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Surface Amine-Implanting Approach for Catalyst Functionalization: Prominently Enhancing Catalytic Hydrogen Generation from Formic Acid

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Abstract: The highly efficient hydrogen generation from formic acid is a vital process in clean energy and chemical industry fields. In this work, a universal and efficient surface amine-implanting approach (SAIA) has been proposed for fabricating highly active nanocatalysts with controllable nucleation and growth of downsized metal nanoparticles (NPs) and desired environments around the active sites. The highly dispersed ultrafine palladium NPs supported by the amine-implanted porous carbon (Pd/APC) exhibited superior catalytic activity and high selectivity for the dehydrogenation of formic acid under mild conditions, which afford nearly three-fold increase of the catalytic activity. Detailed investigation demonstrates that the amine species densely implanted on the pore surface of carbon by hydrothermal treatment with ammonium hydroxide play important roles in both dispersing the metal NPs and promoting the catalytic processes. The approach provides a powerful entry into highly active catalysts to elicit enhanced catalytic performance for various catalytic reactions and promote the dehydrogenation of formic acid for practical applications.

Introduction

The supported metal nanoparticles (NPs) have been aroused substantial attention due to their excellent performance in many fields, especially in heterogeneous catalytic reactions.^[1] There are plenty of researches showing that the metal NP size, support materials and their synergetic effect are crucial to facilitate the heterogeneous catalysis system. It is well accepted that ultrafine metal NPs possess greatly abundant catalytic active sites due to their small size effect and quantum size effect.^[2] However, their large fraction of exposed surface atoms, high specific surface area and surface energy make them tend to aggregation, which is detrimental to their catalytic application. Several endeavors have been made for preparing and stabilizing the ultrafine metal NPs; however, the synthesis of ligand-free ultrafine and stable metal NPs still encounters many challenges and limitations.^[3] Supporting metal NPs on the high-surface-area supports, such as porous carbon, silica, metal oxides, and metal-organic frameworks (MOFs), is an efficient way to support and disperse the metal NPs.[1d, 4] Moreover, it is widely known



that the catalytic performance of the immobilized metal NPs significantly depends on the nature of the support materials. The rational modification of surface nature of supports not only can downsize and prevent aggregation of the metal NPs, but also can optimize their surface electronic properties.^[5] Recently, Nfunctionalized carbon materials has attracted particular attention for heterogeneous catalytic applications.^[6] The ultrafine metal NPs can be anchored by the N-sites of the functionalized carbon to realize higher dispersion, strong synergetic effects between metal and N-contained sites, which may accelerate the catalytic reaction rates and improve the reaction selectivity.^[2c, 7] Particularly, the incorporation of the electron-rich and alkaline amine groups into a carbon may further strengthen these advantages, which, however, is rarely reported. Although several efforts have been made for incorporating N-contained species to carbon supports, the tedious, complex and poor manoeuvrability of the modification processes restrain the widespread applications. Therefore, the strategies for facile and efficient surface implanting of the amine groups onto the pore surface of carbons for significantly enhancing the catalytic performance and providing necessary environments for catalysis are highly desired.

Hydrogen is considered as a most sustainable and clean energy carrier without any damage for environment during use.^[5] However, gaseous hydrogen is hard to be stored by condensing because of its low boiling point and low gravimetric capacity under atmospheric conditions.^[8, 2b] Liquid chemical hydrides with high potential for hydrogen storage and generation have been extensively studied by researchers due to their significant advantages including high volumetric/gravimetric hydrogen density, easy transportation, and safety.^[9] Formic acid (FA, HCOOH) has been identified as an excellent liquid hydrogen carrier due to theirs high hydrogen content (4.4 wt.-%), high volumetric hydrogen density (53 g L-1), safe storage and transportation, nontoxicity, excellent stability.^[9a] Furthermore, FA could be yielded in large scale by biomass processes and catalytic hydrogenation of CO2 generated from industrial processes.^[10] In the past few years, several studies have been done for the dehydrogenation of FA.^[11] However, the challenges of highly efficient and selective dehydrogenation of FA to H₂ + CO₂ without CO generation under ambient conditions still remain. Hence, it is imperative to design and synthesis of excellent performance catalysts by a simple and efficient method for hydrogen generation from FA.

Herein, we reported an simple but effective surface amineimplanting approach (SAIA) to functionalize the inner surface of porous carbon, which shows great ability to disperse and immobilize the ultrafine metal NPs and provides strong metalmolecular support interactions. The ultrafine Pd NPs immobilized on the amine-implanted porous carbon (APC) showed remarkably enhanced catalytic activity for the hydrogen generation from FA. For optimizing the properties of supports to realize better catalytic activity, APCs with different contents of amine groups were prepared by altering ammonium hydroxide concentration, time and temperature of the hydrothermal

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treatment with ammonium hydroxide, respectively. Detailed studies imply that the amine species of APC not only can benefit to the dispersion and downsizing of Pd NPs, but also provide necessary local environments to promote the deprotonation of FA, absorption between reactants and catalysts, and thereby the overall catalytic process.^[12]

Results and Discussion



Scheme 1. Schematic Illustration for Preparing Pd/APC Nanocatalyst.

The preparation of Pd/APC nanocatalyst by SAIA is illustrated in **Scheme 1**. Briefly, 100 mg pristine porous carbon (PPC) was hydrothermally treated at 200 °C for 10 h with 25 wt% ammonium hydroxide, resulting in the formation of APC. Then, aqueous K_2PdCl_4 solution was injected into aqueous suspension of the resultant APC with ultrasonic treatment for 30 min. Finally, rapid addition of NaBH₄ aqueous to the above suspension afforded the ultrafine Pd NPs immobilized on APC. For the comparison, Pd/PPC was synthesized by using PPC instead of APC.

The crystallinity of as-synthesized catalysts was characterized by powder X-ray diffraction (PXRD) patterns. The characteristic peaks of Pd⁰ were observed, indicating that the Pd NPs were successfully immobilized on porous carbon support (Figure S1). The X-ray photoelectron spectroscopic (XPS) measurements confirm that the electron-rich amine species successfully implanted onto the pore surface of APC. The N 1s signal at 399.9 eV could be attributed to amine groups (e.g., -NH-, -NH₂) (Figures 1c and S2d).^[13] The binding energy for Pd in Pd/APC at Pd 3d_{5/2} level is observed at 336.0 eV, which can be assigned to Pd⁰, while the Pd 3d_{5/2} level at 337.5 eV could be ascribed to Pd²⁺ caused by oxygenizing of highly active surface atoms of Pd NPs and/or strong interaction between Pd precursors and amine species of APC making Pd²⁺ difficult to be reduced to Pd⁰ (Figures 1d and S3b).^[14] The Pd loading in Pd/APC was determined to be 4.62 wt.-% by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) measurement, while 4.37 wt.-% Pd was loaded onto PPC (Table S2), demonstrating that the implanted amine species can promote Pd precursors and/or Pd NPs to anchor on porous carbon supports.^[14a] The Pd content of the recycled Pd/APC catalyst was determined to be 4.58 wt.-%, indicating no leaching of Pd from catalyst during the catalysis. N2 adsorption/desorption isotherms were measured at 77 K to determine porous structure information of the samples. The calculated Brunner-Emmett-Teller (BET) surface areas of PPC, APC, Pd/PPC and Pd/APC were 1643, 1483, 1117 and 868 m² g⁻¹, respectively (Figure S8). Compared to the carbon supports, the appreciable decreases of surface areas of Pd/PPC and Pd/APC demonstrate that part of Pd NPs has been successfully embedded into the pores of carbon frameworks. In addition, APC shows slightly lower BET surface areas than that of PPC, which could be attributed to the incorporation of N-contained species into the pores of carbon by amine-implanting approach.[12b]



Figure 1. XPS survey spectrum (a) and high-resolution XPS spectra of C 1s (b), N 1s (c) and (d) Pd 3d for Pd/APC.

The morphologies and microstructures of the as-prepared catalysts were characterized by transmission electron microscopy (TEM) and high angle annular dark field scanning TEM (HADDF-STEM). The TEM and HADDF-STEM images of Pd/APC show that the Pd NPs well dispersed on the APC support with rare aggregation and an average particle size of about 2.3 nm (Figures 2a, c and S4b, d). However, the PPC supported Pd NPs show a larger average particle size of 3.2 nm with inferior dispersion (Figures 2b, d and S4a, c). Therefore, it further demonstrates that the implanting of amine group to carbon support can downsize the Pd NPs and improve their dispersion, implying that Pd/APC could exert a better catalytic activity.

The catalytic performance of the as-synthesized catalysts for hydrogen generation from FA was tested. Remarkably, the Pd/APC exhibited tremendously enhanced catalytic performance for the dehydrogenation of FA at FA-SF system at ambient

conditions, compared with Pd/PPC (Figure 3). It is worth noted that the Pd/APC catalyst presented an exceptional TOF of 2230 h⁻¹ at 50 °C, which is almost three times higher than the counterpart without amine functionality, and among the highest values ever reported for heterogeneously catalyzed hydrogen generation from FA at ambient conditions. Such catalyst can efficiently catalyze the hydrogen generation from FA at relatively low temperatures, which may significantly decrease costs and be conveniently operated during industrial process. The average rates of H₂ generation during FA dehydrogenation process could be calculated as 17 L $H_2\mbox{ min}^{-1}\mbox{ }g_{Pd}{}^{-1},$ corresponding to the appreciably high energy density (~30 W min⁻¹ g_{Pd}⁻¹), which promisingly facilitates FA as a competitive hydrogen carrier for practical applications. The catalytic selectivity of Pd/APC for the dehydrogenation of FA was confirmed by chromatography (GC) analysis (Figure S9). No CO was detected by GC in the released gaseous product, indicating highly selective decomposition of FA to H₂ and CO₂ over Pd/APC and strictly restraint of the undesired dehydration pathway (HCOOH \rightarrow H₂O + CO), which is crucial for its practical applications, such as proton exchange membrane fuel cells (PEMFCs). The catalyst poison experiment was conducted and found that the catalytic activity of Pd/APC decreased sharply after exposure of the catalyst to CO, suggesting the low tolerance of the catalysts to CO (Figure S17). Moreover, the catalytic performance of the dehydrogenation of pure FA over Pd/PPC and Pd/APC was further conducted $(n_{Pd}/n_{FA} = 0.011, 50 \text{ °C})$, which also elucidated that Pd/APC possesses higher catalytic performance for hydrogen generation from FA (Figure S13).



Figure 2. TEM and HADDF-STEM images of (a,c) Pd/APC and (b,d) Pd/PPC.



Figure 3. Volume of the generated gas $(CO_2 + H_2)$ versus time for the dehydrogenation of FA over (a) Pd/APC and (b) Pd/PPC ($n_{Pd}/n_{FA} = 0.011$, FA/SF = 1:1, 50 °C). Inset: TOF values of dehydrogenation of FA over Pd/APC and Pd/PPC.

The rate of hydrogen generation from FA over Pd/APC highly depends on operation temperature. The catalytic reactions were completed in 10.3, 6.3, 3.6 and 3.3 minutes at 30, 40, 50 and 55 °C (FA/SF= 1:1, n_{Pd}/n_{FA} = 0.011), respectively. The apparent activation energy of Pd/APC and Pd/PPC was calculated to be 46.31 KJ mol⁻¹ and 41.37 KJ mol⁻¹ by fitting Arrhenius plot of InTOF *vs* 1/T (Figures 4a and S15). In addition, it is noted that the molar ratio of FA/SF has profound effect on the activity of the as-prepared catalyst. The activity of the catalyst increases initially until FA/SF = 1:1 and then slightly decreases with further increasing SF molar percentage in FA/SF mixed solution (Figure S14). Therefore, it can be concluded that the best molar ratio of FA/SF for hydrogen generation over this catalyst is 1:1.



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Figure 4. (a) Volume of the released gas $(H_2 + CO_2)$ versus time and (b) corresponding TOF values for the dehydrogenation of FA at different temperatures over Pd/APC (n_{Pd}/n_{FA} = 0.011, FA/SF= 1:1, 50 °C). Insert: Arrhenius plot (InTOF vs. 1/T).

To gain more details about the effects of the amine groups in APCs on the enhancement of catalytic performance of the Pd/APC catalysts, various comparative experiments were carried out. With the increases of temperature, time and ammonium hydroxide concentration for hydrothermal treatment of the porous carbon by ammonium hydroxide; the TOF values achieved by the corresponding Pd/APC catalysts initially increased, and then a similar maximum value was reached and maintained (Figures S10, S11 and S12), which is consistent with the changes of the amine contents of APC determined by elemental analysis (Table S3). Consequently, the catalytic performance of Pd/APC is highly dependent on the content of amine group in APC. Fundamentally, the explanation for the prominent enhancement of the catalytic performance of Pd/APC could be down to the high dispersion of ultrafine Pd NPs and strong metal-molecular support interactions. On the one hand, the amine groups on the pore surface can disperse and downsize Pd NPs immobilized on APC by enhancing the interactions between metal precursors/NPs and electron-rich supports.^[5a] On the other hand, the weakly alkalization of the amine-implanted porous support plays another indispensable role to provide the alkaline and electron-donating environments around the active sites for promoting the de-protonation of FA, absorption between reactants and catalyst. Another catalyst, Pd/APC*, with mean particle size of 3.5 nm also has been prepared by using the APC support. Despite the larger particle size, the Pd/APC* catalyst displayed a much higher catalytic activity than that of Pd/PPC, further confirming that amine species doped within carbon supports can promote the dehydrogenation of formic acid (Figures S18 and S21). The possible pathway of hydrogen generation over amine-implanted porous carbon supported Pd NPs could be speculated that the amine species on the supports acts as proton scavengers providing alkalized environment, which promote O-H bond dissociation in FA to produce -[H2NH]+ and Pd-formate species.^[15, 7a] Subsequently, Pd-formate species undergo βhydride elimination to produce CO₂ and palladium hydride species.^[15a] The H₂ release followed by the combination of -[H₂NH]⁺ and palladium hydride species. On the basis of above analysis, the assist of the amine species and synergetic effects between Pd NPs and alkaline supports are responsible for the significantly enhanced catalytic activity.

From the views of practical applications, the stability and recyclability of catalyst plays a crucial role in industrial process. The stability and recyclability of the as-synthesized catalyst were evaluated at 50 °C ($n_{Pd}/n_{FA} = 0.011$, FA/SF = 1:1). The catalytic activity displayed slightly loss after 4 runs of reaction, which indicated the excellent recyclability of the Pd/APC catalyst (Figure S16). No obvious change was found for Pd NP crystalline phase and size after catalysis as indicated by PXRD, TEM measurements (Figures S19 and S20), suggesting the high stability of the catalyst during hydrogen generation from FA. In addition, the performance of Pd/APC after 4-cycle tests still hugely surpass Pd/PPC, suggesting amine-implanted porous carbon supported ultrafine Pd NPs are much more competitive.

Conclusions

In summary, a universal and efficient SAIA approach has been successfully developed to prepare amine-implanted porous carbon supported metal NPs. Compared with pristine porous carbon, the amine-implanted ones can afford more highly dispersed Pd NPs with necessary local catalytic environments. which exhibited much more preferable catalytic activity and excellent recyclability with 100% selectivity for hydrogen generation from FA under mild conditions, giving a TOF value among the best vet reported. The superior catalytic performance of Pd/APC could be ascribed to the improved affinity between amine-implanted carbon supports and metal precursor/NPs, and thus the prevention of the aggregation and over-growth of Pd NPs and the enhanced metal-molecular support interactions. Moreover, the alkalization of the carbon supports with amine groups could further facilitate the decomposition of FA to release hydrogen. The catalyst functionalization method and results are expected to not only promote the fabrication of efficient nanocatalysts, but also expand the practical applications of hydrogen storage and generation using FA as hydrogen carrier for fuel cells and other energy fields of chemical industry.

Experimental Section

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Preparation of catalysts

Synthesis of amine-implanted porous carbon supports: Typically, 100 mg pristine porous carbon (PPC) powder was dispersed in 25 wt % ammonium hydroxide (15 mL). Subsequently, the mixture was transferred into a Teflon-lined steel autoclave and heated under 200 °C for 10 h. Finally, the amine-implanted porous carbon (APC) was obtained by filtering and wishing with de-ionized water for several times and then dried at 50 °C for 5 h in vacuum.

Control experiments were conducted to explore the optimum conditions for the treatment of porous carbon. The PPC samples were treated at 80 °C, 120 °C, 180 °C and 200 °C for 10 h with 25 wt.-% ammonium hydroxide, named as APC-80 °C, APC-120 °C, APC-180 °C and APC-200 °C, respectively. The PPC samples were treated with hydrothermal reaction at 200 °C with 25 wt.-% ammonium hydroxide for 2 h, 6 h, 10 h and 14 h, named as APC-2 h, APC-6 h, APC-10 h and APC-14 h, respectively. The PPC samples were treated with hydrothermal reaction with 5 wt.-%, 10 wt.-%, 15 wt.-% and 25 wt.-% ammonium hydroxide at 200 °C for 10 h, named as APC-5 %, APC-10 %, APC-15 % and APC-25 %, respectively.

Synthesis of Pd/APC and Pd/PPC: The Pd NPs supported by APC were synthesized by a facile sodium hydroxide-assisted reduction approach.^[4a] Firstly, the as-obtained APC (100 mg) was dispersed in deionized water (2.5 mL), and mixed with an aqueous solution of K2PdCl4 (0.30 M, 0.30 mL). Then, the resulted aqueous suspension was further homogenized by sonicating 0.5 h. Subsequently, NaBH₄ (20 mg) dissolved in NaOH aqueous (0.5 M, 0.50 mL) was rapidly injected into the above obtained aqueous suspension. The mixture was stirred for another half an hour at room temperature to fully deposit the metallic Pd NPs onto the support. Finally, the desired Pd/APC catalyst was collected by centrifuging and washing with de-ionized water for three times, and then dried in vacuum at room temperature for further catalytic activity tests. In addition, the reduction temperature was further increased from room temperature to 50 °C, and the resultant catalyst was denoted as Pd/APC*. For comparison, Pd/PPC was prepared following the same synthetic procedures, except that PPC was used instead of APC.

Catalytic Activity Testing

Procedures for the dehydrogenation of formic acid: Reaction apparatus for measuring the H₂/CO₂ evolution from the FA/SF system is the same as previously reported.^[4a] In general, a mixture of assynthesized catalyst and distilled water (2 mL) was placed in a two-necked reaction tube (50 mL), which was placed in a water bath at a preset temperature (30-55 °C) under ambient atmosphere. A gas burette filled with water was connected to the reaction flask to measure the volume of released gas (temperature kept constant at 25 °C during measurements). The reaction started when 1.5 mL of the mixed aqueous solution containing FA (5.5 M) and SF with different molar ratios was injected into the mixture. The molar ratios of Pd/FA were theoretically fixed at 0.011 in all the catalytic reactions. The volume of the evolved gas was monitored by recording the displacement of water in the gas burette.

Recyclability testing of the catalysts: For the recyclability test, the Pd/APC catalyst was recycled for the next test cycle by washing with deionized water for several times after the completion of the hydrogen generation from FA. Such test cycles of the catalyst for the dehydrogenation of FA were carried out for 4 runs at 50 °C ($n_{Pd}/n_{FA} = 0.011$, FA/SF = 1:1).

Catalyst poison experiment: The as-synthesized Pd/APC was used for catalyst poison test. Typically, the CO gas flow was pumped into the two-necked reaction tube (50 mL) placed with Pd/APC or Pd/PPC for 30 min. Then, the procedures for the dehydrogenation of FA were carried out.

Acknowledgements

We thank the Recruitment Program of Global Youth Experts, the NSFC (21233009), the Strategic Priority Research Program of CAS (XDB20010200), and the 973 Program (2014CB845603) for financial support.

Keywords: heterogeneous catalyst • functionalized carbon • hydrogen generation • formic acid • metal nanoparticles

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A universal and efficient surface amine-implanting approach (SAIA) has been proposed for fabricating highly active nanocatalysts, which exhibited superior catalytic performance for the dehydrogenation of formic acid under mild conditions. The amine species densely implanted on the pore surface of carbon play important roles for enhancing the catalytic activity.

TOF = 2230 h⁻¹ , 323 K

Heterogeneous catalysis

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