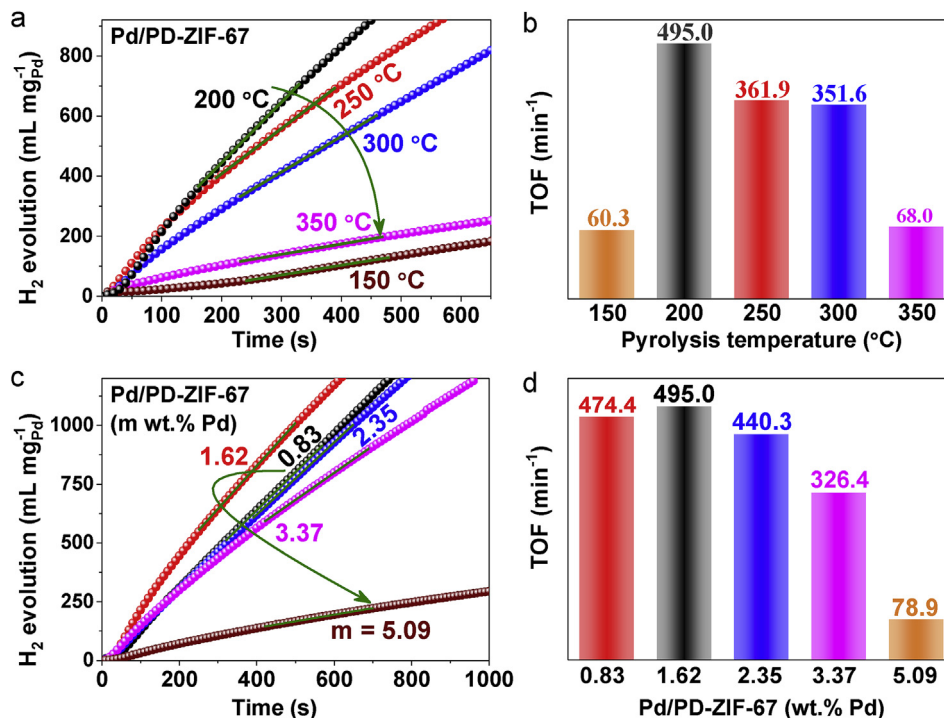


Fig. 3. (a) The effect of reduction temperatures on the synthesis of Pd/PD-ZIF-67 catalysts in H₂ atmosphere (1.62 wt% Pd) for H₂ generation from hydrolysis of 150 mM NaBH₄ + 0.4 wt% NaOH solution. (b) The TOF values are obtained from a. (c) The effect of Pd loadings on Pd/PD-ZIF-67 (H₂, 200 °C) catalysts for H₂ generation by hydrolysis of alkalized NaBH₄. (d) The TOF values are summarized from c.

NaBH₄ hydrolysis as well [51]. Notably, the morphologies and structures of Pd/PD-ZIF-67 catalyst suffer a certain degree of decomposition after 5th cycles (Fig. S11). Therefore, the catalyst deactivation could be due to the Pd agglomerations, structural damages and catalyst poisoning by BO₂⁻ species [52].

3.3. Catalytic mechanism analysis

As mentioned above, the Pd/PD-ZIF-67 (H₂, 200 °C, 1.62 wt%) catalyst exhibits the highest specific H₂ evolution rate and TOF value, where the enhanced catalytic performance is defined by the

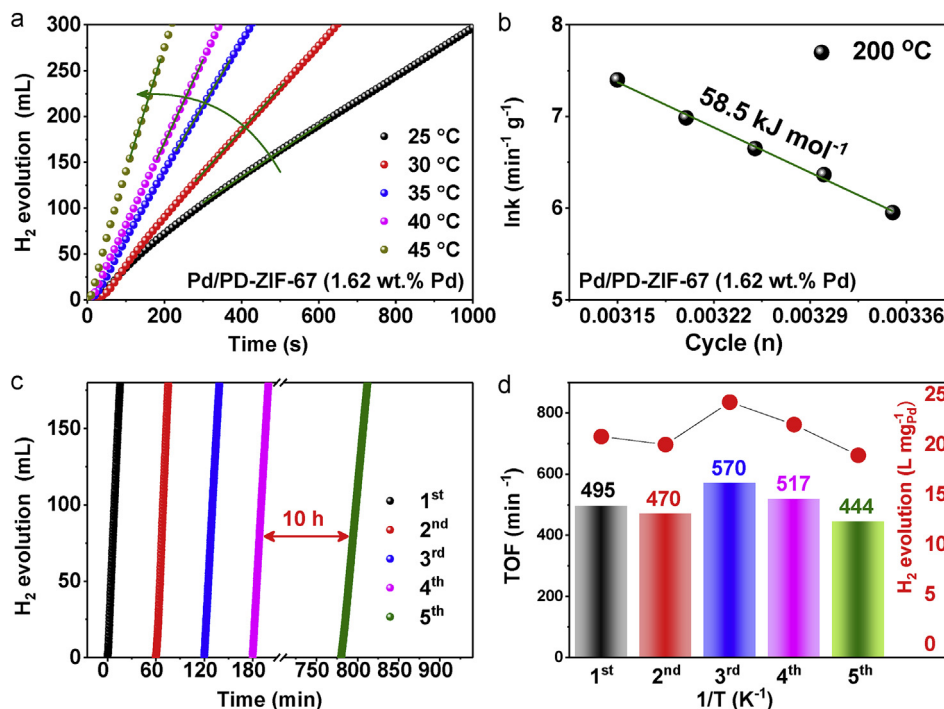


Fig. 4. (a) The effect of hydrolysis temperatures for H₂ production on the Pd/PD-ZIF-67 catalyst (H₂, 200 °C, 1.62 wt% Pd) by hydrolysis of alkalized NaBH₄ solution. (b) The summarized Arrhenius plot from c. (c) The reusability of Pd/PD-ZIF-67 catalyst (H₂, 200 °C, 1.62 wt% Pd) for continuous hydrolysis of 150 mM NaBH₄ + 0.4 wt% NaOH solution. (d) The summarized TOF values and specific H₂ evolution from a.

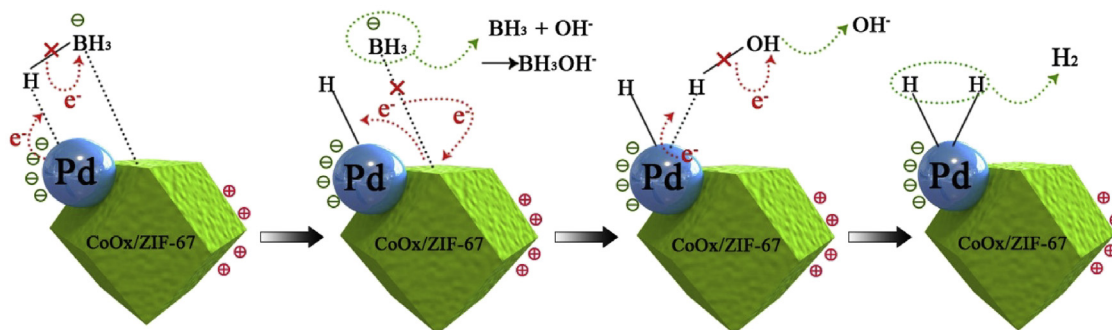


Fig. 5. Catalytic mechanism diagram of the Pd/PD-ZIF-67 catalyst for H_2 generation by hydrolysis of alkalinized $NaBH_4$ solution.

synergistic effect of the particle size and size distribution of Pd nanoclusters, conductivity of the metal-organic frameworks resulted by the Co-oxide species. The experimental results show that the electron transfer to Pd can be enhanced considerably by altering the content of CoO_x species in the ZIF-67. The actual reason is unknown to us at this stage. One may suggest that the partial oxidation of ZIF-67 could generate free NH groups on the surface that ready to be chelated with Pd^{2+} subsequently improve the synergetic effect between the active sites and support thereof enhance catalytic activity. Moreover, the proposed mechanism is described in Fig. 5. The partial charge separation has resulted because of the different work functions of Pd, Co_3O_4 and CoO, which are about 5.22, 4.5 and 3.7 eV respectively. Thus, the PD-ZIF-67 surface is partially positive while the Pd nanoclusters are partially negative (Fig. S12). As a result, the BH_4^- ions are more inclined to adsorb onto the support whereas one of H belong to BH_4^- ions will adsorb onto the active sites of Pd nanoclusters while the B is adsorbed by PD-ZIF-67 surface [53]. As the B–H bond breaks, $Pd-H_{ads}$ and $PD-ZIF-67-(BH_3^-)_{ads}$ are promptly formed on the catalyst surface. After that, with the adsorbed BH_3 peels off, one electron will release onto the active sites of PD-ZIF-67 [54]. Due to the metallic property of Pd and good conductivity of the PO/ZIF-67, the electron can be quickly transferred to the Pd nanoclusters, and then interact with H_2O molecules to form another $Pd-H_{ads}$. Finally, the resulted neighboring $Pd-H_{ads}$ intermediates combine quickly and subsequently release H_2 . The BH_4^- ions are eventually hydrolyzed to $B(OH)_4^-$ ions ($B(OH)_4^- \leftrightarrow BO_2^- + 2H_2O$) after three cycles [55].

4. Conclusion

In summary, a novel Pd/PD-ZIF-67 hybrid catalyst with low noble metal loading is developed by a solution deposition followed by a H_2 -assisted reduction method at $200^\circ C$. The effects of the Pd loading and annealing temperatures on $NaBH_4$ hydrolysis are systematically optimized. The optimized catalyst of the Pd/PD-ZIF-67 (H_2 , $200^\circ C$, 1.62 wt%) exhibits outstanding catalytic performance and high stability. The synergistic effects between different species of the hybrid catalyst as well as the improved conductivity of the support are proposed to be the two main factors that largely alter the catalytic performance of the Pd/PD-ZIF-67. Accordingly, we suggested possible reaction mechanism. These findings provide a mechanical insight in to the dynamics associated with Pd loading and support conductivity and hence offer valuable guidance for rational design of efficient catalyst for $NaBH_4$ hydrolysis.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.renene.2018.09.070>.

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