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Chemistry A European Journal



Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.202003640

Link to VoR: https://doi.org/10.1002/chem.202003640

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CoPd Nanoalloys with MOF as Template for Both *N*-doped Carbon and Cobalt Precursor: Efficient and Robust Catalysts for Hydrogenation Reactions

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Abstract: In this work, a series of MOF-derived CoPd nanoalloys have been prepared. The nanocatalysts exhibited excellent activities in the hydrogenation of nitroarenes and alkenes in green solvent (ethanol/water) under mild conditions (H₂ balloon, room temperature). Using ZIF-67 as template for both carbon matrix and cobalt precursor coating with a mesoporous SiO₂ layer, the catalyst CoPd/NC@SiO₂ were smoothly constructed. Catalytic results revealed the synergistic effect between Co and Pd components in the hydrogenation process due to the enhanced electron density. Mesoporous SiO₂ shell effectively prevented the sintering of hollow carbon and metal NPs at high temperature, furnishing the well-dispersed nanoalloy catalysts and better catalytic performance. Moreover, the catalyst was durable and showed negligible activity decay in recycling and scale-up experiments, providing a mild and highly efficient way to access amines and arenes.

Introduction

Hydrogenation process, especially for nitroarenes and alkenes to access amines and arenes which arguably finds the most application in pharmaceutical and fine chemical industries, has always been the center of attention of both academic and industrial researchers.^[1] Considering the atom economy, it is not surprising that transition metal catalyzed direct hydrogenation based on gaseous H₂ continue to attract interest, since the pioneering work by von Wilde using Pt/H₂ tracing back to 1874.^[2] The vast majority of catalysts were then extended to other precious metals, such as ruthenium and rhodium with palladium being the most common one due to its unique activity and selectivity for the hydrogenation.^[3] Heterogeneous catalysis is thus highlighted to recover and reuse the precious transition metal; and catalysts based on stabilized nanoparticles (NPs) have proven to be a powerful tool with the consensus that catalytic reactivity could be enhanced by increasing the number of exposed active sites.[4]

Traditional synthesis of Pd NPs relies on thermal (pyrolysis or calcination) or chemical reduction of the respective metal precursors on heterogeneous supports.^[5] Recently, the use of metal organic frameworks (MOFs) as versatile support materials has emerged as a rational method to avoid sintering of the active species and regulate selectivity due to their well-ordered crystalline structure, high porosity and tunable pore size.^[6] Moreover, MOF is of particular interest when serving as structure controlling templates^[7] to design heterogeneous catalysts via direct pyrolysis.^[8] Zeng and Wang further extended the strategy independently with MOF as sacrificial precursors.^[9] In their elegant works, mesoporous silica shell covered ZIF-MOF was used as precursor to prepare supported Pd, Pt or other nanoparticles, which prevented nanoparticles from sintering at high temperature and leaching in catalytic process (Scheme 1a).

On the other hand, the availability and high price of Pd as a noble metal also hinder its widespread applications and long-term use. In this regime, intensive efforts have been made to design lower-cost alternatives and in particular, alloying an inexpensive and earth-abundant metal with the precious metal seems attractive to minimize the usage of noble metal and retain the activity at the same time.^[10] Moreover, the hybrid structure of the alloyed catalyst provides much promise to possess not only the properties of individual constituents but also synergistic effect leading to improved catalytic activity, selectivity and stability.^[11] Piccolo reported that nanolayers obtained by segregation of palladium at an alloy surface displayed increased catalytic activity with respect to bulk materials by maintaining hydrogen atoms in the near-surface region.^[12] The challenge may mainly lie in the complicated fabrication process for alloy and uneven distribution of each metal constituent. Considering the templating method as a straightforward and facile way, the utilization of MOF as precursor provides great opportunities for the controllable fabrication of functional bimetallic NPs embedded within a support. Li's group has performed representative works in this area with the construction of low-cost bimetallic nanocatalysts,[8h,13] for

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example, nanostructured PtNi catalyst on nitrogen-doped carbon and NiCo/Fe $_3O_4$ heteroparticles within MOF-74.



Scheme 1. (a) previous work on ZIF-MOF derived NPs within SiO₂ shell; (b) previous work on cobalt catalysed Hydrogenation Reactions; (c) this work.

Despite of the efforts made in this area, there is yet much work to be done. For example, although MOFs have been extensively used as sacrificial templates to fabricate hollow carbon materials, the feasibility that MOFs paly roles in delivering both carbon support and metal constituent for alloy have rarely been reported.^[10a,10b] Besides, when utilization Pd species in hydrogenation process, elevated hydrogen pressure, high temperature, safety measures and special reactors are usually required for hydrogenation process which is difficult and dangerous to control. It is envisaged that combining Pd with a lowcost metal constituent may be achieved with the MOF derived strategy and presenting a highly active and versatile nano-alloy. Recently, there is a general agreement that cobalt plays an indispensable role in enhancing hydrogenation activity. Several N-doped carbon supported cobalt materials prepared by the carbonization of MOFs or a mixture of cobalt salts and organic complex has been demonstrated which exhibited good activity in hydrogenation reactions (Scheme 1b).[10c,14]

Inspired by the leading reports, herein, we describe the successful synthesis of CoPd alloys as a versatile nanocatalysts for hydrogenation of nitroarenes and alkenes with substantially enhanced catalytic activity (Scheme 1c). Co-zeolitic imidazole MOF (ZIF-67) was utilized as Co precursor and acted as sacrificial template as well after coating with a silica layer. The resulting bimetallic nanocatalyst supported on *N*-doped carbon not only is effectively prevented from sintering upon high temperature calcinations, but also exhibiting great synergistic effect between Co and Pd when applied for catalytic hydrogenations under mild conditions for nitroarenes and alkenes (EtOH/H₂O solvent, hydrogen balloon and room temperature).

Results and Discussion

The study was initiated by preparing the MOF derived CoPd nanoalloys as illustrated in Figure 1. ZIF-67 nanocubes which act as both Co precursors and morphological carbon matrix were first prepared by mixing cobalt(II) nitrate hexahydrate and 2methylimidazole in deionized water followed by crystallization. After the impregnation process with palladium solution, Pd²⁺ was introduced into ZIF-67 to form Pd2+/ZIF-67 as another component for the alloy. To increase the surface area and achieve better distribution of CoPd/NC upon calcination, a thin layer of silica was then coated on the surface of the Pd2+/ZIF-67 with hydrolysis of TEOS to afford Pd2+/ZIF-67@SiO2. Finally, the as-synthesized Pd²⁺/ZIF-67@SiO₂ was treated with high temperature under inert atmosphere which led to the in-situ formation of alloy nanoparticles supported on nitrogen-doped porous carbon as ultimate catalyst denoted as CoPd/NC@SiO2. After the carbonization process, hollow ZIF-67 containing metal ions and heteroatoms could be topotactically transformed into heteroatomdoped porous carbon materials containing homogeneously embedded metal alloy NPs, which brings out unique chemical and physical properties that are not attainable from single MOF or Co precursors.^[15]



Figure 1. Schematic illustration of the process for the synthesis of CoPd/NC @SiO_2.

To determine the pyrolysis temperature and analyze its influence on catalyst preparation, TGA-DSC study of $Pd^{2+}/ZIF-67@SiO_2$ was performed (Figure 2a). A slight weight loss together with an endothermic peak were witnessed at 330°C, which was assigned to the decomposition of the ligand for Pd. ZIF-67 precursor was stable up to 540°C where it began to decompose. To achieve fully carbonization, the pyrolysis temperature was thus started from 700°C and different calcination temperatures (700, 800 and 900°C) were tried, denoted as C700, C800 (CoPd/NC@SiO₂) and C900 respectively.

X-ray diffraction (XRD) of the prepared samples were investigated to reveal the phase structure and composition (Figure 2). Peaks located at 7.2°, 10.3°, 12.7°, 18.0° were observed in XRD patterns of ZIF-67 (curve a), correspond exactly to the (011), (002), (112) and (222) plane of its standard simulation (CCDC-671074).^[16] When comparing the results of ZIF-67 and $Pd^{2+}/ZIF-67@SiO_2$, no obvious difference was detected except for the broad peak appeared around 20-30° attributed to the existence of SiO2,[17] which indicated the successful coating of silica. It also disclosed that the structure of the ZIF-67 remained intact during the introduction of Pd2+ and coating process. After calcination, CoPd/NC@SiO2 exhibited diffraction peak at two theta of 41.1° which was ascribed to (111) plane of Pd metal.^[9b,18] It was suggested that the reduction of Pd²⁺ to metallic Pd NPs through pyrolysis under inert atmosphere was feasible. Moreover, peaks at 44.1° and 51.5° appeared, assigning

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to the (111) and (200) planes of Co respectively (JCPDS-15-0806).^[19] The slightly shift of the peaks to lower values compared with face-centered cubic pattern of crystalline Co further confirmed that the starting Pd²⁺ and Co²⁺ have been converted into CoPd alloys successfully through the carbothermic reduction.^[10c,20] The peaks for Pd and Co were relatively weak and wide, resulting from the encapsulation of silica and small particle size of catalysts. When increasing the calcination temperature from 700 to 900°C (inserted Figure 2b), the signals tended to be stronger and sharper due to the better crystalline at higher temperature.



Figure 2. (a) TG(I) and DSC (II) curves of CoPd/NC@SiO₂; (b) XRD patterns of (I) ZIF-67, (II) Pd²⁺/NC@SiO₂ and (III) Pd²⁺/ZIF-67@SiO₂; inserted: XRD patterns of samples with different calcination temperature; (c) N₂-adsorption-desorption isotherms of CoPd/NC@SiO₂ and CoPd/NC; (d) Pore size distribution of CoPd/NC@SiO₂.

The N₂ adsorption-desorption isotherms of CoPd/NC@SiO₂ and CoPd/NC were shown in Figure 2c, which displayed type IV curves for both samples. The former one showed a hysteresis loop at $P/P_0 = 0.4-0.8$, suggesting the presence of mesoporous structure inside the catalyst. As can be seen from Figure 2(d), CoPd/NC showed micropores mainly of 1.7 nm, while CoPd/NC@SiO₂ were proved to be mesoporous materials with pore size of 4.1 nm and few micropores involved. Using the Brunauer-Emmett-Teller (BET) method, the specific surface area and total pore volume of the CoPd/NC@SiO2 was calculated to be 392 m²/g and 0.447 cm³/g. Without the coating of mesoporous SiO₂ shell, the values for CoPd/NC decreased to 259 m^2/g and 0.363 cm³/g accordingly. The coating of silica shell led to higer surface area of the samples, which could furnish better distribution of CoPd/NC upon calcination. In this way, the agglomeration of inner metals was prevented and smaller particle size was obtained.

The samples were further characterized by means of scanning electron microscopy (SEM) and the images were shown in Figure 3. As can be seen, the as prepared ZIF-67 displayed regular nanocube structure with diameter of ~200 nm. The cubic structure was remained almostly after coating of silica shell but the size increased to about 220 nm, testifying the successful covering of a thin SiQ₂ layer. Owning to the protection of SiO₂, subsequent thermal treatment showed no significant influence on the morphology of CoPd/NC@SiO₂, exhibiting similar cubic shape but with rough facets despite of tiny irregularities. As for comparison, CoPd/NC without SiO₂ showed severe agglomeration and irregular morphology (Figure 3d).



Figure 3. SEM images of (a) ZIF-67, (b) Pd²⁺/ZIF-67@SiO₂, (c) CoPd/NC@SiO₂, (d) CoPd/NC.

The morphology and microstructure of the samples were further monitored by transmission electron microscopy (TEM) and highresolution transmission electron microscopy (HRTEM). As illustrated in Figure 4(a), Pd²⁺/ZIF-67@SiO₂ was of a core-shell cubic shape with SiO₂ coating of about 33 nm thickness. The structure maintained for CoPd/NC@SiO₂ but a slightly smaller size was observed, which was attributed to the partial surface collapse of Pd²⁺/ZIF-67@SiO₂ during the pyrolysis process, resulting in a shrinked overall structure (Figure 4b). The alloy nanoparticles of about 10-15 nm were homogeneously dispersed within the SiO₂ surface on nitrogen doped carbon matrix and with no considerable formation of aggregates. HRTEM images of CoPd/NC@SiO₂ revealed the lattice fringes with an interplanar distance of 0.225 nm and 0.210 nm which were corresponding to the (111) plane of Pd and (111) plane of Co respectively, indicating the existence of Pd and Co after carbothermic reduction under inert atmosphere. The relative element mapping analysis was performed and demonstrated the well distribution of Pd, Co, C, N and Si. It was found that the Pd species spatially distributed with Co species in the nitrogen doped carbon matrix, which indicated that with the protection of SiO₂, Co and Pd formed bimetallic alloys on the NC support. The line scanning in Figure 4(e) and (f) also revealed the coexistence of Co and Pd in the particle, and their superficial ratia was about 3:1. Further investigation found that changing the thickness of SiO2 shell would result in different particle sizes. When increasing the loading of TEOS, the SiO2 shell thickened from 33 nm to 67 nm with larger nanoparticle obtained from 12 nm to 18 nm owing to "Ostwald ripening" without additional passivation (Figure S1). The combined results of SEM and TEM indicated that SiO₂ shell effectively prevent the sintering of hollow carbon and metal NPs at high temperature, furnishing the well-dispersed nano-alloy catalyst. As also evidenced clearly by the TEM images in Figure S2, the alloy catalysts tended to aggregate into larger nanoparticles with uneven distribution when increasing the calcination temperature. The C700, C800 and C900 catalyst exhibited size distributions of 12, 18 and 30 nm respectively.

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Figure 4. TEM images of (a) Pd²⁺/ZIF-67@SiO₂; (b) and (d) CoPd/NC@SiO₂; HR-TEM images of (c) CoPd/NC@SiO₂; (e, f) Line scanning of Co and Pd, element mapping images of (g) Co, (h) Pd, (i) Co+Pd, (j) C, (k) N and (l) Si for CoPd/NC@SiO₂ catalyst.

X-ray photoelectron spectroscopy (XPS) was further carried out to analyze the composition and chemical state of the catalysts. Figure 5a showed the wide-scan spectra which indicate the existence of Pd, Co, N, O, C, and Si elements in CoPd/NC@SiO₂ without other impurities. In the N 1s XPS spectra (Figure 5b), peaks located at 399.0 eV and 401.1 eV were identified as pyridine type N and graphitic type N respectively,^[21] suggesting the successful doping of N into carbon support with ZIF-67 as a sacrificial template. The C 1s spectra could be deconvoluted into two peaks at 286.7 eV and 284.8 eV respectively which was attributed to the graphitic type C-C bond and C-N bond.^[22] The high-resolution XPS spectrum of the Pd 3d region (Figure 5b) presented doublet peaks at 335.4 eV and 340.8 eV, corresponding to the Pd 3d_{5/2} and Pd 3d_{3/2} respectively for metallic state Pd(0) species.^[23]

In case of Co 2p (Figure 5d), the core level spectra could be deconvoluted into eight peaks indicating the existence of Co(0), Co(II), Co(III) and satellite peak. The characteristic peaks at 778.3 eV and 792.6 eV could be attributed to Co(0) $2p_{3/2}$ and Co(0) $2p_{1/2}$,^[9c,24] which were in accordance with the formation of metallic Co in CoPd alloy. The peak at 780.9 eV and 782.5 eV can be assigned to Co(II) and Co(III) peak in Co-N species and Co oxides.^[25] The content of Co(0) *vs* total Co(II) and Co(III) estimated by the area ratio of two doublet peaks was approximately 1:4. XPS for metallic Pd(0) and Co(0), together with the TEM and line scanning results confirmed the formation of CoPd alloy. As Pd is generally more electronegative compared with Co, it would gain electrons from Co, which is supposed to be

compensated by the nitrogen doped carbon matrix. Therefore, the surface electron density of the bimetallic CoPd alloy is enhanced compared with monometallic Pd.^[26] Moreover, the superficial Co/Pd ratio determined by XPS was about 3:1, similar to the line scanning result; while the ICP data for the whole CoPd alloy was 8:1. The distinct result could be rationalized that XPS determine only the superficial elements and may give deviation for the hybrid catalyst. The ICP result is considered to be more accurate.



Figure 5. XPS spectrum of (a) full scan; (b) N1s; (c) C 1s; (d) Pd 3d and (e) Co 2p respectively.

With the synthesized CoPd alloy catalyst in hand, initial attempts to perform hydrogenation reactions were conducted in EtOH/H₂O system using nitrobenzene as the substrates. To our delight, over 95% conversion of nitrobenzene toward the desired aniline was obtained in the presence of only 0.4 mol% catalyst and a H₂ balloon within 120 min at room temperature. The catalytic activity employing other samples including monometallic Pd/NC@SiO2, Co/NC@SiO2, CoPd/NC with no SiO2 shell and commercial Pd/C were further tested and compared as outlined in Figure 6a. To be noted, CoPd/NC@SiO2 outperformed both Pd/NC@SiO₂ and Co/NC@SiO₂, which gave only 65% and trace conversion after 180 min of reaction respectively. When compared with the result of commercial Pd/C in this system (14%, 180 min), the advantage of using the nanoalloy was still highlighted. It was indicated that Pd serve as the active centre and Co was supposed to accelerate process through the synergistic effect with Pd. The enhanced electron density of the bimetallic CoPd allov (as illustrated above) which would be favorable for H₂ adsorption and activation may account for the improved catalytic performance. In terms of CoPd/NC as catalyst, the conversion of nitrobenzene decreased to only 25% after 180 min. The effect of SiO₂ shell was thus manifested that prevented the alloy nanoparticles on carbon support from agglomeration.

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Figure 6. (a) Hydrogenation performance of different catalysts for nitrobenzene; the influence of Pd contents (b), SiO₂ thickness (c) and calcination temperature (d) on hydrogenation of nitrobenzene. Reaction conditions: nitroarene (1 mmol), CoPd/NC @SiO₂ (40 mg, 0.4 mmol% Pd), solvent 10 mL, EtOH:H₂O=2:1), H₂ balloon, room temperature; conversions were determined by GC-MS.

To gain some more insights into the catalytic process, CoPd/NC@SiO₂ of different calcination temperature, SiO₂ thickness and Pd contents were tested. For comparison, catalyst loading for all the materials were adjusted to the same Pd concentration. As shown in Figure 6c and 6d, among the prepared catalysts, CoPd/NC@SiO2 with a moderate SiO2 thickness and Pd contents calcinated at 800°C was shown to provide the best performance. Considering the TEM results, it was suggested that appropriate pyrosis temperature was necessary to carbonize ZIF-67 precursor and lead to the alloy with Pd constituent, but higher temperature may result in inhomogeneous growing of the alloy as well as larger particle size. The effect of NC@SiO₂ support to stabilize and disperse the alloy particles was weakened at 900°C and thus decreased catalytic performance was observed. As for SiO₂ thickness, the influence mainly lies in two aspect. Firstly, different SiO₂ thickness means different surface area upon calcination. With thicker SiO₂ shell and larger surface area, CoPd/NC would disperse better, leading to smaller particle size of CoPd NPs. Secondly, mass transfer effect would be influenced by different SiO₂ thickness. Excessive SiO₂ shell may hinder the diffusion of substrates during the catalytic process and prevent the coordination of the substrates on particle surface, thus resulting in low efficiency. Thus, it was supposed that an appropriate amount of SiO₂ was necessary and catalyst of 67 nm SiO₂ shell gave the best catalytic performance with the smallest particle size (Figure 6c and Figure S1). Thicker samples were prepared but afforded decreased catalytic performance, which further confirmed the conjecture. On the other hand, CoPd/NC@SiO₂ with different Pd contents showed similar catalytic activities for this transformation, indicating their excellent efficiency and applicability due to the alloying of Co.

Based on the preliminary results, subsequent efforts were devoted to examine the applicability of this attractive protocol using a wide range of nitroarenes containing diverse substituent groups, as listed in Table 1. Generally, nitrobenzenes bearing either electron-donating (-alkyl, -alkoxyl, hydroxyl) or electron-withdrawing (-fluoro, -chloro, -bromo, -acyl) substituents proceeded quite well to afford corresponding anilines with quantitative yields without observation of obvious electronic effect. For chlorinated substrates, the influence of the position seems inconspicuous and ortho-, meta-, and para-substituted nitrobenzenes were all well tolerated (**2b-2d**). Moreover, -COOH, -CHO, -COOEt and -SCH₃ remained intact after the reaction

without cleavage or hydrogenation of C=O bonds, exhibiting great selectivity of the system (2i-2l). As for amino group, the hydrogenation process was retarded significantly and prolonged reaction time was needed to achieve the process (2m-2o). This differentiation might be rationalized by relative differences in the stability and reactivity of intermediates affected by the substitution groups. Tri-substituted substrates also performed well under the standard conditions and notably, dinitro compound was evaluated which turned into the desired 1,3-diamine smoothly in good yield (2p). For substrate 1q, cascade coupling reaction was occurred in the system furnishing 2q in 57% yield, probably due to the activation of *ortho*- methyl for the leaving of CI. To understand the origin of product 2q, 3-chloro-2-methylaniline was tested in the system, which delivered the coupling product 2q under the Co-Pd catalysis.



Encouraged by the promising results, the substrate scope was further extended to evaluate he hydrogenation of various alkenes using 2 mol% CoPd/NC@SiO₂ under a H₂ balloon at room temperature. As the alkenes are difficult to dissolve in H₂O/EtOH solvent, EtOH was used instead to perform the reactions and the results were summarized in Table 2. It could be observed that the nano-alloy catalyst still exhibited outstanding catalytic performance and styrenes containing alkyl, alkoxy, or chloro substitutions afforded the corresponding hydrogenated products

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with good to excellent conversions $(4a-4f).\alpha$ -methyl styrene, however, impaired the reaction and afforded cumene in poor yield (4g). The system shows compatibility for cinnamaldehyde and its derivatives with great selectivity giving conversions ranging from 91% to 98% (4h-4m). To be noted, 3-(furan-2-yl)acrylaldehyde, though considered difficult to activate, proceeded smoothly in this regime with extended reaction time (4n), which further extended the substrate scope greatly. However, aliphatic substrates were proved to be inefficient in the system for both long-chain and cyclic ones with no prodect detected even at refluxing temperature (4o-4q).



In terms of a heterogeneous catalyst, the stability and recyclability always cause concern and thus the recycling test of the CoPd/NC@SiO₂ was performed and compared with CoPd/NC and Pd/C. As shown in Figure 7, the recovered CoPd/NC@SiO₂ catalyst could be reused for at least 8 times in hydrogenation of nitrobenzene without remarkable loss of activity (96% and 92% conversion in the eighth run respectively). As for CoPd/NC, without the protection of SiO₂, relatively poor reusability was shown and the activity dropped obviously. The kinetic curves in Figure 7(b) further confirmed that the catalyst was reusable but with lower initial reaction rate, which was due to the gradual collapse and aggregation of catalyst when increasing the recycling times. As disclosed by SEM imaged in Figure 7(c), increased proportion of the broken catalyst was observed after 8th recycling, but CoPd/NC still adheres strongly to the SiO₂ wall which to some certain prevented serious loss or aggregation of the NPs. Hot filtration was further performed as shown in Figure 7(b) (inserted). The TEM image of the recovered CoPd/NC@SiO₂ after eighth cycle (~15 nm) as well as the hot filtration result and ICP data of Pd (0.83%) and Co (6.60%) before the reaction and after the eighth cycle (0.79%, 5.41%) collectively suggested that leaching of Pd was not obvious during the hydrogenation process, further displaying the outstanding stability of the nanoalloy

stabilized by the carbon support and SiO_2 shell. As for Co, considering that it was located in both carbon matrix and nanoalloy, and Co itself could not achieve the catalytic transformation, the partial loss of Co showed less impact on the catalytic performance.



Figure 7. The recycling study of catalyst CoPd/NC@SiO₂; (a) recycling performance in hydrogenation of nitroarenes; (b) comparison of kinetic curves before and after recycling with hot filtration tests inserted; (c) SEM images of recovered CoPd/NC@SiO₂; (d) TEM images of broken part of recovered CoPd/NC@SiO₂ with relative size distribution inserted.





To demonstrate the practical applications of this attractive protocol for hydrogenation, scale-up experiments were performed with nitrobenzene and styrene as substrates. As shown in Figure 8, only slight decline of conversion was observed with 10 mmol substrate under the standard conditions for both of the transformations. When the processes further amplified to 100 mmol, high conversions (87% and 82% respectively) were still maintained for nitrobenzene and styrene with extended reaction time of 4 h.

Conclusion

In summary, a CoPd nanoalloy catalyst supported on *N*-doped carbon within mesoporous silica shell was successfully developed with ZIF-67 served as both template for carbon and cobalt precursor. When applying the catalyst in hydrogenation of nitroarenes and alkenes, a clean, mild and efficient system was

disclosed using a hydrogen balloon at room temperature in ethanol/water solvent. The reaction tolerated various functional groups for both kinds of substrates, delivering the target products in good to excellent yields. Notably, due to the synergistic effect between Co and Pd, the alloy outperformed monometallic Pd and Co nano-catalyst. The mesoporous SiO₂ shell has been proved to play a key role in preventing the sintering of hollow carbon and metal NPs at high temperature, furnishing the well-dispersed nanoalloy catalyst. The present work might open a new avenue to design MOFs-templated catalyst alloying noble and earth abundant metals, exhibiting enhanced activity as well as reduced cost compared with monometallic noble catalyst.

Experimental Section

General information: Solvents and reagents of reagent grade were used without purification unless otherwise noted. Thermogravimetric analysis was performed on TGA/SDTA851e under N2 atmosphere from 50 °C to 800 °C, with a heating rate of 10 °C/min and N₂ flowing rate of 30 mL/min. Inductively coupled plasma-mass spectra (ICP-MS) were taken from Optima 7300 DV (PerkinElmer). XRD data were collected with CuKa radiation on Bruker C8 ADVANCE. The Brunauer-Emmett-Teller (BET) specific surface area (SSA) of the samples were determined by collecting N2 gas adsorption/desorption isotherms on a Micromeritics ASAP 2020 Instrument. All samples were degassed at 200 °C for 18 h before the SSA determination. Transmission electron microscopy (TEM) pictures were taken on a FEI-Tecnai G2 F30 at an accelerating voltage of 75 kV with the chloroform dispersion of catalyst was drop-cast onto a 300 mesh carbon coated copper grid. The elemental mappings were performed on a scanning transmission electron microscope (STEM) unit with a high-angle annular-dark-field (HAADF) detector (HITACHI S-5500) operating at 200 kV.

Typical procedure for the synthesis of ZIF-67 nanocubes^[16a]: In a typical preparation, 20 mg of hexadecyl trimethyl ammonium bromide (CTAB) and 580 mg of cobalt(II) nitrate hexahydrate were dissolved into 20 mL of deionized water to form a clear solution; and another solution was obtained by dissolving 9.08 g 2-methylimidazole in 140 mL of deionized water. Under vigorous stirring, the cobalt containing solution was poured into the ligand containing solution and kept stirring at room temperature for 20 min. Finally, purple precipitates were produced, centrifuged and washed with ethanol for three times before and drying under vacuum at room temperature for 12 h.

Typical procedure for the synthesis of Pd²⁺/ZIF-67: The Pd²⁺/ZIF-67 was prepared via a conventional impregnation method. Typically, 600 mg of ZIF-67 was dispersed in 20 mL of acetone and was sonicated for about 20 min until uniform dispersion. Afterwards, a solution containing a certain amount of Pd(CH₃COO)₂ (30, 50, 100, 150 mg) and 5 mL acetone and was added dropwise into the above solution under magnetic stirring. The obtained suspension was subjected to ultrasonic treatment for 20 min before magnetically stirred for 24 hours at room temperature. The resulting product was washed by acetone for three times and dried under vacuum for 24 hours before further use.

Typical procedure for the synthesis of Pd²⁺/ZIF-67@SiO₂: The Pd²⁺/ZIF-67@SiO₂ according to the following reported method.^[9a] Briefly, 200 mg of as-prepared Pd²⁺/ZIF-67 was dispersed in 60 mL of ethanol. After sonicated for 5 min, the suspension was mixed with another solution containing 4 g of 2-methylimidazole (MeIM) and 64 mL deionized water. The mixture was sonicated foe another 5 min followed by the addition of 4 mL CTAC aqueous solution (5 wt%) and stirring for 20 min. Afterwards, TEOS (0.5, 1, 1.5, 2 mL) was added dropwise within 3 min and the mixture stirred for another 2 hours. The final product was harvested through

centrifugation and washed with ethanol for three times before drying under vacuum overnight.

Typical procedure for synthesis of CoPd/NC@SiO₂: The prepared $Pd^{2+}/ZIF-67@SiO_2$ above was calcinated at 800°C with a heating rate of 2°C/min under nitrogen atmosphere and was cooled down to room temperature naturally, furnishing the final alloy catalyst denoted as CoPd/NC@SiO₂. For comparison, Pd/NC@SiO₂ without Co,^[9b] Co/NC@SiO₂ without Pd and CoPd/NC without silica shell were prepared as well using a method similar to the above one. The Pd/NC@SiO₂ was prepared according to a reported literature.

Typical procedure for the hydrogenation of nitroarenes: To a 25 mL vial equipped with hydrogen balloon was added nitroarenes (1 mmol), catalyst (0.4 mol % Pd) and mixed solvent (10 mL, EtOH: $H_2O = 2:1$) respectively. The reaction was then allowed to react at room temperature for certain time until the complete consuming of starting materials monitored by TLC. When completed, the catalyst was recovered from the system through centrifugation; the samples were diluted to 15 mL with water, extracted with Et₂O for three times, and dried over anhydrous Na₂SO₄ before being analyzed by GC-MS. Substrate could be recharged into the aqueous phase to achieve recycling. To achieve recycling, the recovered catalyst washed with ethanol for several times with ethanol, dried under vacuum and reused as the catalyst in the next run.

Typical procedure for the hydrogenation of alkenes: To a 25 mL vial equipped with hydrogen balloon was added alkenes (0.5 mmol), catalyst (2 mol % Pd) and 5 mL EtOH respectively. The reaction was then allowed to react at room temperature for certain time until the complete consuming of starting materials monitored by TLC. After completion of the reaction, the catalyst was removed from the solution through centrifugation, and the liquid phase was subsequently analyzed by GC-MS.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 11972195 and 11702141) for support of this work.

Keywords: CoPd nanoalloy • MOF derived • Hydrogenation • Nitroarenes • Alkenes

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CoPd nanoalloys were prepared with MOF as Template for Both *N*-doped Carbon and Cobalt Precursor. The catalyst encapsulated in silica shell afforded a clean, mild and efficient system for hydrogenation of nitroarenes and alkenes. Improved activity was witnessed due to the synergistic effect between Co and Pd components as well as improved stability due to the protection of silica shell.