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Conceptual Insights:

Although noble metal nanoparticles (NPs) exhibit excellent catalytic behavior in various reactions, the high cost and limited storage restrict their application. In reverse, the price of non-noble metal NPs is acceptable while the activity is usually inferior to the former. More importantly, the reduction of non-noble metal precursors is generally carried out with strong reductant or under harsh conditions that some supports, employed for stabilizing metal NPs, hardly sustain. Therefore, it is highly desired to obtain highly active non-noble metal nanocatalysts with moderate reducing agent under very mild conditions. In this work, for the first time, we developed a novel, general and facile one-step in-situ noble metal seed-mediated (NMSM) synthetic approach to reduce non-noble metal cations under ambient conditions, by taking advantage of the trace amount of noble metal cations as an initiator and NH_3BH_3 as a moderate reducing agent. The obtained non-noble NPs stabilized by a metal-organic framework (MOF) are low-cost and display superior catalytic activity in the hydrolytic dehydrogenation of NH_3BH_3 under ambient conditions. This general and facile approach paves a way to the synthesis of non-noble metal NPs under ambient conditions with a moderate reductant.



Journal Name

COMMUNICATION

A Seed-Mediated Approach to General and Mild Synthesis of Non-noble Metal Nanoparticles Stabilized by A Metal-Organic Framework for Highly Efficient Catalysis

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A novel and facile in-situ seed-mediated synthetic approach has been developed to reduce non-noble metal precursors (Ni^{2+} , Co^{2+} , Fe^{2+} , etc.) at room temperature, by taking advantage of a trace amount of noble metal cations (Ag^+ , Pd^{2+} , Pt^{2+} , Au^{3+} , etc.) as a seed/initiator and NH_3BH_3 as a moderate reducing agent. The obtained noble metal-seed-mediated (NMSM) non-noble metal nanoparticles (NPs) stabilized by a metal-organic framework are low-cost and display superior catalytic activity in the hydrolytic dehydrogenation of NH_3BH_3 under ambient conditions. As a representative catalyst, Ag-doped Ni/MIL-101 (with Ag/Ni molar ratio as low as 1/200), exhibiting much higher activity than any other corresponding counterparts.

Introduction

Metal nanoparticles (NPs) have attracted great attention because of their unique catalytic properties.¹ Although noble metal NPs exhibit excellent catalytic behavior in various reactions, the high cost and limited storage restrict their application in an industrial scale. In contrast, the price of non-noble metal NPs is desirable while the activity is usually inferior to the former. More importantly, the non-noble metal precursors have low reduction potentials and thus their reduction is generally carried out under harsh conditions, such as NaBH_4 with strong basicity or H_2 reduction under high temperature or/and pressure.² Given tiny metal NPs with high catalytic activity possess high surface energies, they are prone to aggregate and grow larger. One of the most effective

solutions to avoid their aggregation is to stabilize them with supports/porous host materials, unfortunately, some structures of which hardly sustain harsh conditions. Moreover, the strong reductants are detrimental to the control of narrow size distribution of metal NPs, which can be easily generated by using moderate reducing agents.³ Therefore, it is highly desired and imperative to obtain highly active non-noble metal nanocatalysts under very mild conditions, which would guarantee the integrity of NP supports/hosts during the synthesis and low cost of the catalysts.

On the other hand, studies have shown that noble metal precursors are readily reduced with moderate reductants.³⁻⁵ Therefore, it is possible to prepare non-noble metal NPs under ambient conditions by judiciously selecting a trace amount of noble metal as an initiator and choosing a suitable reductant, such as ammonia borane (NH_3BH_3 , AB), which is not only a good/moderate reducing agent but also a promising hydrogen material with high hydrogen capacity up to 19.6 wt.%, exceeding that of gasoline.⁶ Hydrogen would be released from NH_3BH_3 over newly generated noble metal NPs to form intermediate M-H species with strong reducibility, which is able to further reduce non-noble metal precursors at room temperature.^{5d} The basic concept in such noble metal-seed-mediated (NMSM) synthesis of non-noble metal NPs under mild conditions is to take advantage of the difference in reduction potentials of the two soluble metal salts and a suitable reducing agent (NH_3BH_3).

Bearing this in mind, a trace amount (1/100-1/200, molar ratio of noble metal/non-noble metal) of noble metal precursors were introduced to non-noble metal precursors in NH_3BH_3 hydrolysis system containing a metal-organic framework (MOF),⁷ a class of crystalline porous material well demonstrated to be ideal support/host providing confinement effect to limit the aggregation and growth of metal NPs.⁸ Strikingly, a trace amount of different noble metal precursors are able to rapidly trigger the reduction of non-noble metal cations at room temperature and the resultant in-situ formed NPs exhibit excellent catalytic performance in the hydrolytic dehydrogenation of NH_3BH_3 . It is noteworthy that all non-

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[‡] Electronic supplementary information (ESI) available: experimental details, and figures referred in the text. See DOI: 10.1039/x0xx00000x

noble metal NPs cannot be obtained without introducing noble metals, unless with very harsh reduction conditions (Scheme 1). The current one-step in situ seed-mediated synthetic approach was conducted at room temperature under ambient atmosphere with a moderated reductant NH_3BH_3 , which is very gentle and thus acceptable for diverse NP supports/host materials. It is worthy to note that although bimetallic Au@Co and AuNi NPs have been reported based on similar Au-induced reduction method,^{5a,b} the amount of noble metal used in this work is dramatically lower. To the best of our knowledge, this is the first general one-pot synthesis of non-noble metal NPs with a moderate reductant and a trace amount of noble metal as the seed/initiator under ambient conditions.



Scheme 1. Schematic illustration showing the preparation of non-noble metal NPs under harsh conditions or via a NMSM synthetic approach with moderate NH_3BH_3 under ambient conditions.

Experimental

General

All chemicals were from commercial and used without further purification. De-ionized water with the specific resistance of $18.25 \text{ M}\Omega\cdot\text{cm}$ was obtained by reversed osmosis followed by ion-exchange and filtration (Cleaned Water Treatment Co., Ltd., Hefei). Powder X-ray diffraction (PXRD) data were collected on a Japan RigakuSmartLabTM rotation anode X-ray diffractometer equipped with graphite monochromatized Cu $\text{K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) were acquired on JEOL-2010 and JEOL-2100F with an electron acceleration energy of 200 kV. The nitrogen sorption isotherms were measured by using an automatic volumetric adsorption equipment (Micromeritics ASAP 2020). Prior to nitrogen adsorption/desorption measurement, the samples were dried overnight at $160 \text{ }^\circ\text{C}$ under vacuum. The contents of metals in the samples or solution were quantified by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES).

Preparation of MIL-101

MIL-101 was synthesized according to the previous report with modifications.⁹ Typically, a mixture of terephthalic acid (332 mg, 2.0 mmol) with $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (800 mg, 2.0 mmol) in the presence of aqueous HF (0.1 mL, 0.5 mmol) and de-ionized water (9.5 mL) was reacted at $200 \text{ }^\circ\text{C}$ for 8 h. The reaction produced microcrystalline green powder of MIL-101 with formula $\text{Cr}_3\text{X}(\text{H}_2\text{O})_2\text{O}[(\text{O}_2\text{C})\text{C}_6\text{H}_4(\text{CO}_2)]_3\cdot n\text{H}_2\text{O}$ ($\text{X} = \text{F}$ or OH , $n \leq 25$). MIL-101 was purified in water at reflux temperature for 12 h, followed by in ethanol at $100 \text{ }^\circ\text{C}$ for 24 h for twice and washed with hot ethanol, and was further purified by NH_4F solution. The resultant green solid was finally dried overnight at $150 \text{ }^\circ\text{C}$ under vacuum prior to the further use. The main paragraph text follows directly on here.

Preparation of Ag/MIL-101, Ag-doped Ni/MIL-101, Au-doped Ni/MIL-101, Pd-doped Co/MIL-101, Pd-doped Ni/MIL-101, Pd-doped Fe, Pt-doped Co/MIL-101 and Pt-doped Ni/MIL-101

The aqueous solution AgNO_3 (0.24 mol/L), $\text{Pd}(\text{NO}_3)_2$ (0.25 mol/L) or $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ (0.02 mol/L) and $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.5 mol/L), $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (0.5 mol/L) or $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.5 mol/L) with desired contents as well as 20 mL pure water were charged into a flask with 40 mg MIL-101, which was dried overnight at $160 \text{ }^\circ\text{C}$ under vacuum prior to use. The reaction proceeded when ammonia borane was added into the flask. The noble metal ions were first reduced by ammonia borane to behave as in situ seeds for the subsequent reduction of non-noble metal ions to produce non-noble based NPs stabilized by MIL-101. It should be noted that magnetic stirring was not preferred and shaking was employed for the reaction in order to avoid the attachment of Ni or Co species onto the magnetic stirring bar. In this work, the molar quantity of (Au+Ni), (Pd+Ni), (Pd+Co), (Pd+Fe), (Pt+Ni), (Pt+Co) and (Ag+Ni) were 0.02, 0.015, 0.015, 0.02, 0.02, 0.02 and 0.015 mmol, respectively. The theoretical molar ratios of Au/Ni, Pd/Ni, Pd/Co, Pd/Fe, Pt/Ni, Pt/Co and Ag/Ni were 1/100, 1/200, 1/150, 1/100, 1/100, 1/100 and 1/200, respectively. In addition, pure Ag-doped Ni NPs with Ag/Ni molar ratio of 1/200 were also obtained in the absence of MIL-101 or other support/stabilizer.

Preparation of Ni/MIL-101 and PVP-stabilized Ni NPs

The aqueous solution of $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (29.8 μL , 0.5 mol/L) and 20 mL of pure water was introduced to 40 mg MIL-101 or PVP placed in the bottom of flask, then NaBH_4 (10 mg) was added into the flask to afford PVP-protected Ni NPs. It should be noted that magnetic stirring was not preferred and shaking was employed for the reaction in order to avoid the attachment of Ni species onto the magnetic stirring bar.

Attempt to prepare Ag-doped Ni/MIL-101 reduced by NaBH_4

The aqueous solution AgNO_3 (0.24 mol/L) and $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.5 mol/L) with desired contents as well as 20 mL pure water were charged into a flask with 40 mg MIL-101, then fresh 0.6 M NaBH_4 aqueous solution was added into the flask for the reduction of metal cations. Similarly, magnetic stirring was not preferred and shaking was employed for the reaction in order to avoid the attachment of Ni species onto the magnetic stirring bar.

Preparation of PVP-stabilized Ag@Ni core-shell NPs

The aqueous solution of AgNO_3 (31 μL , 0.24 mol/L), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (15 μL , 0.50 mol/L) and 20 mL of pure water was introduced into 40 mg PVP that placed in the bottom of flask, then NH_3BH_3 (30 mg) was added into the flask with vigorous shaking to afford PVP stabilized Ag@Ni core-shell NPs. It should be noted that magnetic stirring was not preferred and shaking was employed for the reaction in order to avoid the attachment of Ni species onto the magnetic stirring bar.

Catalytic activity characterization

In general, a two-necked round-bottomed flask (50 mL) with a mixture of 40 mg MIL-101, metal precursors with desired concentration and 20 mL of pure water was placed in a mechanical oscillator in order to avoid the attachment of Ni or Co NPs onto the magnetic stirring bar. A gas burette filled with water was connected to the reaction flask to measure the volume of hydrogen evolved. The reaction started when 30 mg NH_3BH_3 was added into the flask. The volume of the evolved hydrogen gas was monitored by recording the displacement of water in the gas burette. The reaction was completed when there was no more gas generated. For the catalytic recyclability/durability experiments, the same amount of NH_3BH_3 (30 mg) was added into the flask to initiate the reaction.

Results and discussion

A representative mesoporous MOF, MIL-101 with molecular formula $\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}[(\text{O}_2\text{C})\text{C}_6\text{H}_4(\text{CO}_2)]_3 \cdot n\text{H}_2\text{O}$ ($n \approx 25$),⁹ was selected as a host matrix based on its high specific surface (BET, $>3000 \text{ m}^2/\text{g}$) and large pore size (2.9 to 3.4 nm), in order to avoid the aggregation and growth of resultant metal NPs. No reaction occurred to the NH_3BH_3 aqueous solution involving only non-noble metal precursor and MIL-101 in the flask. Upon the introduction of a trace amount of noble metal precursor (1/100-1/200, molar ratio of noble metal/non-noble metal), the reaction was initiated immediately, accompanying by the color evolution of the reaction solution (ESI[†], Fig. S1[†]). Based on this NMSM synthetic approach, diverse non-noble metal NPs can be obtained by using kinds of noble metal precursors as reduction initiators. Typically, Pd-doped Ni, Pd-doped Co, Pt-doped Ni, Pt-doped Co, Ag-doped Ni and Au-doped Ni NPs stabilized by MIL-101 have been successfully synthesized involving only trace amount of noble metal species. Due to the high reduction potentials of the soluble noble metal salts ($E_{\text{Pd}^{2+}/\text{Pd}}^\circ = +0.915 \text{ eV vs SHE}$, $E_{\text{Pt}^{2+}/\text{Pt}}^\circ = +1.18 \text{ eV vs SHE}$, $E_{\text{Au}^{3+}/\text{Au}}^\circ = +1.498 \text{ eV vs SHE}$ and $E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ eV vs SHE}$), the noble metal ions were first reduced to be NPs by NH_3BH_3 as the initiator for the subsequent reduction of non-noble metal precursors.

The high dispersion of Pd-doped Ni, Pd-doped Co, Au-doped Ni, Pt-doped Ni, Pt-doped Co and Ag-doped Ni NPs can be evidenced by transmission electron microscopy (TEM) observation (Fig. 1a-f), which shows that their average sizes are 2-3 nm and indicates the universality of this noble metal-triggered synthetic approach (Fig. 1f). To gain further structure information of these metal NPs, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), high-resolution TEM (HRTEM) and energy-dispersive X-ray spectroscopy (EDS) have been employed to

investigate Ag-doped Ni/MIL-101 nanocomposite as a representative (Fig. 1g-i). The lattice fringes with a spacing of 0.206 nm are assigned to the (111) planes of the face-centered cubic (fcc) Ni, which are clearly observable from the HRTEM image for Ag-doped Ni/MIL-101 (Fig. 1h). The SAED pattern (Fig. 1h, inset) shows the diffuse diffraction rings, indicating that the Ni is mostly in an amorphous phase.^{2a,6i} The EDS spectrum for Ag-doped Ni NPs can identify Ni species only, revealing the very low content of Ag doping in the Ni NPs (Fig. S2[†]). For comparison, PVP-protected Ni NPs with much larger particle sizes have been obtained by the reduction of NaBH_4 (Fig. S3b[†]) and the lattice fringes demonstrate the NP is composed by Ni.

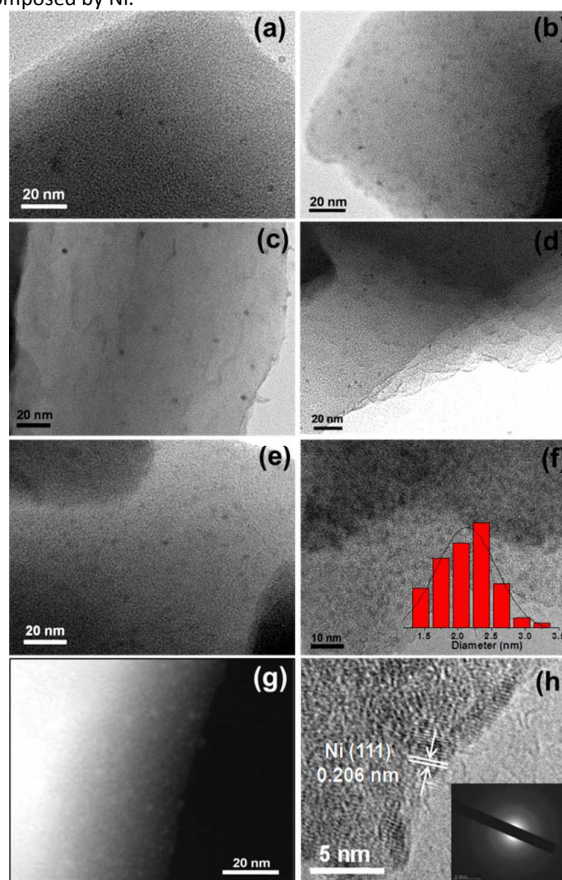


Fig. 1 TEM images of (a) Pd-doped Ni, (b) Pd-doped Co, (c) Au-doped Ni, (d) Pt-doped Ni, (e) Pt-doped Co, and (f) Ag-doped Ni NPs stabilized by MIL-101 (inset: size distribution). (g) HAADF-STEM image, and (h) HRTEM image of Ag-doped Ni/MIL-101 catalyst (inset: SAED pattern).

For further comparison, TEM observation for Ni/MIL-101 (reduced by NaBH_4), Ag/MIL-101 (reduced by NH_3BH_3), Ni^{2+} /MIL-101, pure Ag-doped Ni (1/200) NPs without stabilizer and PVP-stabilized Ag@Ni core-shell NPs (reduced by NH_3BH_3) with Ag/Ni molar ratio of 1/1 were also performed (Fig. S3[†]). The Ni/MIL-101 reduced with NaBH_4 shows relatively larger Ni NPs, possibly because the structure of MIL-101 was partly damaged by the strong reductant of NaBH_4 (Fig. S3c[†]). In contrast, Ag/MIL-101 shows their average sizes are $\sim 2 \text{ nm}$ with confinement of MIL-101 (Fig. S3d[†]). However, the Ag-doped

Ni NPs presents apparent aggregation to ~20 nm in the absence of support (Fig. S3e†). Ni²⁺/MIL-101 almost presents no particles (Fig. S3g†). In order to validate the seed role of noble metals for introducing the reduction of non-noble metal, as a representative, the PVP stabilized Ag@Ni core-shell NPs with increasing Ag content have been synthesized with NH₃BH₃. The TEM image clearly shows the core-shell structure for Ag@Ni and the HRTEM further confirms the Ag core (Fig. S3h†), suggesting the in situ formation of Ni NPs triggered by Ag seed.

Attempt to prepare Ag-doped Ni/MIL-101 reduced by strong reductant NaBH₄ even under ambient condition has been demonstrated to be failed, as the powder X-ray diffraction (PXRD) peak intensity for resultant composite is very weak, suggesting the partly collapsed MIL-101 structure (Fig. S4a†). In contrast, the PXRD profiles show that there is no apparent loss of crystallinity and no identifiable peaks for metal NPs after the reduction with NH₃BH₃, indicating the retained integrity of the MIL-101 framework and tiny metal NPs (Fig. S4b,c†). The impact of metal NP loading on the porosity of MIL-101 was established by using the N₂ adsorption/desorption at 77 K, which reveals that the highly porous structure of MIL-101 was remained. The appreciable decrease in the amount of N₂ sorption and its surface area indicates that the cavities of the host framework could be occupied by dispersed metal NPs or blocked by the NPs located on the surface (Fig. S5†).

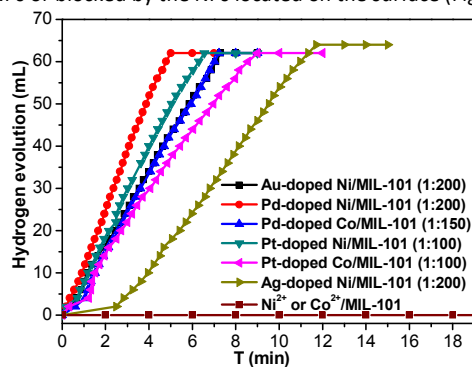


Fig. 2 Plots of time vs volume of hydrogen generated from the catalytic hydrolysis of NH₃BH₃ (0.875 mmol in 20 mL water) over Pd-doped Ni/MIL-101, Pd-doped Co/MIL-101, Au-doped Ni/MIL-101, Pt-doped Ni/MIL-101, Pt-doped Co/MIL-101 and Ag-doped Ni/MIL-101 catalysts at 25 °C. The data in the parentheses indicate the molar ratios of noble metal/non-noble metal in the catalysts.

To investigate the catalytic performance of the resultant noble metal-doped non-noble metal NPs, the hydrolytic dehydrogenation of NH₃BH₃ is employed. The very high hydrogen capacity of 19.6 wt. %, excellent solubility, nontoxicity, stability in water and easy storage of NH₃BH₃ make it one of the most attractive candidates for chemical hydrogen storage. Among various catalysts for hydrolytic dehydrogenation of NH₃BH₃,^{6g-i,10} platinum possesses the highest activity.^{10a} It is clearly a desired goal to prepare low-cost catalysts with high catalytic performance and rapid kinetics of hydrogen release under ambient conditions for the ultimate practical application of this reaction system in fuel cell. In this work, the reaction was initiated by adding NH₃BH₃ to the flask containing MIL-101, noble metal (Ag⁺, Pd²⁺, Pt²⁺, Au³⁺, etc.) and non-noble metal

(Ni²⁺, Co²⁺, etc.) precursors with desired concentrations under vigorous shaking and ambient conditions. Fig. 2 shows plots of the H₂ generation versus time during the catalytic hydrolysis of NH₃BH₃ over different NMSM non-noble metal-based catalysts with noble metal/non-noble metal molar ratio as low as 1/100-1/200. The results indicate that the catalytic activity of the in-situ formed non-noble metal NPs is significant and all hydrogen can be released from NH₃BH₃ in less than 10 min (H₂/NH₃BH₃ ≈ 3). Among these noble metals, Ag is the most inexpensive and a good initiator to trigger the reduction of non-noble metals. Meanwhile, Ni is one of the most intensively studied non-noble metals with high catalytic activity toward the hydrolytic dehydrogenation of NH₃BH₃.^{2c,6i,10b,i} Therefore, Ag-doped Ni/MIL-101 catalyst as a representative was further investigated in detail. Fig. 3 shows the catalytic activity for the hydrolysis of NH₃BH₃ over Ag-doped Ni/MIL-101 with Ag/Ni molar ratios varied from 10/1 to 1/200, while the molar ratio of total metal/NH₃BH₃ was fixed at a constant of 0.017. The result revealed that the catalytic activity had no significant change even the molar ratio of Ag/Ni was decreased sharply. Remarkably, a trace amount of Ag dopant is able to trigger the reduction of Ni²⁺ (Ag/Ni molar ratio = 1/200) and the resultant Ag-doped Ni/MIL-101 catalyst presents superior catalytic activity with completion of the hydrolysis in 12 min (containing ~2 min of initiation/induction period). The same parallel tests with various noble/non-noble metals molar ratios for other samples such as Pd-doped Ni/MIL-101, Pd-doped Co/MIL-101, Au-doped Ni/MIL-101, Pt-doped Ni/MIL-101 and Pt-doped Co/MIL-101 have been also conducted for better comparison (Fig. S6†).

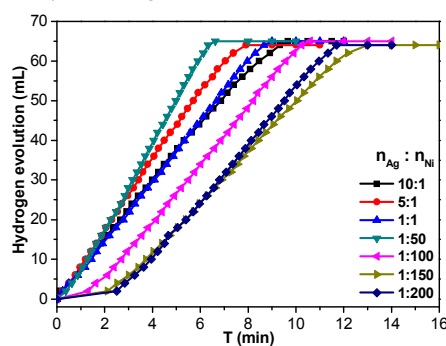


Fig. 3 Plots of time vs volume of hydrogen generated from the catalytic hydrolysis of NH₃BH₃ over Ag-doped Ni/MIL-101 with different Ag/Ni molar ratios at 25 °C. The molar ratio of (Ag+Ni)/NH₃BH₃ is fixed at a constant of 0.017 for all catalysts.

When the very few noble metal precursors were introduced, the induction time was observed to initiate the reaction (Fig. 2 and 3). Interestingly, the induction time is not only dependent on the content of Ag⁺, but also related to the reaction temperature as well as the concentration of NH₃BH₃.⁶ⁱ The higher reaction temperature or concentration of NH₃BH₃ leads to a shorter or even no induction period. The induction process is attributed to the slow generation of Ag-H reductive species with trace amounts of Ag precursor or at low temperature or low concentration of NH₃BH₃, and thus the Ni²⁺ would be reduced slowly. The detectable hydrogen started to release out until a certain amount of Ni NPs as very active species

was produced and following that, a nearly linear rate of hydrogen was rapidly generated and all Ni^{2+} cations would be fully reduced further to efficiently catalyze the hydrolytic reaction. Although Ag amount is very low, the limited Ag-H is able to induce the reduction of a small amount of Ni^{2+} , during which the formation of Ni-H as new reductant occurs.^{10e,11} Subsequently, more Ni^{2+} is reduced and more Ni-H can be successively formed until all Ni^{2+} ions are reduced.

Importantly, although the negligible Ag doping in the resultant Ag-doped Ni NPs, the catalytic activity of which is much higher than those of the monometallic counterparts Ag and Ni NPs (Fig. 4). Moreover, the Ni/MIL-101 obtained by NaBH_4 reduction also takes longer time (over 22 min) to complete the reaction. The Ag/MIL-101 catalyst obtained by the reduction of NH_3BH_3 also performed low activity and the hydrolysis of NH_3BH_3 cannot be completed even after 60 min. In addition, no H_2 was generated without the introduction of Ag^+ salt because the Ni^{2+} cannot be directly reduced by NH_3BH_3 under ambient conditions. For comparison, Ag-doped Ni NPs with Ag/Ni molar ratio of 1/200 reduced by NH_3BH_3 in the absence of MIL-101 support and MIL-101/PVP-protected Ni NPs reduced by NaBH_4 were also applied as catalysts in the hydrolysis of NH_3BH_3 (Fig. 4). The incomplete dehydrogenation of NH_3BH_3 over PVP-protected Ni NPs was observed and only ~40 mL hydrogen was released after 45 min, which presented much slower catalytic kinetics than that of in situ formed Ag-doped Ni/MIL-101. The catalytic dehydrogenation of NH_3BH_3 over Ag-doped Ni NPs without MIL-101 support was much slower and the complete hydrogen release took more than 60 min under identical reaction conditions, possibly due to the agglomeration of Ag-doped Ni NPs in the absence of the confinement effect of MIL-101. The above results indicate that the electronic structure modification-induced synergistic effects between Ag and Ni species in Ag-doped Ni NPs, which has been documented in previous reports.^{1d,12} The trace amount of Ag triggered in situ formation of Ni nanocatalyst is very efficient for the hydrolytic dehydrogenation of NH_3BH_3 and presents superior activity to other corresponding catalysts. Evidently, each of Ag, Ni and MIL-101 in the Ag-doped Ni/MIL-101 catalyst plays respective critical role for its excellent catalytic performance.

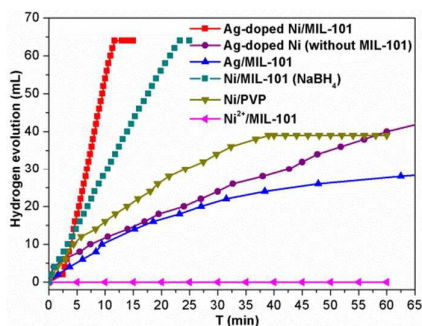


Fig. 4 Plots of time vs volume of hydrogen generated from the catalytic hydrolysis of NH_3BH_3 over Ag-doped Ni/MIL-101 (Ag/Ni molar ratio of 1/200), Ag-doped Ni NPs (Ag/Ni molar ratio of 1/200) in the absence of MIL-101, Ag/MIL-101, Ni/MIL-101 and PVP-protected Ni NPs. The total amount of (Ag+Ni) is fixed to be (Ag+Ni)/ $\text{NH}_3\text{BH}_3 = 0.017$ (molar ratio) for all catalysts.

The catalytic reaction rate constant (k) and the total turnover frequency (TOF) values of Ag-doped Ni/MIL-101 catalysts with different Ag contents for hydrolytic dehydrogenation of NH_3BH_3 are shown in Table S1[†]. It is noteworthy that the catalyst with the lowest Ag/Ni molar ratio of 1/200 in Ag-doped Ni/MIL-101 performs excellent catalytic activity with a high TOF value of $20.2 \text{ mol}_{\text{H}_2} \cdot \text{mol}_{\text{metal}}^{-1} \cdot \text{min}^{-1}$, which is higher than most of non-noble metal such as Ni catalysts toward the hydrolysis of NH_3BH_3 (Table S2[†]). Inductively coupled plasma atomic emission spectrometry (ICP-AES) has confirmed that the actual Ag/Ni molar ratio (1/170) is very close to the nominal value (1/200) (Table S3[†]). From the Arrhenius plots of the reaction over the Ag-doped Ni/MIL-101 (Ag/Ni molar ratio of 1/200) obtained at different temperatures ranging from 25 to 40 °C (Fig. S8[†]), the activation energy (E_a) is calculated to be 25 kJ/mol (Fig. S9[†]), being lower than most of the reported catalysts (Table S2[†]), indicating the superior catalytic performance of the catalyst.

Another remarkable benefit of the Ag-doped Ni/MIL-101 catalyst for the hydrolysis of NH_3BH_3 is its good stability and reusability. It can be seen that no significant decrease of activity during the five consecutive use without any treatment or activation for the catalyst (Fig. 5a). The Ag-doped Ni NPs have well remained sizes (about 2.5 nm) even after several runs, showing the good confinement effect of MIL-101 due to its porous structure (Fig. 5b[†]). The powder XRD profiles show that there is no apparent loss of crystallinity and no identifiable peaks for metal NPs after five cycles (Fig. S11[†]), suggesting the good recyclability and stability of the catalyst.

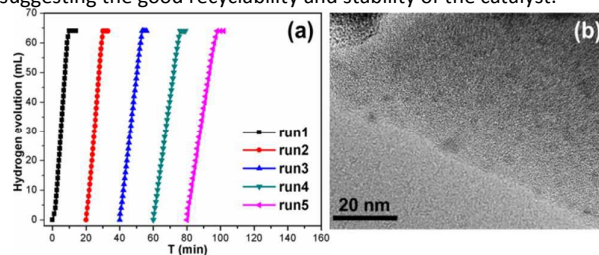


Fig. 5 (a) Recyclability test for the hydrogen generation from aqueous NH_3BH_3 solution (0.875 mmol in 20 mL H_2O , $T = 30^\circ\text{C}$) over Ag-doped Ni/MIL-101 catalyst. (b) TEM image for the Ag-doped Ni/MIL-101 catalyst with Ag/Ni molar ratio of 1/200 after several cycles of NH_3BH_3 hydrolysis reaction.

Conclusions

In summary, for the first time, we have successfully developed a novel, general and simple one-step in-situ NMSM synthetic approach to reduce non-noble metal precursors under very mild conditions by taking advantage of noble metal, even in a trace amount, as seed and initiator. The obtained catalysts are low-cost and perform superior catalytic activity in the hydrolytic dehydrogenation of ammonia borane to the corresponding monometallic counterparts. Nevertheless, these non-noble metal NPs cannot be obtained in the absence of noble metal as seed/initiator unless with harsh reduction conditions. As a representative, the Ag-doped Ni/MIL-101 catalyst (Ag/Ni molar ratio of 1/200) has superb catalytic

activity in the hydrolysis of NH_3BH_3 . Furthermore, the catalyst also exhibits a very low activation energy of 25 kJ/mol and good recyclability for hydrolytic dehydrogenation of NH_3BH_3 . This general and facile approach paves a way to the synthesis of non-noble metal NPs under ambient conditions with a moderate reductant, such as NH_3BH_3 . In addition, the outstanding catalytic performance of such non-noble metal nanocatalysts via a NMSM synthetic approach presents a promising step for the application of ammonia borane as a feasible chemical hydrogen storage material.

Acknowledgements

We gratefully thank the reviewers for their valuable suggestions. This work is supported by the NSFC (21371162 and 51301159), the 973 program (2014CB931803), NSF of Anhui Province (1408085MB23), Research Fund for the Doctoral Program of Higher Education of China (20133402120020), the Recruitment Program of Global Youth Experts and the Fundamental Research Funds for the Central Universities (WK2060190026).

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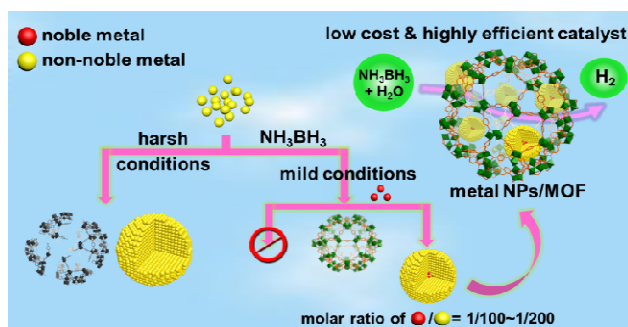
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Graphical Abstract



A novel noble metal-seed-mediated approach has been developed to reduce non-noble metal precursors under mild conditions to afford non-noble metal nanoparticles with superior catalytic performance.