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Introduction

It is of importance to develop robust and simple strategies for converting nitroaromatic compounds such as 2,4,6-trinitrotoluene (2,4,6-tNT) and 2,4,6-trinitrophenol (2,4,6-tNP) to NH₂containing compounds, due to not only the toxicity of nitroaromatic compounds towards humans, fish, algae and invertebrates,^{1,2} but also the explosive nature of some nitroaromatic compounds resulting from the nitro groups as explosophores.^{3,4}

Metal nanoparticles have attracted great attention in the field of catalysis because of their outstanding catalytic performance.^{5,6} In 2001, Pal's group firstly reported that the reduction reaction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by sodium borohydride (NaBH₄) could be employed as a model reaction to evaluate the catalytic performance of metal nanoparticles.^{7,8} Since this pioneering work was reported, a series of investigations on the catalytic conversion of 4-NP to 4-AP have been extended by employing various metal nanostructures including Au, Ag, and Cu nanoparticles as nanocatalysts.⁹⁻³⁰ For example, Sahi *et al.*⁹ reported a simple and green method for the intracellular formation and growth of spherical Au nanoparticles in plant tissues. The resulting Au nanoparticles bearing biomatrix of *Sesbania* demonstrated the *in situ* catalytic performance for the reduction of 4-NP to 4-AP by NaBH₄. Rao

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Developing robust and facile catalytic systems for converting nitroaromatic compounds to NH_2 -containing compounds are of importance to decrease or even eliminate their toxicity or risk in the environment. In view of *in situ* formed metal nanoparticles, the metal ion (Cu^{2+} , Ag^+ , $AuCl_4^-$, Co^{2+} and Ni^{2+})/NaBH₄ systems were employed to catalyze the reduction reaction of nitroaromatic compounds. By employing the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) as a model reaction, the effects of concentration of NaBH₄, 4-NP and metal ions on the rate constants of the catalytic reduction reactions were systematically investigated. Apparent activation energies of these metal ion/NaBH₄ catalytic systems were further measured and compared. *In situ* formed metal NPs could be characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Furthermore, these metal ion/NaBH₄ systems were successfully employed to catalyze the reduction reaction of a series of other nitroaromatic compounds. These metal ion/NaBH₄ catalytic systems investigated in this protocol are simple and do not require the preparation of metal nanoparticles in advance, compared with previous related reports.

et al.¹⁰ also prepared Au and Ag nanoparticles from the stem extract of Breyniarhamnoides. It was further found that the sizes of these metal nanoparticles could be tuned by the extract concentration, and the as-prepared metal nanoparticles could effectively facilitate the catalytic reduction of 4-NP. Ballauff et al.11 reported a nanoreactor system of thermosensitive coreshell networks integrated by Ag nanoparticles and the activity of the nanocatalysts could be modulated by temperature over a wide range. The reduction of 4-NP to 4-AP by NaBH₄ was chosen as a model reaction to be repeatedly performed to investigate the catalytic activity of the nanoreactor. Besides that Au and Ag nanoparticles could be employed as nanocatalysts, Cu nanoparticles or other Cu nanostructures could also demonstrate the catalytic capability for the reduction reaction of 4-NP.11-14 To make it easier to recover the catalysts, some immobilized metal nanostructures could be served as nanocatalysts for the reduction of 4-NP with favourable bifunctional properties, reusability and catalytic performance.13,18,19,22,30 In addition, it should be noted that, Co and Ni nanoparticles prepared in hydrogel systems could also show good catalytic performance towards the reduction of 4-NP and 2-nitrophenol (2-NP) since these systems can be used repetitively up to five times with approximately 100% conversion resulting from the hydrogels as supports.27,28

With regard to the catalytic mechanism of metal nanoparticles for the model reduction reaction of 4-NP to 4-AP by NaBH₄, it can be discussed according to the Langmuir–Hinshelwood model.^{31–34} In general, in reaction aqueous solution, firstly BH_4^- can be adsorbed on and react with the surface of metal nanoparticles, thereby the active metal hydride can be



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created at the surface of metal nanoparticles. At the same time, 4-NP can also be adsorbed on the surface of metal nanoparticles. The two steps are reversible and are fitted into a Langmuir isotherm model. It should also be noted that the diffusion of both reactants to the surface of metal nanoparticles and the adsorption/desorption equilibriums of these reactants on the surface can be considered to be fast. Therefore, the reduction of 4-NP to corresponding 4-AP will occur in view of the reaction of adsorbed 4-NP with the metal hydrides bound by metal nanoparticles surface. When formed 4-AP detaches from the metal nanoparticles surface, the next cycle of new catalytic reduction can be triggered again.

However, it should be pointed out that, in most of reported cases involve the catalytic reduction of 4-NP by metal nanoparticles/nanostructures, firstly the metal nanoparticles/nanostructures were required to be prepared, and then they were employed as nanocatalysts for the reduction conversion of 4-NP to 4-AP by NaBH₄. In general, the procedures of preparing metal nanoparticles with high quality are troublesome, and metal nanoparticles are known to be intrinsic unstable for storage and application since they are easily oxidized and aggregated in the presence of oxygen. Therefore, it is difficult to construct highly effective and reproducible catalytic systems for the reduction of other nitroaromatic compounds based on preformed metal nanoparticles. In light of these facts, developing a robust and facile catalytic system for the reduction conversion of 4-NP or nitroaromatic compounds is crucial. It should be pointed out that, although the work of Pal et al. and Tilve et al. on coinage metal nanoparticles in situ formed could afford an intriguing clue for the solution of this problem,7,8,35 detailed investigations on the metal ion/NaBH₄ systems towards the catalytic reduction of 4-NP and other nitroaromatic compounds are still lacking up to now. Obviously, metal ions as precatalysts stored in aqueous solutions are much more stable, comparing with metal nanoparticles solutions.

Herein, we report that the metal ion $(Cu^{2+}, Ag^+, AuCl_4^-, Co^{2+},$ and Ni²⁺)/NaBH₄ systems which were detailedly investigated could effectively catalyze the reduction reaction of 4-NP to 4-AP due to *in situ* created metal nanoparticles. By employing 4-NP as a model compound, the effects of concentration of 4-NP, NaBH₄, and metal ions on the rate of these catalytic reduction reactions were systematically investigated. Apparent activation energies of metal ion/NaBH₄ systems were further measured and compared. These catalytic systems could also be employed to facilitate the reduction reaction of a series of nitroaromatic compounds including 2-NP, 3-NP, 2,4-dinitrophenol (2,4-dNP), 2,5-dNP, 3,4-dNP, 2,4,6-tNP and 2,4,6-tNT (Fig. 1), by NaBH₄. These catalytic systems investigated in this protocol are simple and do not require a prerequisite for preparing metal nanoparticles in advance, comparing with previous related reports.

Experimental

Materials

2-NP (99.7%, GC) and 3-NP (99%, GC) were purchased from Aladdin (China). 3,4-dNP (97.0%) was purchased from Aldrich. 2,5-dNP (99.0%) was obtained from TCI (Japan). 2,4-dNP (99%,



Fig. 1 Molecular structures and abbreviations of the tested nitroaromatic compounds.

AR) was purchased from Gracia (China). 2,4,6-tNP (99.8%) was obtained from YUEQIAO (China). AgNO₃ (99.95%), NaBH₄ (96%), 4-NP (99.5%), HAuCl₄·4H₂O, Cu(NO₃)₂·3H₂O (99–102%), Co(NO₃)₂·6H₂O (99%), Ni(NO₃)₂·6H₂O (98.5%) and other reagents were obtained from GuoYao (Shanghai, China). 2,4,6-tNT (99.9%) was generously offered by Dr Tao Yu from Beijing Institute of Pharmaceutical Chemistry. All chemicals were used in the experiments without further purification.

Characterization

X-ray power diffractions (XRD) were performed on Panalytical X'pert PRO diffractometer equipped with Cu K α radiation (λ = 1.5418 Å). For obtaining the XRD samples, the catalytic reduction reactions were amplified for 3 orders of magnitude, comparing with the spectra measurements. After finishing the reactions, the resulting solutions were centrifuged by a high speed freezing centrifugal apparatus (Shuke TGL-22) at 20 000 rpm speed for 30 min. The resulting solids were washed by ultrapure water and centrifuged for 3 times, repeatedly. And then the resulting solids were vacuum freeze-dried by employing a home-made vacuum freeze-drier at -80 °C. Transmission electron microscopy (TEM) experiments were conducted on HITACHI H-7650 system. UV-vis absorption spectra were recorded on Thermo Evolution 300 absorption spectrophotometer equipped with a temperature controller. For the experiments of spectra measurement, except for the experiments of measuring activation energy, temperature of the experiments was set at about 24 °C.

Catalytic reduction of nitroaromatic compounds

In a typical experiment of catalytic reduction of nitroaromatic compounds, 100 μ L nitroaromatic compounds stock solution (concentrations of all stock solutions were 1 mM; except for 1 : 1 by volume of alcohol–water solution was used in 2,4,6-tNT case, and 1 : 99 by volume of alcohol–water solution was used in both 2,5-dNP and 3,4-dNP cases, pure aqueous solution was used in other nitroaromatic compound cases) was mixed with a certain amount of NaBH₄ in a quartz cell (4.0 mL) with a path length of 1 cm, and after a certain amount of metal ions (20 μ L of 0.1 mM

Cu(NO₃)₂ solution, 10 μ L of 0.1 mM AgNO₃ solution, 13.4 μ L of 0.05 mM HAuCl₄ solution, 100 μ L of 1 mM Co(NO₃)₂ solution, 47 μ L of 1 mM Ni(NO₃)₂ solution) were added and then certain amount of water were added to make the total volume to be 1 mL, the spectra changes in the solution were monitored at a certain time intervals by employing a UV-vis spectrophotometer equipped with a temperature controller. The concentration of 4-NP (*C*_t) could be calculated from the measurement of UV-vis absorption spectrum.

Results and discussion

In this protocol, the reduction of 4-NP to 4-AP by NaBH₄ was employed as a model reaction to evaluate the catalytic performance of the metal ion (Cu²⁺, Ag⁺, AuCl₄⁻, Co²⁺ and Ni²⁺)/ NaBH₄ systems. It was found that the maximum peak of UV-vis absorption spectrum of 0.1 mM 4-NP solution was shifted to 400 nm from original 317 nm when a certain amount of NaBH4 was introduced, accompanied by the solution color change from original light yellow to intense yellow. This color or spectra change is because that adding NaBH₄ could substantially enhance the pH value of 4-NP solution, leading to an increase of the amount of 4-nitrophenolate anion which is a strong electron donor.³⁶ This deprotonation could lower the energy gap of charge transfer (CT) transition due to the change from weak donor (D)-acceptor (A) CT of -NO2 and -OH to strong D-A CT of -NO₂ and -O⁻. Therefore, the catalytic reduction reaction could be easily monitored by UV-vis absorption spectra. In the absence of tested metal ions, the absorption at 400 nm wavelength of the mixing solution of 4-NP and NaBH₄ could be kept untouched even the reaction time was prolongated to several hours.

However, after introducing a certain concentration of metal ion (Cu2+, Ag+, AuCl4-, Co2+ and Ni2+; except HAuCl4 was employed as Au^{III} source, other M^{n+} were obtained from their nitrates) into the mixing solution of 4-NP and NaBH₄, surprisingly, the absorption peak of 4-nitrophenolate anion at 400 nm was found in all cases to gradually decrease and even disappear with prolongating reaction time, accompanied by the appearance of a new absorption peak at 300 nm wavelength, as shown in Fig. 2 and 3. These experimental phenomena are similar to those of the reported cases of preformed metal nanoparticles as nanocatalysts.7-30 Considering the reduction capability of NaBH₄, it was considered that metal nanoparticles could be in situ created in our present case and this deduction could be confirmed by the following experiments. The new emerging absorption peak could be ascribed to resulting amino group.37 Therefore, this observation indicated that nitro group of 4-NP could be reduced into amino group in the metal ion/NaBH₄ catalytic systems.³⁸ This conversion could also be directly observed from the discoloration of resulting solutions. Since the concentration of NaBH₄ employed in these metal ion/NaBH₄ catalytic systems was at least 100-fold higher than that of 4-NP, the concentration of NaBH4 could be considered as a constant during the catalytic reduction reaction. Therefore, pseudo firstorder kinetics could be applied to evaluate the apparent kinetic



Fig. 2 The evolution of UV-vis absorption spectra of 4-NP with prolongating time in the presence of NaBH₄ and (a) Cu²⁺, (b) Ag⁺, and (c) AuCl₄⁻, respectively. [4-NP] = 0.1 mM; [NaBH₄] = 10 mM; [Cu²⁺] = 2 μ M; [Ag⁺] = 1 μ M; [AuCl₄⁻] = 0.67 μ M.



Fig. 3 The evolution of UV-vis absorption spectra of 4-NP with prolongating time in the presence of NaBH₄ and (a) Co²⁺, and (b) Ni²⁺. [4-NP] = 0.1 mM; [NaBH₄] = 20 mM; [Co²⁺] = 0.1 mM; [Ni²⁺] = 47 μ M.

rate constant of catalytic reduction reaction, according to the first-order kinetics equation of

$$-\mathrm{d}C_t/\mathrm{d}t = KC_t \tag{1}$$

in which C_t is the concentration of 4-NP at certain reaction time (*t*) and *K* is the rate constant. Linear relationship between $\ln(C_t/C_0)$ and *t* could be observed in all metal ion/NaBH₄ catalytic systems, indicating that these catalytic reduction reactions were followed by the pseudo-first-order kinetics. From the slope of linear fitting, the rate constant *K* could be calculated (*t* employed for calculating *K*, please see the Table S1†). It should be pointed out that the concentration of Co^{2+} and Ni^{2+} are much higher than those of Cu^{2+} , Ag^+ and AuCl_4^- , and significantly uprising baseline was observed in the cases of Co^{2+} . The uprising baseline is probably because Co nanoparticles with large size or large aggregates of Co nanoparticles were *in situ* formed, leading to significant light scattering.

The effect of concentration of NaBH₄ on the rate constant of the metal ion/NaBH₄ catalytic systems towards 4-NP was investigated, and the results were shown in Fig. 4. Experimental results revealed that for the cases of Cu²⁺, Ag⁺ and AuCl₄⁻, when low concentration of NaBH₄ was employed, the reaction rate constant was generally enhanced with increasing the concentration of NaBH₄; however, when the concentration of NaBH₄ was enhanced to a certain extent, the reaction rate constant was nearly constant or somewhat decreased. This observation was probably resulted from that the surface of *in situ* formed metal nanoparticles was saturated by BH₄⁻ when high concentration of NaBH₄ was used. The reaction rate constant was observed as nearly a constant with changing the concentration of NaBH₄ from 10 mM to 40 mM in the case of Co^{2+} . However, for the $\mathrm{Ni}^{2+}/$ NaBH₄ catalytic system, the reaction rate constant was found to be enhanced with increasing the concentration of NaBH4 within the range of 20 mM to 60 mM. It should be noted that much higher concentration of NaBH₄ could not be further used in the case of Ni²⁺ since the disturbance by bubbles resulted from the hydrogen production from NaBH₄ in spectra measurement occurred.

We further investigated the effect of the concentration of 4-NP on the reaction rate constant of the metal ion/NaBH₄ catalytic systems. Detailed experimental conditions and the results were shown in Fig. 5, when 20 mM and 30 mM NaBH₄ for the cases of Ag^+ and $AuCl_4^-$ and for the cases of Cu^{2+} , Co^{2+} and Ni^{2+} , respectively, was employed. It has a tendency for an increase of the concentration of 4-NP from 70 μ M to 130 μ M could generally lead to an increase of the reaction rate constant and even reaching a platform in all cases, except for the cases of Au and Ni. This observation might be explained by that increasing concentration of 4-NP at certain extent could effectively inhibit the aggregation of metal nanoparticles, since much more surface of *in situ* formed metal nanoparticles were occupied by 4-nitrophenolate anion, thereby resulting in an apparent increase in the catalytic activity. It should be pointed out that



Fig. 4 Dependence of the apparent rate constant on the concentration of BH₄⁻ under fixed concentration of metal ions and 0.1 mM 4-NP in the catalytic reduction of 4-NP by the metal ion/NaBH₄ systems. (a) For the cases of Cu²⁺, Ag⁺ and AuCl₄⁻; (b) for the cases of Co²⁺ and Ni²⁺. [Cu²⁺] = 2 μ M; [Ag⁺] = 1 μ M; [AuCl₄⁻] = 0.67 μ M; [Co²⁺] = 0.1 mM; [Ni²⁺] = 47 μ M.



Fig. 5 Dependence of the apparent rate constant on the concentration of 4-NP under fixed concentration of BH₄⁻ (20 mM NaBH₄ in the cases of Ag⁺ and AuCl₄⁻, 30 mM NaBH₄ in the cases of Cu²⁺, Co²⁺ and Ni²⁺) and metal ions in the catalytic reduction of 4-NP by the metal ion/NaBH₄ systems. [Cu²⁺] = 2 μ M; [Ag⁺] = 1 μ M; [AuCl₄⁻] = 0.67 μ M; [Co²⁺] = 0.1 mM; [Ni²⁺] = 47 μ M.

for the case of Au, the reaction rate constant did not change much within the range of the tested concentration of 4-NP from 70 μ M to 130 μ M likely due to relatively good dispersity of Au nanoparticles. However, for the case of Ni, the reaction rate constant decreased with increasing the concentration of 4-NP, probably resulting from the insufficient concentration of NaBH₄ employed due to relatively high NaBH₄ concentration per catalyst unit required in the case of Ni comparing with that of the case of Co.^{27,28}

The effect of concentration of metal ions on the reaction rate constant of the metal ion/NaBH₄ catalytic systems towards 4-NP were also investigated. The experimental results suggested that in all cases the reaction rate constant linearly increased with increasing the metal ion concentration (Fig. 6). It was considered that much more surface vacancies for the 4-NP or BH₄⁻ could be provided with increasing the concentration of metal ions. Therefore, the electron transfer rate between absorbed



Fig. 6 Dependence of the apparent rate constant on the concentration of metal ions under fixed concentration of BH_4^- (20 mM and 30 mM NaBH₄ were employed in the cases of Ag⁺ and AuCl₄⁻ and in the cases of Cu²⁺, Co²⁺ and Ni²⁺, respectively) and 0.1 mM 4-NP, in the catalytic reduction of 4-NP by the metal ion/NaBH₄ systems.

 BH_4^- and 4-NP could be accelerated. If all of the experimental conditions including the concentration of metal ions, 4-NP and NaBH₄, temperature, and pH, were set to the same in the Cu²⁺, Ag⁺, AuCl₄⁻, Co²⁺ and Ni²⁺/NaBH₄ systems, the catalytic activity could be clearly distinguished by following the order of Co \approx Ni \ll Cu < Ag < Au (Fig. S1[†]).

Considering reduction capability of NaBH₄ for metal ions in the metal ion/NaBH₄ systems, TEM experiments were conducted to confirm this reduction after finishing the catalytic reduction reaction towards 4-NP. The TEM results were shown in Fig. 7 and 8. The results substantially revealed that the catalytic reduction reaction systems could in situ create metal nanoparticles. For the cases of Cu, Ag and Au, the particle size was followed by the order of Ag < Au < Cu, and their sizes were located at the level of several or a dozen of nanometers (Fig. 7 and Fig. S2[†]); for the cases of Co and Ni, the particle size was followed by the order of Ni < Co, and their sizes were located at the level of dozens of nanometers or even more than one hundred nanometers level (Fig. 8 and S3[†]). Comparing with the good dispersity of the cases of Cu, Ag and Au, in situ formed Co and Ni nanoparticles showed serious aggregation. These results also suggested that 4-nitrophenolate anion adsorbed on the surface of the in situ formed metal nanoparticles could play as surface ligands which are capable of effectively limiting the growth of metal nanoparticles and have an effect on stabilizing metal nanoparticles. Therefore, in the metal ion/NaBH₄ catalytic reduction systems, in situ formed metal nanoparticles could serve as effective nanocatalysts for the reduction reaction of 4-NP by NaBH₄.

To further probe *in situ* formed metal nanoparticles, these catalytic reduction reactions were amplified, and after the



Fig. 7 TEM images of Cu (a), Ag (b) and Au nanoparticles (c) formed in the catalytic reduction of 4-NP by the Cu²⁺, Ag⁺ and AuCl₄⁻/NaBH₄ systems.



Fig. 8 TEM images of Co (a) and Ni nanoparticles (b) formed in the catalytic reduction of 4-NP by the Co^{2+} and $Ni^{2+}/NaBH_4$ systems.

catalytic reduction reactions were finished, resulting solid samples were collected by centrifugation, washed, and vacuum freeze-dried. XRD experiments were then conducted. For the cases of Cu, Ag and Au, distinct XRD diffraction peaks appeared, and correspondingly, these diffraction peaks could be assigned to different diffraction planes of Cu, Ag, and Au nanoparticles, respectively (Fig. 9). Therefore, the XRD results also suggested that the *in situ* formed metal nanoparticles were fcc structure in Cu^{2+} , Ag⁺, and AuCl₄⁻ cases. It should be noted that no impurity peaks could be observed in these samples, indicating the same structure of formed metal nanoparticles. However, no distinct XRD diffraction peaks could be observed in both Co and Ni cases (Fig. S4[†]), revealing that both in situ formed Co and Ni nanoparticles were amorphous. Furthermore, according to the results of XRD, the mean particle size could be alternatively estimated by the well-known Scherrer equation,

$$D = 0.89\lambda/(\beta\cos\theta) \tag{2}$$



Fig. 9 XRD patterns of the in situ formed Cu, Ag and Au nanoparticles.



Fig. 10 Arrhenius plots for the catalytic reduction of 4-NP by Cu²⁺, Ag⁺, AuCl₄⁻, Co²⁺ and Ni²⁺/NaBH₄ systems. [4-NP] = 0.1 mM; [Cu²⁺] = 2 μ M; [Ag⁺] = 1 μ M; [AuCl₄⁻] = 0.67 μ M; [Co²⁺] = 0.1 mM; [Ni²⁺] = 47 μ M; 20 mM NaBH₄ in the cases of Ag⁺ and AuCl₄⁻, and 30 mM NaBH₄ in the cases of Cu²⁺, Co²⁺ and Ni²⁺.

 Table 1
 Summary of reported examples and our present work involving in catalytic system, tested nitroaromatic compounds, and activation energy

No.	Catalytic system	Nitroaromatic compounds	$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$	Ref.
1	Au nanoparticles	4-NP	30.1	23
2	Au nanostructures	4-NP	28-55	25
3	Au nanoparticles/Fe ₃ O ₄	4-NP	51.2	16
4	Au nanoparticles, Ag nanoparticles	2,4-DNP	29.72 (Au), 35.33 (Ag)	29
5	Ag nanoshells	4-NP	24.08	26
6	Cu nanostructures	4-NP	22.44-54.26	37
7	Co nanoparticles	4-NP, 2-NP	27.8 (4-NP), 39.3 (2-NP)	27
8	Ni nanoparticles	4-NP, 2-NP	25.70 (4-NP), 38.69 (2-NP)	28
9	Cu^{2+} , Ag^{+} , $AuCl_4^{-}$, Co^{2+} and $Ni^{2+}/NaBH_4$ systems	4-NP	74.0 (Cu), 173.1 (Ag), 32.6 (Au), 34.7 (Co), 216.4 (Ni)	This work

in which, *D* is the diameter of nanoparticles, λ is the wavelength of the incident X-ray, β is full width at half-maximum, and 2θ is diffraction angle. Although the calculated diameter of Cu nanoparticles had some deviation, comparing with that from TEM result, the order of Ag < Au < Cu particle size obtained from XRD results was consistent with the finding from TEM (Table S2†).

The catalytic reduction of 4-NP by the metal ion/NaBH₄ systems were further investigated at different temperatures. Therefore, the activation energy (E_a) of these catalytic reduction systems could be obtained. Based on the Arrhenius equation,

$$K = A e^{-E_a/RT} \tag{3}$$

following equation could be written as:

$$\ln K = \ln A - E_{\rm a}/RT \tag{4}$$

Herein, *A* is a constant, *K* is the apparent rate constant, *T* is the absolute temperature of the system, E_a is the activation energy and *R* is the gas constant.

Under optimized experimental conditions, temperature effect on the catalytic reduction of 4-NP by the metal ion/NaBH₄ systems were performed. When the relationship between $\ln K$ and 1000/T were plotted, a linear relationship could be observed (Fig. 10), indicating that the reaction rate constant increased with increasing temperature. After linear fitting of ln K versus 1000/T, $E_{\rm a}$ could be obtained from the slope. Therefore, the activation energy of catalytic reduction of 4-NP by the metal ion/ NaBH₄ systems were calculated as: E_{Cu} of 74.0 kJ mol⁻¹, E_{Ag} of 173.1 kJ mol⁻¹, E_{Au} of 32.6 kJ mol⁻¹, E_{Co} of 34.7 kJ mol⁻¹ and E_{Ni} of 216.4 kJ mol⁻¹. Comparing with the previously reported cases, although most of these activation energies are somewhat high (as listed at Table 1), the metal ion/NaBH₄ catalytic systems for the reduction of 4-NP could show some merits. For example, the operation procedure was simple and it did not require the preparation of metal nanoparticles in advance.

Taking into account of the environmental toxicity and explosive nature of other nitroaromatic compounds, we also employed the present metal ion/NaBH₄ systems to check whether the reduction reaction of a series of nitroaromatic compounds by NaBH₄ could be effectively catalyzed. These tested aromatic nitro compounds include 2-NP, 3-NP, 4-NP, 2,4-DNP, 2,5-DNP, 3,4-DNP, 2,4,6-tNT and 2,4,6-tNP. In particular, 2,4,6-tNT and 2,4,6-tNP bearing three nitro groups are widely employed as explosives in the fields of industry and military.³

Time-dependent UV-vis absorption spectra revealed that, under the optimized experimental conditions, the reduction of all tested nitroaromatic compounds could be facilitated by the metal ion/NaBH₄ catalytic systems, similar to that of 4-NP. In the absence of metal ions, the absorption spectra of 2-NP, 3-NP, 2,4-dNP, 2,5-dNP, 3,4-dNP and 2,4,6-tNP solution containing NaBH₄ exhibited absorption peaks at 414, 390, 357, 438, 387 and 386 nm wavelength, respectively. However, when a certain amount of tested metal ions were added into these mixing nitroaromatic compounds and NaBH₄ solution, corresponding characteristic absorption peaks decreased or even disappeared with increasing the reaction time (Fig. S5-S34[†]). It should be noted that, 2,4,6-tNT, without any characteristic absorption peak in its original mixing solution of water and ethanol (1:1, by v/v), could demonstrate a strong absorption peak at 425 nm after adding a certain amounts of NaBH₄ into the 2,4,6-tNT solution for ca. 20 seconds. The new absorption peak was found to gradually decrease with extending the reaction time (Fig. S35-S39[†]). Similar to previous investigations, control experiment indicated that in alkaline NaBH₄ solution partial hydrolysis reaction of 2,4,6-tNT could occur, forming Meisenheiner complex or 2,4,6-tNT anion.1,39 However, the rate of hydrolysis is much smaller than that in metal ion/NaBH₄ catalytic systems (Fig. S40[†]), since introducing metal ions could substantially accelerate the hydrolysis and facilitate the catalytic reduction of nitro group to amino group. It should also be noted that in the dinitro or trinitro compounds' cases some intermediates like 2-amino-4-nitrophenol could be produced at first stage after introducing the metal ion/NaBH₄ catalytic systems.24,40

Conclusions

Taking into consideration of some nitroaromatic compounds are dangerous or environmentally toxic, it is of importance to develop effective and simple catalytic strategies for the reduction conversion of nitroaromatic compounds. In this work, the metal ion (Cu²⁺, Ag⁺, AuCl₄⁻, Co²⁺ and Ni²⁺)/NaBH₄ systems were employed to in situ form metal nanoparticles, and to detailedly investigate the catalytic reduction of 4-NP to 4-AP by NaBH₄ which was used as the model reaction. The effects of concentration of NaBH₄, metal ions, and 4-NP on the catalytic reduction system were systematically studied. The activation energies of the metal ion/NaBH₄ systems towards catalytic reduction reaction of 4-NP have also been investigated. These catalytic reduction systems show some merits, for instance, (i) the operation procedure is simple; (ii) it does not require to synthesize metal nanoparticles in advance, which could overcome the shortcoming of intrinsic aggregation or oxidation of metal nanoparticles during storage, since storing up metal ions solutions is more facile than that of metal nanoparticles solutions; (iii) a series of metal ion/NaBH₄ systems could be demonstrated the good catalytic performance towards nitroaromatic compounds, indicating the diversity of this catalytic system. In situ formed metal nanoparticles in the metal ion/ NaBH₄ catalytic systems towards the reduction reaction of 4-NP were probed by XRD and TEM, and catalytic reduction reaction was facilely tracked by employing UV-vis absorption spectroscopy. The reduction of a series of other nitroaromatic compounds by NaBH₄ including 2-NP, 3-NP, 2,4-dNP, 2,5-dNP, 3,4-dNP, 2,4,6-tNP and 2,4,6-tNT could also be achieved by employing these metal ion/NaBH4 catalytic systems. This study is expected to not only afford a robust and simple strategy for the catalytic reduction of one-, two-, and tree-nitro group containing aromatic compounds, but also be helpful for developing novel bimetal nanomaterial catalytic systems.

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