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Size-Controlled Synthesis of Tetrametallic Ag@CoNiFe Core–Shell Nanoparticles Supported on Graphene: A Highly Efficient Catalyst for the Hydrolytic Dehydrogenation of Amine Boranes

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Tetrametallic core-shell Ag@CoNiFe nanoparticles (NPs) supported on graphene have been synthesized by a facile onestep in situ procedure for the first time. We tuned the reducing ability of the reductants to control the structure and particle size of the as-synthesized NPs. The use of weaker reducing agents, such as ammonia borane (AB) and methylamine borane (MeAB), result in the core-shell structure, whereas the stronger reducing agent NaBH₄ results in alloy NPs. The as-synthesized core-shell NPs reduced by MeAB possess a smaller particle size and exhibit a superior catalytic activity compared to the core-shell NPs reduced by AB and alloy NPs reduced by NaBH₄ for the hydrolytic dehydrogenation of AB. Moreover, the turnover frequency of the as-synthesized tetrametallic core-shell NPs is 118.5 mol_{H2}min⁻¹mol_{Ag}⁻¹, which is higher than that of Ag-based trimetallic, bimetallic core-shell, and alloy counterparts and even higher than that of most reported noble-metal-based NPs. Kinetic studies indicate that the catalytic hydrolysis of AB and MeAB by the Ag@CoNiFe/graphene NPs is a first-order reaction. Furthermore, the as-prepared NPs exert good catalytic activities and recycle stabilities towards the hydrolysis of AB. Additionally, the as-prepared NPs display magnetic recyclability, which makes the practical recycling of the NPs more convenient.

Introduction

Heterometallic nanoparticles (NPs) have attracted increasing attention because of their fascinating applications in a variety of fields, such as chemical sensing,^[1] drug delivery,^[2] plasmonics,^[3] optoelectronics,^[4] magnetic memory,^[5] and catalysis.^[6] Among them, core-shell architectures have attracted more attention in the application of nanocatalysts because of their new and efficient catalytic activity compared with their monometallic counterparts and alloys.^[7] Tremendous efforts have been devoted to the size- and shape-controlled synthesis of bimetallic coreshell NPs, however, to date, the controlled synthesis of multiple metal NPs ($n \ge 3$) has been relatively unexplored. For instance, Wang and Yamanchi,^[8] Xu et al.,^[9] Sun et al.,^[10] and Yan et al.^[11] have developed different strategies to obtain trimetallic core-shell NPs. To the best of our knowledge, reports on tetrametallic core-shell NPs are rare.^[12] Therefore, to investigate the possible applications of multimetallic NPs in comparison to bi-

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metallic and monometallic NPs, the development of an efficient method to produce multimetallic NPs with a desirable structure is of great importance.

The safe and efficient storage of hydrogen is still a major hurdle for a prospective hydrogen economy.^[13] Over the past few decades, many methods have been proposed for the storage of hydrogen, among them, amine borane compounds have attracted much attention because of their high gravimetric hydrogen densities and favorable kinetics of hydrogen release.^[14] As the parent amine borane, ammonia borane (AB) has been considered to be the most promising candidate for on-board hydrogen storage applications because of its 19.6 wt% hydrogen content, high stability, and environmental benignity.[15] The hydrogen stored in AB can be released through different ways,^[16] but the hydrolysis of AB by transition-metal-nanocatalysts under ambient conditions seems to be the most promising route for on-board applications.^[17] So far, not only monometallic NPs^[18] but also bimetallic^[19] and trimetallic NPs^[9,11] have been tested for the catalytic hydrolysis of AB. It is well known that the catalytic process takes place on the metal surfaces, on which the smaller metal NPs have higher surface areas and exhibit higher catalytic activity.^[20] As classical Lewis acid-base adducts, amine boranes have weak reducibility, which offers much better control of the reduction rate and selective reduction of metal ions over traditional strong reducing agents such as borohydrides. The reducing strength decreases if the alkyl substitution on the nitrogen atom is increased: H₃NBH₃ > MeNH₂BH₃ > Me₂NHBH₃ >

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Me₃NBH₃.^[21] Recently, we have succeeded in the production of graphene-supported bimetallic Ag@Co, Ag@Ni, and Ag@Fe core–shell NPs^[22] and trimetallic Ag@CoNi, Ag@CoFe, and Ag@NiFe core–shell NPs by using amine boranes as the reductant.^[23,24] The trimetallic core–shell NPs exhibit superior catalytic activity towards the hydrolysis of AB than the bimetallic core–shell NPs and monometallic counterparts.

Herein, we report a facile method for the size-controlled synthesis of graphene-supported tetrametallic Ag@FeCoNi coreshell NPs for the first time. Graphene was chosen as the support because of its superior electrical conductivity, high mechanical strength, chemical stability, and high surface-tovolume ratio.^[25,26] It has been demonstrated that the enhanced catalytic activity of graphene-supported metal NPs is caused mainly by charge transfer across the graphene-metal interface caused by the graphene-metal spacing and Fermi level difference.^[27] Interestingly, the tetrametallic core-shell NPs exhibit higher catalytic activity than the trimetallic and bimetallic Agbased core-shell NPs towards the hydrolysis of AB. The catalytic hydrolysis of methylamine boran (MeAB) was also studied.

Results and Discussion

Synthesis and characterization

In a typical synthesis of graphene-supported Ag@CoNiFe coreshell NPs, an aqueous solution of AB, MeAB, or NaBH₄ was introduced into a round-bottomed flask that contained an aqueous solution of AgNO₃, CoCl₂, NiCl₂, FeCl₂, and graphene oxide (GO). The Ag⁺ with a high reduction potential $(E^{0}(Ag^{+}/Ag)) =$ +0.80 eV vs. the standard hydrogen electrode (SHE)) was first reduced by AB or MeAB to form the Ag NPs to serve as the in situ seeds to induce the successive growth of the rest of the metal NPs as the shell, which may be generated by Ag-H species or H₂ released from AB/MeAB catalyzed by the Aq seeds^[9, 28, 29] to form the Ag@CoNiFe core-shell NPs. Without Ag cores, Co²⁺, Ni²⁺, and Fe²⁺ cannot be reduced by AB or MeAB directly because of their low reduction potentials $(E^{0}(Co^{2+}/Co) = -0.28 \text{ eV vs. SHE}; E^{0}(Ni^{2+}/Ni) = -0.25 \text{ eV vs. SHE};$ $E^{0}(Fe^{2+}/Fe) = -0.44 \text{ eV vs. SHE}$) and the weak reduction capability of AB/MeAB. If a stronger reducing agent such as NaBH₄ was used, the metal precursors were reduced simultaneously to form AgCoNiFe alloy NPs.

The microstructures of $Ag_{0.1}@[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.1}]_{0.9}/graphene NPs reduced by AB and MeAB were characterized by TEM. A distinct contrast between the core and shell can be observed clearly in Figure 1a and c; the as-synthesized NPs were well dispersed on graphene, which helps to prevent their agglomeration. The high-resolution transmission electron microscopy (HRTEM) image is shown in Figure 1b; the$ *d*spacing of the crystallized core is ~0.235 nm, which is consistent with the spacing of the Ag (111) plane. This result indicates that Ag is reduced initially by MeAB or AB, and subsequently acts as the seed to reduce Co, Ni, and Fe to form the shell. The energy-dispersive X-ray (EDS) spectrum shown in Figure 1h confirms the presence of Ag, Co, Ni, and Fe, and the molar ratio of the four metals is 10:44:39:7, which is close to the target value. If



Figure 1. a) and b) TEM images of Ag@CoNiFe/graphene NPs; c) and d) TEM images of NPs reduced by AB and NaBH₄; e) and f) TEM image of Ag@Co-NiFe NPs without support; g) TEM image of Ag@CoNiFe/graphene NPs after five cycles; h) EDS spectrum of Ag@CoNiFe/graphene NPs; a)–c) inset: particle size of Ag@CoNiFe/graphene NPs reduced by MeAB, AB, and NaBH₄, respectively.

a stronger reducing agent, NaBH₄, was used, AgCoNiFe/graphene alloy NPs were formed as shown in Figure 1d. The mean diameter of the as-synthesized NPs in Ag@CoNiFe/graphene reduced by MeAB was around 12 nm, in Ag@CoNiFe/graphene reduced by AB it was around 15 nm, and in AgCo-NiFe/graphene reduced by NaBH₄ it was around 20 nm. This result indicates that the use of weaker reducing agents could result in much slower reduction kinetics and more size control over the nucleation of the NPs to turn the nanostructures from

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alloy to core-shell, which could affect their catalytic activity (vide infra). A TEM image of as-synthesized core-shell NPs reduced by MeAB without graphene is shown in Figure 1 e and f. It is clear that without the support of graphene, the NPs exhibit severe agglomeration.

The formation process of the NPs has been further examined and monitored by UV/Vis spectroscopy by withdrawing samples at different stages of the reaction, and a mechanism is proposed as illustrated in Figure 2. The UV/Vis spectrum of the



Figure 2. Schematic view of the formation of the Ag@CoNiFe NPs monitored by UV/Vis spectroscopy a) before adding the reductant MeAB, b) during the reaction, and c) after the reaction finished.

solution before the reductant was added is shown in Figure 2(a), and there is no peak in the spectrum. A distinct peak around $\lambda = 400 \text{ nm}$ is seen in the spectrum shown in Figure 2b,^[30] which arises from the formation of Ag seeds on the addition of MeAB, and this characteristic peak almost disappears completely by the end of reaction (c) for Ag@CoNiFe NPs covered fully with Co, Ni, and Fe, which is in accord with the results obtained from the TEM images. The powder XRD patterns of the as-prepared graphene-supported NPs reduced by MeAB and AB and Ag@CoNiFe without support by graphene reduced by MeAB are shown in Figure 3b, c, and e, respectively. There are two peaks at $2\theta = 38.1$ and 44.3° , which is in good agreement with the values for Ag (111) and Ag (200). However, no diffraction peaks of Co, Ni, and Fe are present, which may be because of the amorphous phase of Co, Ni, and Fe as indicated in the TEM images. The XRD pattern of the asprepared graphene-supported NPs reduced by NaBH₄ is shown in Figure 3 d, and there are no obvious peaks. The XRD pattern of NPs reduced by NaBH₄ after they were annealed at 500 °C for 4 h under a N₂ atmosphere is shown in Figure 3 f, and the intensity of the peaks is increased distinctly. The peak at $2\theta =$ 38.1° is attributed to Ag (111), the peak that results from Ag (200) is shifted slightly to higher angles, and the peak at $2\theta =$ 51.7° is a little higher that of than Co (200). These phenomena indicate that the catalysts reduced by NaBH₄ are alloys, which is in accord with the strong reducibility of NaBH₄. Furthermore, the most intense peak at around $2\theta = 9.6^{\circ}$ that correspond to GO disappears, and new peaks at around $2\theta = 24.4^{\circ}$ are observed in the as-prepared graphene-supported NPs, which indicates that the GO is reduced successfully to graphene. In the Raman spectra (Figure 4), the GO and graphene-supported NPs



Figure 3. XRD patterns of a) GO, b)–d) graphene-supported AgCoNiFe NPs reduced by MeAB, AB, and NaBH₄; e) NPs without support reduced by MeAB, f) graphene-supported NPs reduced by NaBH₄ after they had been annealed at 500 °C for 4 h under a N₂ atmosphere.



Figure 4. Raman spectra of GO and Ag@CoNiFe/graphene NPs.

exhibit two peaks centered at $\tilde{\nu} = 1358$ and 1596 cm^{-1} , which correspond to the D and G bands of the carbon products, respectively. The intensity ratio of the D to G bands (I_D/I_G) is generally accepted to reflect the degree of graphitization of carbonaceous materials and defect density. After Ag@CoNiFe was loaded, the I_D/I_G of GO is increased from 1.03 to 2.48. The relative changes in I_D/I_G confirm the reduction of GO during the in situ fabrication. The FTIR spectra of GO and graphene-supported Ag@CoNiFe core-shell NPs are shown in Figure 5. The disappearance of the C=O peak at $\tilde{\nu} = 1724 \text{ cm}^{-1}$ and the C–O peak at $\tilde{\nu} = 1052 \text{ cm}^{-1}$ of GO after the formation of the graphene-supported core-shell NPs can be seen clearly, which further indicates that the GO is reduced to graphene during the process.

Catalytic activities for the hydrolysis of AB and MeAB by Ag@CoNiFe/graphene NPs

The as-synthesized Ag@CoNiFe/graphene NPs reduced by MeAB with different compositions were tested for the hydrolysis of AB. Without the addition of Ag, the precursor Co, Ni, and

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Figure 5. FTIR spectra of GO and Ag@CoNiFe/graphene NPs.

Fe cannot be reduced by MeAB. In our study, the molar ratio of Co and Ni was kept at 1. The $Ag_{0.1}@[(Co_{0.5}Ni_{0.5})_{1-x}Fe_x]_{0.9}$ NPs demonstrate different catalytic activities if the ratio of (Co+Ni) to Fe is changed (Figure 6a). The best ratio of (Co+Ni) and Fe in $Ag_{0,1}@[(Co_{0,5}Ni_{0,5})_{1-x}Fe_x)_{0,9}$ is 9:1, and AB cannot be catalytically decomposed completely. However, with a ratio of (Co+Ni) to Fe of 9:1, the effects of the Ag ratio were studied by changing the y value from 0.1 to 0.9. The best Ag ratio in $Ag_{v}@(Co_{0.5}Ni_{0.5}Fe_{0.1})_{1-v}$ is 0.1. Unexpectedly, as the molar ratio of Ag (y value) increases from 0.1 to 0.9, the catalytic activities of the as-synthesized NPs decrease gradually. The activity in terms of turnover frequency (TOF) is 118.5 $mol_{H_2}min^{-1}mol_{Ag}^{-1}$ for the as-synthesized $Ag_{0.1}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.1}]_{0.9}/graphene NPs$, which is higher than that of trimetallic and bimetallic coreshell Ag-based NPs and most reported noble-metal-based NPs if the TOF is normalized in terms of moles of noble metal (Table 1).

For comparison, Ag@CoNiFe/graphene NPs generated by AB as the reducing agent, and AgCoNiFe/graphene alloy NPs re-

duced by NaBH₄ were also prepared and applied to the catalytic hydrolysis of AB. It has been reported that the catalytic activity increased if the size of the metal NPs was decreased because of the higher surface areas of the smaller metal NPs.^[20] $Ag_{0,1}[(Co_{0,5}Ni_{0,5})_{0,9}Fe_{0,1}]_{0,9}/gra$ phene NPs reduced by MeAB with the smallest size exhibit the highest catalytic activity toward hydrolysis of AB, followed by the core-shell NPs reduced by AB, and the alloy NPs reduced by NaBH₄ exhibit the lowest activity (Figure 7). These results indicate that it is possible to achieve much more control over the nucleation and growth processes



Figure 6. a) Hydrolysis of AB catalyzed by $Ag_{0.1}@[(Co_{0.5}Ni_{0.5})_{1-x}Fe_x]_{0.9}/graphene (x = 0.1-0.9) NPs, A: Ag_{0.1}[(Co_{0.5}Ni_{0.5})_{0.1}Fe_{0.9}]_{0.9}, B: Ag_{0.1}[(Co_{0.5}Ni_{0.5})_{0.5}Fe_{0.7}]_{0.9}, C: Ag_{0.1}[(Co_{0.5}Ni_{0.5})_{0.5}Fe_{0.5}]_{0.9}, D: Ag_{0.1}[(Co_{0.5}Ni_{0.5})_{0.7}Fe_{0.3}]_{0.9}, E: Ag_{0.1}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.1}]_{0.9}, b) Hydrolysis of AB catalyzed by Ag_{9}@(Co_{0.5}Ni_{0.5}Fe_{0.1})_{1-y}/graphene (y = 0.1-0.9) NPs, A: Ag_{0.1}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.1}]_{0.9}, B: Ag_{0.3}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.1}]_{0.7}, C: Ag_{0.5}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.1}]_{0.7}, D: Ag_{0.5}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.5}]_{0.7}, D: Ag_{0.5}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.5}]_{0.7}, D: Ag_{0.5}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.5}]_{0.7}, D: Ag_{0.5}[(Co_{0.5}Ni_{0.5})_{0.7}Fe_{0.5}]_{0.7}, D: Ag_{0.5}[(Co_{0.5}Ni_$

 $Ag_{0.7}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.1}]_{0.3}, \ E: \ Ag_{0.9}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.1}]_{0.1}, \ catalyst/AB \,{=}\, 0.05.$

of the metal NPs over graphene by changing the reducing agents, which further affects their catalytic activities. Additionally, to study the effects of the supported materials on the cat-

 Table 1. Catalytic activity of different noble-metal-based catalysts used for the hydrolytic dehydrogenation of

 AB. (PSSA-co-MA = poly(4-styrenesulfonic acid-co-maleic acid), RGO = reduced graphene oxide)

Catalyst	TOF $[mol_{H_2}mol_M^{-1}min^{-1}]$ M = Ru, Pd, Ag	TOF [mol _{H2} mol _{metal} ⁻¹ min ⁻¹]	E _a [kJ mol ⁻¹]	Ref.
Ni _{0.74} Ru _{0.26} alloy NPs	194.8	50.65	44	[19e]
PSSA-co-MA-stabilized Ru nanoclusters	187.6	187.6	54	[31]
Ag@CoNiFe/graphene	118.5	11.85	36.63	This study
Ni@Ru	114	30.56	-	[32]
Ag@CoNi/graphene	106.4	10.64	36.15	[23]
Ag@Co/graphene	102.4	10.24	20.03	[22]
Ag@Ni/graphene	77.0	7.70	49.56	[22]
Ru@Al ₂ O ₃	39.6	39.6	48 ± 2	[33]
RuCo (1:1)/γ-Al2O3	32.9	16.45	47	[34]
Ru/γ-Al2O3	23.05	23.05	67	[35]
PSSA-co-MA-stabilized Pd nanoclusters	19.9	19.9	44	[31]
RuCu (1:1)/γ-Al ₂ O ₃	16.4	8.2	52	[34]
Ag@C@Co	8.93	8.93	-	[35]
RGO/Pd	6.25	6.25	51	[37]
Ag/C/Ni	5.32	5.32	38.91	[30]

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Figure 7. Time plots of catalytic dehydrogenation of AB by $Ag_{0.1}@[(Co_{0.5}N_{i0.5})_{0.9}Fe_{0.1}]_{0.9}/graphene NPs reduced by MeAB and AB, respectively, and <math>Ag_{0.1}@[(Co_{0.5}N_{i0.5})_{0.9}Fe_{0.1}]_{0.9}/graphene reduced by NaBH_4$, catalyst/ AB = 0.05.

alytic performances of the as-synthesized core-shell NPs, Ag@-CoNiFe/C, Ag@CoNiFe/SiO₂, and Ag@CoNiFe/ γ -Al₂O₃ NPs were prepared and their catalytic activities towards the hydrolysis of AB ware studied. Their catalytic activities are all inferior to that of Ag@CoNiFe/graphene NPs (Figure 8), which highlights the dominant factor of graphene to facilitate the hydrolysis of AB in our system.

As the Ag_{0.1}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.1}]_{0.9}/graphene catalyst reduced by MeAB exhibits the highest activity, we used it for the further kinetic study. The plots of hydrogen generation from the hydrolysis of AB and MeAB solution in the presence of different Ag@-CoNiFe/graphene NP concentrations at (25 ± 0.2) °C are shown in Figures 9 and 10, respectively. The initial rate of hydrogen generation was determined from the nearly linear initial portion of each plot. The line slope of the plot of hydrogen evolution rate versus catalyst concentration on a log–log scale is 1.06 and 1.09 for AB and MeAB, respectively, which indicates that the hydrolysis of AB and MeAB catalyzed by Ag@CoNiFe/ graphene NPs is first order with respect to the catalyst concentration.



Figure 8. Time plots of catalytic dehydrogenation of AB by Ag@CoNiFe NPs reduced by MeAB with different supported materials, catalyst/AB = 0.05.



Figure 9. a) Plots of hydrogen evolution vs. time for the Ag@CoNiFe/graphene-catalyzed hydrolysis of AB at different catalyst concentrations; b) plot of hydrogen generation rate vs. the concentration of Ag@CoNiFe/graphene (both in logarithmic scale).

To obtain the activation energy (E_a) of the hydrolysis of AB and MeAB catalyzed by Ag@CoNiFe/graphene NPs, hydrolytic reactions were performed in a temperature range of 25–40 °C. The values of the rate constant k at different temperatures were calculated from the slope of the linear part of each plot shown in Figures 11 a and 12 a. The Arrhenius plot of ln k vs. 1/T for the catalyst is plotted in Figures 11 b and 12b for the hydrolysis of AB and MeAB, respectively, from which the apparent E_a values of hydrolysis was determined to be approximately 36.63 and 35.33 kJ mol⁻¹, respectively, which are lower than most of the reported E_a values (Table 1) and indicates the superior catalytic performance of the as-synthesized Ag@CoNiFe/graphene NPs.

Recyclability

The reusability of a catalyst is crucial in practical applications. The recyclability of $Ag_{0.1}@[Co_{0.5}Ni_{0.5}]_{0.9}Fe_{0.1})_{0.9}$ /graphene NPs up to the fifth run for the hydrolysis of AB and MeAB is shown in Figure 13.

The as-prepared catalysts retain 69.3 and 80.3% of their initial catalytic activities in the hydrolysis of AB and MeAB, respectively, in the fifth run (Figure 13). The TEM image of Ag@-CoNiFe/graphene NPs after the fifth run of the durability test is

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Figure 10. a) Plots of hydrogen evolution vs. time for the Ag@CoNiFe/graphene-catalyzed hydrolysis of MeAB at different catalyst concentrations; b) plot of hydrogen generation rate vs. the concentration of Ag@CoNiFe/ graphene (both in logarithmic scale).

shown in Figure 1 g. As can be seen clearly from the TEM image, there is no noticeable change in the morphology of the as-synthesized NPs on graphene. These results indicate that graphene can stabilize the as-synthesized NPs at least for five cycles. The X-ray photoelectron spectra (XPS) of the as-synthesized Ag@CoNiFe/graphene catalysts before and after five cycles are shown in Figure 14. The XPS Ag 3d peak of the catalyst is shown in Figure 14a and b. Two peaks can be seen at a binding energy (BE) of 372.4 and 366.6 eV. This is in good agreement with the values for zero-valent Ag, which corresponds to $Ag 3d_{5/2}$ and $Ag 3d_{3/2}$. The peaks of Co 2p are shown in Figure 14c and d. There are two peaks at BE = 779.5 and 776.7 eV, which correspond to oxidized Co and zero-valent Co, respectively. The peaks of Ni2p are shown in Figure 14e and f; the two peaks at BE = 854.5 and 851.0 eV represent oxidized Ni and zero-valent Ni. The peaks of Fe 2p are shown in Figure 14 g and h, in which the peak at BE = 711.4 eV represents oxidized Fe. These results indicate that the core Ag metal is stable, whereas the outside shell of Co, Ni, and Fe are oxidized to varying degrees maybe during the sample preparation^[38] and during the catalytic process.^[23] Therefore, the decrease in the catalytic activity may be because of the oxidation of the shell metals. Meanwhile, the increased viscosity of the solution and the deactivation effect of the increasing metaborate concentra-



Figure 11. a) Plots of hydrogen evolution vs. time for the Ag@CoNiFe/graphene-catalyzed hydrolysis of AB at four different temperatures in the range of 25-40 °C, catalyst/AB = 0.05; b) Arrhenius plot obtained from the data shown in a). Figure 11 a.

tion during the hydrolysis of AB or MeAB should also be taken into account. Moreover, from Figure 13, we can see that the in situ synthesized Ag@CoNiFe/graphene NPs are magnetic and thus can be separated from the reaction solution by an external magnet, which makes the practical recycling of the NPs more convenient.

Conclusions

We have developed a facile in situ one-step method for the synthesis of graphene-supported tetrametallic core-shell magnetic Ag@CoNiFe nanoparticles (NPs). Their catalytic activities towards the hydrolytic dehydrogenation of AB and MeAB under ambient conditions were also studied. Compared with those reduced by AB and NaBH₄, the as-synthesized Ag@Co-NiFe/graphene catalysts reduced by MeAB exert the highest catalytic activity with a turnover frequency (TOF) value of 118.5 mol_{H2}min⁻¹ mol_{Ag}⁻¹. Furthermore, the as-synthesized Ag@CoNiFe/graphene NPs showed a good durability, stability, and magnetic recyclability for the hydrolytic dehydrogenation of AB and MeAB, which makes the practical recycling of the catalyst convenient. Moreover, this simple synthetic method can be extended to other mutilmetallic core-shell systems for more applications.

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Figure 12. a) Plots of hydrogen evolution vs. time for the Ag@CoNiFe/graphene-catalyzed hydrolysis of MeAB at four different temperatures in the range of 25-40 °C, catalyst/MeAB = 0.05; b) Arrhenius plot obtained from the data shown in a).

Experimental Section

Materials

Ammonia borane (AB, Aldrich, 90%), sodium borohydride (NaBH₄, Sinopharm Chemical Reagent Co., Ltd., >96%), methylamine hydrochloride (CH₃NH₂·HCl, Sinopharm Chemical Reagent Co., Ltd., \geq 96%), tetrahydrofuran (C₄H₈O, Sinopharm Chemical Reagent Co., Ltd., \geq 99%), dimethyl ether anhydrous (C₄H₁₀O, Sinopharm Chemical Reagent Co., Ltd., >99.7%), silver nitrate (AqNO₃, AR), cobalt chloride hexahydrate (CoCl₂·6H₂O, Sinopharm Chemical Reagent Co., Ltd., \geq 99%), nickel(II) chloride hexahydrate (NiCl₂·6H₂O), ferrous chloride tetrahydrate (FeCl₂·4H₂O, Sinopharm Chemical Reagent Co., Ltd., \geq 99%), graphite power (Sinopharm Chemical Reagent Co., Ltd., >99.85%), potassium permanganate (KMnO₄, Shanghai Chemic Co., Ltd., > 99.5%), hydrogen peroxide (H₂O₂, Sinopharm Chemical Reagent Co., Ltd., \geq 30%), phosphoric acid (H₃PO₄, Sinopharm Chemical Reagent Co., Ltd., AR), sulfuric acid (H₂SO₄, Sinopharm Chemical Reagent Co., Ltd., 95~98%), Ketjen black EC-300 J (Triquo Chemical Co., Ltd.), neutral silica power (SiO₂, Branch of Qingdao Haiyang Chemical Co., Ltd.), and aluminum oxide neutral (y-Al₂O₃, Sinopharm Chemical Reagent Co., Ltd., FCP) were used as obtained. We used ordinary distilled water as the reaction solvent.

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Figure 13. a) and b) Hydrogen generation from AB and MeAB catalyzed by Ag@CoNiFe/graphene NPs from the first to fifth cycles, catalyst/AB = 0.05; b) inset: photographs of the Ag@CoNiFe/graphene NPs before (left) and after (right) magnetic separation.

Graphene oxide (GO) preparation

GO was synthesized according to the literature.^[39] In an improved synthesis of GO, a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) was added to a mixture of graphite flakes (3.0 g) and KMnO₄ (18.0 g). The mixture was then heated to 50 °C and stirred for 12 h. The reaction was cooled to RT and poured onto ice (~400 mL) with 30% H_2O_2 (3 mL). The addition of portions of H_2O_2 (2 mL) was continued until the observation of a permanent yellow color, which indicated the complete oxidation of graphite. The resultant solution was centrifuged to obtain the product. The product was washed with deionized water, 30% diluted hydrochloric acid, and absolute ethyl alcohol many times and dried under vacuum at 25 °C.

Preparation of methylamine borane (MeAB)

MeAB was synthesized according to the method reported in the literature.^[40] Sodium borohydride (3.783 g, 0.1 mol) and methylamine hydrochloride (6.752 g, 0.1 mol) were added to a 500 mL twonecked round-bottomed flask equipped with a condenser. THF (200 mL) was transferred into the flask with vigorously stirring. The reaction was performed at RT under a nitrogen atmosphere. After 12 h, the resultant solution was filtered by suction filtration, and the filtrate was concentrated under vacuum at RT. The product was purified by ether.



Figure 14. XPS spectra of Ag@CoNiFe/graphene NPs before (left) and after (right) five cycles.

In Situ synthesis of Ag@CoNiFe/graphene catalysts

In a typical experiment, GO (10 mg) was put into a 25 mL twonecked round-bottomed flask, and cobalt chloride (0.9 mL), nickel chloride (0.9 mL), and ferrous chloride (0.2 mL) aqueous solutions (0.0225 mol L⁻¹), and silver nitrate aqueous solution (0.1 mL; 0.05 mol L⁻¹) were added. One neck was connected to a gas burette, and the other was connected to a pressure equalizer, which used to introduce MeAB. An aqueous solution (1.9 mL) that contained MeAB (90.0 mg, 2 mmol) was kept in the pressure equalizer (90.0 mg). The reaction was started when the MeAB solution was added to the flask with vigorous stirring, and the evolution of the gas was monitored by the gas burette. When the hydrogen generation reaction was completed, aqueous solution (2 mL) that contained AB (1 mmol) was added to the flask, and the evolution of the gas was monitored. A water bath was used to control the temperature of the reaction solution. For comparison, the Ag@CoNiFe catalyst without GO reduced by MeAB, Ag@CoNiFe/graphene reduced by AB, and AgCoNiFe/graphene reduced by NaBH₄ were synthesized by a similar method.

Other Ag@CoNiFe NPs with different Ag, (Co+Ni), and Fe compositions were synthesized by a similar method to that described

above. If the molar ratio of $(Co^{2+}+Ni^{2+})/Fe^{2+}$ was kept constant at 1, the molar ratio of Ag⁺/(Ag⁺+(Co²⁺+Ni²⁺)+Fe²⁺) was changed to several values (0.1, 0.3, 0.5, 0.7, 0.9). If the molar ratio of Ag⁺/(Ag⁺+(Co²⁺+Ni²⁺)+Fe²⁺) was kept as 0.1, the value of $(Co^{2+}+Ni^{2+})/Fe^{2+}$ was changed from 0.1 to 0.9 (0.1, 0.3, 0.5, 0.7, 0.9).

Catalytic hydrolysis of AB and MeAB

Sets of experiments with different concentrations of Ag_{0.1}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.1}]_{0.9}/graphene (0.02, 0.03, 0.04, 0.05 mmol) were performed at RT, and the AB concentration was kept the same (1 mmol) to determine the rate law of the catalytic hydrolysis of AB. For MeAB, sets of experiments with different concentrations of Ag_{0.1}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.1}]_{0.9}/graphene (0.03, 0.035, 0.04, 0.05 mmol) were performed at RT. The temperature was varied at (25±0.2), (30±0.2), (35±0.2), and (40±0.2)°C, and the concentration of Ag_{0.1}[(Co_{0.5}Ni_{0.5})_{0.9}Fe_{0.1}]_{0.9}/graphene (0.05 mmol) and AB (or MeAB) (1 mmol) were kept constant to obtain the activation energy.

Stability test for the hydrolysis of AB and MeAB

A solution of MeAB (1.9 mL, 90.0 mg, 2 mmol) was added to cobalt chloride (0.9 mL), nickel chloride (0.9 mL), and ferrous chloride solution (0.2 mL; 0.0225 molL⁻¹), silver nitrate solution (0.1 mL, 0.05 molL⁻¹), and GO (10 mg). The evolution of gas was monitored as described above. After the hydrogen generation reaction was completed, new aqueous AB or MeAB solution (1 mmol, 2 mL) was added into the reaction flask. The evolution of gas was monitored again by using the gas burette. Such tests of the catalyst for the hydrolysis of AB and MeAB were performed five times in air.

Different supports

Sets of experiments with different supports (such as SiO₂, γ -Al₂O₃, and carbon black) were performed at RT. All the experiments were performed as described above.

Characterization

TEM images were recorded by using a FEI Tecnai G20 TEM instrument operating at 200 kV. Powder XRD patterns were measured by using a Bruker D8-Advance X-ray diffractometer using a CuK_a radiation source ($\lambda = 0.154178$ nm) with a velocity of 6° min⁻¹. FTIR spectra were collected at RT by using a Thermo FTIR-iS10 instrument using KBr discs in the 400–4000 cm⁻¹ region. Raman spectra were measured by using a confocal Raman microscope (Renishaw, RM-1000) at 514.5 nm excitation. XPS measurements were performed by using a Kratos XSAM 800 spectrophotometer. UV/Vis spectra were recorded by using a Persee TU-1810 spectrophotometer.

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FULL PAPERS

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Size-Controlled Synthesis of Tetrametallic Ag@CoNiFe Core-Shell Nanoparticles Supported on Graphene: A Highly Efficient Catalyst for the Hydrolytic Dehydrogenation of Amine Boranes



Core-shell casts a spell: Well-dispersed tetrametallic core-shell Ag@CoNiFe/graphene nanoparticles exert a satisfactory catalytic activity and recyclability to-wards the hydrolysis of ammonia borane and methylamine borane.