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Article

Engineering Nickel/Palladium Heterojunctions for Dehydrogenation of Ammonia Borane: Improving the Catalytic Performance with 3D Mesoporous Structures and External Nitrogen-Doped Carbon Layers

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ABSTRACT: Catalysts based on metallic NPs have shown high activities in heterogeneous catalysis, due to their high fractions of surface-active atoms, which, however, will lead to the sacrifices in stability and recycle of catalysts. In order to balance well the relationship between activity, stability, and recovery, in this paper, we have constructed a 3D mesoporous sphere structure assembled by N-doped carbon coated Ni/Pd NP heterojunctions (Ni/Pd@N-C). This obtained Ni/Pd@N-C has shown high catalytic activity, durability and recyclability for the hydrolytic dehydrogenation of ammonia borane (AB). Further investigations, including experimental and theoretical results, have shown that the unique structural features, the synergistic effect between Ni and Pd, and the coating of N-doped carbon layer are responsible for the good catalytic performance of Ni/Pd@N-C mesoporous spheres.

1. INTRODUCTION

Heterogeneous catalysis, as a major technology in energy and environmental fields, has attracted numerous attention. Tremendous efforts have been made to heterogeneous catalysts based on metallic nanoparticles (NPs) due to their excellent catalytic performances.² Narrowing down the particle size of metallic NPs with enlarged fractions of surface atoms has been proven as one of the most effect strategies to enhance catalytic activities.³ However, the decreased particle size can lead to the sacrifices in stability and recovery of catalysts, which are also the basic factors of heterogeneous catalysis.⁴ Therefore, we need to balance the relationship between the activity, stability, and recovery when designing metallic NP catalysts.⁵ As so far, the usage of capping agents has been widely applied to make sure the good stability of metallic NP catalysts during the catalytic processes, while this method are unhelpful to the recovery and may cause possible decreases on the activity due to the unclear surfaces.⁶ Metallic NPs immobilized or grafted onto inorganic supports can improve their stabilization and recycling ability, but this requires strong metal-support interactions to avoid the aggregation of NPs. Thus, far, a rational fabrication of metallic NP catalysts without the usage of capping agents and supports, which have high activity, stability, and recycling ability, are still highly desired.

Constructing three-dimensional (3D) mesoporous structures assembled by metallic nanoparticles and with controlled shapes seems to be a good option for catalysts to meet the above-mentioned targets. 3D mesoporous structures assembled



NH₃BH₃

Pd

0 nm

N

Moreover, the activity of the metallic NP-based catalysts should be further improved, in addition to the strategy of exposing large amounts of surface atoms. As another effective strategy, constructing bimetallic composites, which can provide synergistic effects between the two compositions by modifying

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Figure 1. (a) Schematic illustration of the synthetic process of Ni/Pd@N–C hierarchical mesoporous sphere; typical SEM image of (b) Ni coordination compound, (c) NiO@N–C, (d) Ni@N–C, and (e) Ni/Pd-2@N–C; (f) the XRD pattern of Ni/Pd-2@N–C; (g) N₂ adsorption/ desorption isotherms and BJH pore size distribution of Ni/Pd-2@N–C.

electronic structures, has been studied well for their abilities to improve the catalytic activities of monometallic NPs.9 In particular, when transition metals (such as Fe, Co, and Ni) are combined with noble metal NPs, the cost can be decreased together with the enhanced catalytic activity, making them as more attractive catalysts.¹⁰ In this paper, we have successfully fabricated a 3D mesoporous structure assembled by Ni-Pd bimetallic NP heterojunctions, i.e., Ni/Pd@N-C, which is coated by a thin layer of N-doped carbon. Except the advantages of morphology and Ni/Pd heterojunctions, the existence of N-doped carbon can show benefits to the adsorption of substrate, further facilitating the catalytic processes.¹¹ Herein, we have chosen the dehydrogenation of ammonia borane as the model reaction to evaluate the catalytic performance of the obtained Ni/Pd@N-C mesoporous spheres. The higher activity, recyclability, and durability of the obtained catalyst can be attributed to the favorable feature of a mesoporous structure assembled by NPs, the synergistic effect between Ni and Pd, and the coating of N-doped carbon layers. The influences of synergistic effect between Ni and Pd on the catalysis have been proved by preparing Ni/Pd@N-C mesoporous spheres with different ratios as catalysts. In addition, both the experimental and calculation results have revealed that the coating of N-doped carbon layer can play a positive role on the catalysis by facilitating the adsorption of water in the hydrolytic process of AB and decreasing the activation energy of the reaction.

2. EXPERIMENTAL DETAILS

Preparation of Ni/Pd@N–C. Ni/Pd@N–C microsphere were synthesized via the reduction process of the obtained Ni@N–C porous microspheres (0.0100 g) with sodium tetrachloropalladate(II) (0.004 g) at an aqueous solution. After a reaction at 30 °C for 3 h, the products were collected via centrifugation and washed several times with deionized water and ethanol, then dried at 60 °C overnight.

Procedures for the Hydrolysis of AB. The method used for evaluating hydrogen evolution from the hydrolysis of AB was as previously reported.¹² In brief, the as-synthesized catalyst (18 mg) and 1 mL of H_2O mixture was carefully poured into a two-necked flask, which was placed in a water bath under ambient atmosphere. A gas buret filled with water was connected to the two-necked flask to collect the generated gas. After 1 mL of H_2O solution containing AB (1 mmol) was added to the flask, the catalytic reaction started and the yield of generated H_2 was recorded by reading the volume of the displacement of water in the gas buret. AB methanolysis was finished when no more gas was generated. Generally, AB methanolysis can be expressed as

 $NH_3BH_3 + 2H_2O \rightarrow NH_4BO_2 + 3H_2$

3. RESULTS AND DISCUSSION

Figure 1a illustrates the detailed formation process of N-doped C-coated Ni/Pd (Ni/Pd@N-C) hierarchical mesoporous



Figure 2. (a) TEM image of Ni/Pd-2@N-C mesoporous spheres, (b) higher magnification TEM image of Ni/Pd-2@N-C mesoporous spheres, (c) HRTEM image of Ni/Pd-2@N-C mesoporous spheres, (d) the corresponding SAED pattern, and (e-i) STEM image and EDX elemental mapping of Ni/Pd-2@N-C mesoporous spheres.

spheres. First, Ni coordination compound with hierarchical mesoporous sphere structure is synthesized according to the previous reported strategy. The experimental details can be found in the Supporting information. Scanning electron microscopy (SEM) images reveal that Ni coordination compound is composed of high monodispersed and uniform mesoporous microspheres (Figure 1b, Figure S1a). EDX elemental mapping images show that the Ni, O, C and N elements are well dispersed in Ni coordination compound microspheres (Figure S1b-f). After calcining Ni coordination compound at 450 °C for 2 h in a nitrogen atmosphere, NiO@ N doped C with maintained morphology can be obtained, which is shown in SEM image (Figure 1c, Figure S3a). The XRD pattern (Figure S2) confirms the presence of cubic NiO phase. The EDX elemental mapping (Figure S3b-f) can indicate the uniform distribution of Ni, O, C and N elements in NiO@N-C microspheres. After reduction treatment in Ar/ H₂ atmosphere, cubic NiO phase can be directly converted into cubic Ni phase (Figure S4a). SEM images (Figure 1d and Figure S4b) indicate that the as-synthesized Ni@N-C products are still hierarchical mesoporous spheres composed of Ni, C, and N elements (Figure S4c-f), but those mesoporous spheres are assembled by nanoparticles due to the absence of O atoms after the reduction process. The deposition of Pd on Ni@N-C can obtained by a galvanic exchange reaction and immersing Ni@N-C mesoporous spheres in a solution containing palladium salts at 60 °C. Duo to the reducibility of metal nickel, Pd²⁺ ions are reduced

to metallic Pd. As shown in Figure 1e is the SEM image of Ni/Pd-2/N doped C particles with specific ratio of Ni/Pd, which maintain the hierarchical mesoporous sphere morphology of the precursors. Their XRD pattern (Figure 1f) shows the peaks assigned to cubic Ni and cubic Pd phases. Brunauer–Emmett–Teller (BET) measurement (Figure 1g) confirms the porosity of Ni–Pd-2@N–C sample, with a surface area of 59.8 m²/g, and the Barrett–Joyner–Halenda (BJH) pore size distribution is not concentrated due to the presence of different kinds of pores (inset of Figure 1g).

The Ni/Pd-2@N-C hierarchical mesoporous spheres have been further characterized by transmission electron microscopy (TEM) to understand the detailed structural information and components. From Figure 2a, we can see that the projection appearance of Ni/Pd-2@N-C are mesoporous sphere structures assembled with small nanoparticles, well consistent with the SEM image. A higher-magnification TEM image (Figure 2b) reveals that these small nanoparticles are below 10 nm and coated with amorphous carbon (marked with blue curves). The high-resolution TEM (HRTEM) image (Figure 2c) shows the connected lattice spacings of 0.203 and 0.223 nm, which should be attributed to the (111) facets of cubic Ni and cubic Pd, respectively. HRTEM image clearly shows a heterojunction between Ni and Pd nanoparticles. The corresponding selected-area electron diffraction (SAED) pattern (Figure 2d) shows two sets of diffraction rings assigned to the cubic Ni and cubic Pd phases, indicating the polycrystalline property of Ni/Pd-2@N-C microspheres. A



Figure 3. High-resolution XPS spectra of Ni/Pd-2@N-C mesoporous spheres, (a) Ni 2p, (b) Pd 3d, (c) C 1s, and (d) N 1s.

typical HAADF-STEM image (Figure 2e) and its corresponding elemental mapping images (Figure 2f–i) clearly show the dispersion of Ni, Pd, C, and N elements. The uniform distributions of Pd and N suggest the uniform deposition of Pd nanoparticles and the uniform doping of N into carbon layers. According to the above results, Ni/Pd-2@N–C can be identified as N-doped carbon layer coated Ni/Pd nanoparticle heterojunctions with hierarchical mesoporous sphere morphology.

Moreover, the chemical valence and electronic structure of Ni/Pd-2@N-C hierarchical mesoporous spheres have been characterized by X-ray photoelectron spectroscopy (XPS). The survey XPS spectrum of the sample shows the existence of Ni, Pd, C, and N elements (Figure S5). The high resolution XPS spectrum of Ni 2p (Figure 3a) indicates that the peaks at 855.9 and 861.6 eV are in agreement with the Ni²⁺ $2p_{3/2}$, and the peaks at 873.9 and 879.9 eV correspond to the Ni²⁺ $2p_{1/2}$, due to the surface oxidation of metallic Ni. The peaks at 852.7 and 871.8 eV are belong to Ni⁰, consistent with the XRD and TEM results. Figure 3b shows the high resolution spectrum of Pd 3d, which clearly indicates the existence of Pd⁰ with the peaks centered at 335.4 and 340.7 eV. The C 1s spectrum for Ni/Pd-2@N-C presented in Figure 3c can be deconvoluted into four major peaks, which correspond to the sp2 C (284.5 eV), N-sp2 C (285.1 eV), N-sp3 C (285.9 eV), and C-O bonds (288.5 eV). The high resolution N 1s spectrum (Figure 3d) can be attributed to N-Graphene (402.6 eV). The above XPS results further revealed the Ni/Pd heterojunctions are coated by Ndoped carbon in the Ni/Pd-2@N-C mesoporous sphere sample.

In order to evaluate the catalytic performance of the obtained Ni/Pd-2@N-C mesoporous spheres, hydrolytic dehydrogenation of ammonia borane (AB), which is an important hydrogen storage system, has been chosen as the model reaction.¹³ As shown in Figure 4a is the hydrogen evolution curves from 1 mmol AB of the Ni/Pd-2@N-C

sample, together with the control samples of Ni/Pd-2 mesoporous spheres without N-doped carbon coating (Figure S6), Pd nanoparticles (Figure S7), Ni@N-C and NiO@N-C (with no activity) mesoporous spheres. Compared with the other samples, Ni/Pd-2@N-C can release a stoichiometric amount of hydrogen (72 mL) within 3.41 min, indicating its highest hydrogen evolution rate and even higher than the Pd nanoparticles. The best activity of Ni/Pd-2@N-C mesoporous spheres can be attributed to the unique structural feature, the synergistic effect between Ni and Pd, and the coating of Ndoped carbon. Moreover, Ni/Pd-2@N-C as the catalyst has expectedly shown good cycle stability (Figure 4b), which should be owning to its 3D mesoporous sphere structure. The SEM and XRD measurement of Ni/Pd-2@N-C (Figure S8) after five catalytic cycles have further indicated its good durability.

Ni/Pd@N-C mesoporous microspheres with different metallic ratios, i.e., Ni/Pd-1@N-C (Figure S9) and Ni/Pd-3@N-C (Figure S10), have been synthesized as the catalysts of the dehydrogenation of AB to investigate the influence of synergistic effect between Ni and Pd (Figures 4, parts b and c). The metal ratios of different samples have been displayed by Table S1. The volcano shape distribution of hydrogen evolution rate toward the metallic ratios of Ni/Pd clearly indicates the synergistic effects between Ni and Pd, and the highest hydrogen evolution rate of Ni/Pd-2@N-C indicates its feeding amount of Pd as the optimized amount. In order to give more adequate evidence about the synergistic effect and rule out the influence of N-doped C, we have also compared the catalytic activity of Ni/Pd-2, Ni (product obtained with Ni @N-C as the calcined precursor, Figure S11), and Pd. Ni/Pd-2 has displayed the highest activity toward the dehydrogenation of AB, which can further reveal the synergistic effect of Ni and Pd (Figure S12). In addition, the positive role played by the coating of N-doped carbon has been clarified by the better activity of Ni/Pd-2@N-C sample than Ni/Pd-2 sample.



Figure 4. (a) Time course plots for the hydrolysis of AB by using Ni/Pd-2@N–C, Ni/Pd-2, Pd, and Ni@N–C as catalysts at 298 K, (b) time course plots for the hydrolysis of AB by using Ni/Pd-1@N–C, Ni/Pd-2@N–C and Ni/Pd-3@N–C as catalysts, (c) hydrogen production rate with various catalysts for the hydrolysis of AB, (d) time course plots for the hydrolysis of AB at different temperatures by using Ni/Pd-2@N–C catalysts, (e) the Arrhenius plots for the reaction activation energy E_a by using Ni/Pd-2@N–C and Ni/Pd-2 catalysts, and (f) the cycle stability of Ni/Pd-2@N–C catalysts.

Hydrogen evolution rates measured at different temperature have been shown in Figure 4d and Figure S13 for Ni/Pd-2@ N–C and Ni/Pd-2, respectively, which indicate temperaturedependences. From the Arrhenius plots calculated from hydrogen evolution rates as the rate constant (Figure 4e), activation energy with Ni/Pd-2@N–C have been determined to be 18.46 kJ mol⁻¹, which is lower than its counterpart with Ni/Pd-2 as the catalyst (26.19 kJ mol⁻¹). These experimental have revealed the positive influence of N-doped carbon on the catalytic process of dehydrogenation of AB. Ni/Pd-2@N–C catalyst also exhibited high cycle stability for hydrolytic dehydrogenation of AB (Figure 4f).

In order to intrinsically understand the lower activation energy of the N-doped C coated Ni/Pd catalyst, theoretical calculation has been conducted. According to the proposed catalytic mechanism of hydrolysis of AB,¹⁴ the breaking of O– H bond has been determined as the rate-determining step. Therefore, the adsorption of H₂O molecular on Ni (111), Pd (111), graphite (001) surfaces, and N-doped graphite (001) surfaces has been investigated by the density functional theory (DFT) calculations, and the corresponding stable adsorption configurations are shown in Figure 5 and Figure S14. The adsorption energies of H₂O adsorbing on Ni (111), Pd (111), graphite (001) surfaces, and N-doped graphite (001) surfaces have been calculated to be -1.54, -1.75, -3.38, and -3.36 eV, respectively. The small difference between the adsorption energies of H_2O on graphite (001) surfaces and N-doped graphite (001) surfaces indicates that the doping of N element on the carbon layer has little influence on the adsorption of water. The corresponding distances between adsorbed H_2O and Ni (111), Pd (111), N-doped graphite (001) surfaces are 2.52, 2.32, and 1.78 Å, respectively. Combined with adsorption energies and distances, it could be concluded that the adsorption of N-doped graphite (001) surface to H_2O molecular is stronger than that of Ni (111) and Pd (111) surfaces, which was attributed to the strong interaction between N–O covalent bond, leading to the lower activation energy of the Ni/Pd-2@N–C than Ni/Pd-2.

4. CONCLUSIONS

In conclusion, we have prepared a unique 3D mesoporous sphere structure assembled by N-doped carbon coated Ni/Pd NP heterojunctions (Ni/Pd@N-C), which has shown great catalytic performance toward the hydrolytic dehydrogenation of AB. The unique morphology of 3D mesoporous structure assembled by metallic NPs, which affords a relative large surface area and exposes high fractions of active sites, the synergistic effect between Ni and Pd, and the coating of N-doped carbon are the reasons that responsible for the high activity of Ni/Pd-2@N-C with an optimized feeding amount

a



Figure 5. Geometry of H_2O adsorbed on Ni (111) surface (a), Pd (111) surface (b), and N-doped graphite (001) surface (c). The bluish violet, deep green, gray, red, and white balls represent Ni, Pd, C, O, and H atoms, respectively.

of Pd. Theoretical calculations have verified that N-doped carbon layer can facilitate the adsorption of water and help improve the catalytic activity of Ni/Pd-2@N-C over the hydrolytic dehydrogenation of AB. Furthermore, with the obtained 3D mesoporous spheres of Ni/Pd-2@N-C as catalysts, good stability and recyclability can also be obtained. Therefore, we, herein, provide a new avenue for the fabrication of metallic NP-based catalysts for heterogeneous catalysis, which can well balance the relationship between activity, stability, and recovery.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03607.

Experimental section and computational details, SEM images and XRD pattern of the various Ni precursors (Figures S1–S4), XPS survey spectrum of Ni/Pd-2@N-C (Figure S5), SEM images and XRD patterns of the corresponding contrast samples (Figures S6–S10); Characterization of Ni/Pd-2@N-C after the catalytic test (Table S1), and temperature-dependent catalytic activity of Ni/Pd-2 (Figure S11) (PDF)

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Author Contributions

[†]X.H. conceived and designed the experiments and cowrote the paper. Yu.Y. and W.Z. performed most of the experiments. L.S. performed the theoretical calculation. X.W. and Ya.Y. guided catalytic experiments. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. The denoted authors contributed equally.

Notes

The authors declare no competing financial interest.

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