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General transfer hydrogenation by activating ammonia-borane over cobalt nanoparticles†

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Cobalt nanoparticles containing both Co^{2+} and Co^0 species supported on carbon nitride can function as heterogeneous nanocatalysts for a general transfer hydrogenation reaction in aqueous ammonia-borane solution at room temperature. The conversions of nitroarenes, olefins, imines, aldehydes, ketones and cyanobenzene are high with superior selectivity under mild conditions. This noble-metal-free catalyst is also cheap and reusable.

Ammonia-Borane (AB), a widely investigated hydrogen-rich compound for hydrogen storage, shows great potential as a solid hydrogen source for hydrogenation reactions.[1,2] The high stability under ambient conditions in combination with its high hydrogen content, low toxicity and high solubility in water makes AB an ideal solid hydrogen source for green organic synthesis. Transfer hydrogenation of unsaturated compounds by using a hydrogen-containing molecule has attracted much attention for organic synthesis. The pioneering work using AB for hydrogenation of various unsaturated carbon and nitrogen bonds promises the availability of such a strategy.[3–5] Transfer hydrogenation of polarized C═C from AB could also proceed even without the presence of catalyst.[3] However, organic or organometallic complexes are usually utilized as homogenous catalysts to activate AB for most transfer hydrogenation reactions due to the relatively high activation barrier for non-activated substrates.[4,5] Recent breakthroughs in applying a unique P(III) ↔ P(V) redox cycle in 1,3,2-diazaphospholene for catalytic hydrogenation of N═N bond with AB rather suggested the critical effect of redox cycle in certain organocatalyst for activating AB and substrates.[4] Redox pairs in inorganic solids, such as Fe^{2+}/Fe^{3+}, Co^{2+}/Co^0 and I^-/IO^{3-}pairs, might also be available to activate small molecules, including AB here, for organic synthesis.

Indeed, various supported noble metal nanoparticles, including single-component nanoparticles or alloy nanoparticles have been investigated as efficient catalysts for transfer hydrogenation reactions using AB or various derivatives.[6] The reusability of these noble metal heterogeneous catalysts could obviously benefit industrial applications. Moreover, powerful catalysts should also offer excellent activity, selectivity and reusability for most reactions under mild conditions.[7,8] All current results promise a great room to develop efficient heterogeneous catalysts for transfer hydrogenation of unsaturated organic compounds using AB,[3–6] although a cheap transition-metal nanoparticle-based catalyst has not been reported for AB-based transfer hydrogenation reaction as far as we know. Obviously, cheap transition metal-based catalysts with reusability are preferred for practical use.[7]

Here, we report a proof-of-concept study that cobalt nanoparticles with Co^{2+} species on the surface can be applied as efficient heterogeneous catalyst for highly effective and selective transfer hydrogenation reactions by AB under mild conditions without sacrificial additives. Our catalytic system is general for transfer hydrogenation of a series of unsaturated organic compounds, including olefins, nitroarenes, ketones, imines and aromatic aldehydes at room temperature.

An *in situ* reduction protocol was applied to fabricate cobalt nanoparticle-carbon nitride dyad (Co/CN), whereby mesoporous carbon nitride (CN) was used as the catalyst support. The formation of Co nanoparticles can be directly confirmed by the powder X-ray diffraction (XRD) pattern of the sample (Fig. S1†). Weak and broad peaks of metallic Co maybe could be distinguished in the sample of Co/CN. The presence of Co components could not be distinguished by low-magnification transmission electron microscopy (TEM) observation due to the similar contrast between Co species and CN components (Fig. S3a†). Nevertheless, the well preservation of the porous structure was confirmed by TEM image (Fig. 1a) after loading Co nanoparticles. Both the specific surface area and the size distribution (Fig. S2 and Table S1†) of the Co/CN sample decreased slightly after deposition of Co species. HRTEM images (Fig. 1b and S3†) revealed the formation of polycrystalline Co nanoparticles with tiny crystal domains sized from several to ten nanometers, matching well with the trend reflected by weak and broad XRD peaks. Clearly, the (111) plane of metallic cobalt with a spacing of 0.204 nm was the dominant plane in our sample, matching well with the XRD results. The

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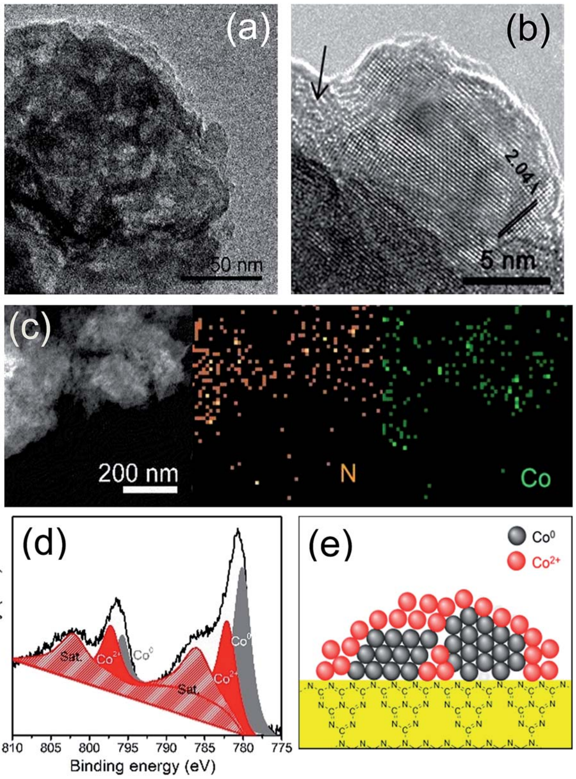

Fig. 1 TEM images (a) of Co/CN with mesoporous structure and corresponding elemental mapping images (c) HRTEM image (b) and XPS Co 2p spectrum (d) of Co species suggested a proposed structure (e).

Table 1 Hydrogenation of nitrobenzene to aniline using AB[a]

Entry	Catalyst	*C* [%]	*S* [%]
1[b]	—	—	—
2[c]	Co/CN	—	—
3	CN	—	—
4	Co	11	68
5	Co/C	41	97
6	Co/N-LC	6	71
7	Co/CN	>99	>99
8[d]	Co/CN	—	—
9[e]	Co*/CN	30	70
10[e]	$Co(OH)_2$/CN	—	—

[a] Reaction condition: 0.5 mmol nitrobenzene, 10 mL of water, 2 mmol AB, 20 mg of catalyst, 298 K, 5 min; conversion (*C*) and selectivity (*S*) were demonstrated *via* GC (byproduct: nitrosobenzene). [b] Without catalyst. [c] Without NH_3BH_3. [d] Hydrogen gas (1 bar) was used as the only hydrogen source, 12 h. [e] 1 h.

elemental mapping images (Fig. 1c) unambiguously demonstrated the homogeneous distribution of Co species on the surface of CN support. More importantly, amorphous domains (marked with an arrow in Fig. 1b) were also observed on the outer surface and at the intersections of Co nanocrystals, proposed to be cobalt oxides or hydroxides as demonstrated by the X-ray photoelectron spectroscopy (XPS) results (Fig. 1d).[9] All these results suggested a hybrid structure of Co nanoparticles with metallic cores and amorphous shells as depicted in Fig. 1e. It should be noted that the amorphous layer mainly formed after the exposure of the sample to air and could be reduced back to metallic Co *in situ* by AB in the catalytic reaction. More importantly, such an amorphous layer could further prevent embedded Co nanoparticles from oxidation. This explains the good stability of Co nanoparticles in Co/CN during the XPS and XRD measurements in air. As a result, the Co/CN catalyst could be easily stored and used under ambient conditions.

Aromatic amines are key intermediates in the synthesis of fine chemicals, biologically active compounds and more.[10] The efficient conversion of nitrobenzene to aniline under mild conditions *via* relatively sustainable methods is thus of great interests. We thus firstly tested the hydrogenation of nitrobenzene at room temperature by using aqueous solution of AB and Co nanocatalysts. Blank tests without catalyst (Entry 1, Table 1) or AB (Entry 2, Table 1) were conducted without obvious conversions of the substrate. Bare Co nanoparticles could give a conversion of 11% and a selectivity of 68% to aniline and 32% to nitrosobenzene (Entry 4, Table 1). Co nanoparticles supported on carbon black (C, surface area: 62.5 $m^2\ g^{-1}$) or nitrogen doped layered carbon (N-LC, surface area: 190 $m^2\ g^{-1}$)[11] could offer moderate conversions and selectivity (Entry 5 and 6, Table 1). Though both the conversions and selectivity need to be optimized, all these results confirmed the possibility of using transition metal nanoparticles for triggering the transfer hydrogenation reaction using AB. Surprisingly, the conversion of nitrobenzene selectivity to aniline over Co/CN (weight percentage of Co: 30%) both reached nearly 100% (Entry 7, Table 1), whilst bare CN offered no conversion (Entry 3, Table 1). These results suggested that the interaction between Co NPs and CN indeed promotes the final activity of Co/CN. The electron transfer from CN to metallic Co nanoparticles at their interface was ambiguously confirmed by the significant decrease in the photoluminance intensity after loading Co NPs (Fig. S4†), whilst the band structure (Fig. S5†) and also chemical structure (Fig. S6†) of CN were not disturbed obviously. The rectified contact between CN and metal significantly facilitated the catalytic activity *via* Mott–Schottky effect.[12,13]

More importantly, the unique coupled structure of Co^0/Co^{2+}-species in Co/CN was found to be the critical factor for ensuring the high activity and selectivity of our catalyst. The Co*/CN catalyst, obtained by using strong reductant ($NaBH_4$), could only offer moderate conversion and poor selectivity under fixed conditions (Entry 9, Table 1). Another control sample $Co(OH)_2$/CN without Co^0 species (Fig. S7†) was totally inert to the same reaction (Entry 10, Table 1).

The catalytic activity of Co/CN catalysts also depended on the loadings of Co species on the surface of CN (Table S2†). As the optimum catalyst for the hydrogenation reaction here, 30% Co/CN was used for all following catalytic reactions.

Nitroarenes substituted by both electron-repelling and electron-attracting groups could be transformed to corresponding amines with high conversions and excellent selectivity (Table 2). Both orientation effect (Entries 1–3 & 6–8, Table 2) and space steric hindrance (Entries 4 and 5, Table 2) of the substituted

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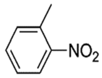
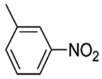
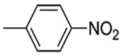
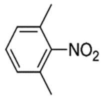
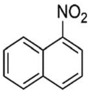
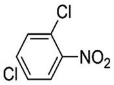
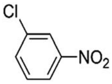
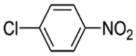
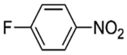
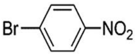
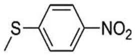
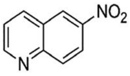
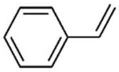
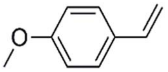
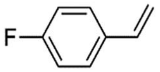
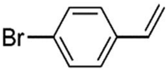
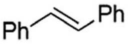
Table 2 Hydrogenation of nitroarenes using Co/CN and AB[a]

Entry	Substrate	*t* [min]	*C* [%]	*S* [%]
1		30	>99	>99
2		20	>99	>99
3		30	>99	>99
4		15	>99	>99
5		30	>99	>99
6		30	>99	>99
7		15	>99	>99
8		30	>99	>99
9		15	>99	>99
10		30	98	>99
11		15	98	>99
12		30	>99	>99

[a] Standard reaction conditions as described in Table 1.

Table 3 Hydrogenation of olefins using Co/CN and AB[a]

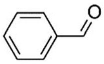
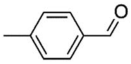
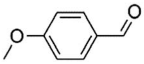
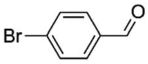
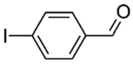
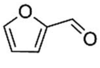
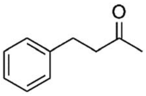
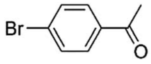
Entry	Substrate	*t* [min]	*C* [%]	*S* [%]
1		25	90	>99
2		20	64	>99
3		25	46	>99
4		20	26	>99
5		20	65	>99
6		5	>99	>99
7		30	—	—

[a] Standard reaction conditions as described in Table 1.

groups didn't disturb the hydrogenation rate of corresponding substrates. No dehalogenation was detected for these halogenated substrates (Entries 6–10, Table 2). The Co/CN catalyst also showed its advantages over noble metal based catalysts on resistance to the poison effect of N or S atoms. Co/CN catalyst could remain active in the presence of sulfur, reducing 4-nitrothioanisole to 4-aminothioanisole (Entry 11, Table 2). 6-Nitroquinoline was also reduced in excellent yields (Entry 12, Table 2) in the same catalytic system.

We further tested the possibility of hydrogenation of olefins (Table 3) over Co/CN using AB as the hydrogen source. Cyclohexene was reduced to cyclohexane (yield: 90%) without other by-product (Entry 1, Table 3). Styrene and substituents (Entry 2–5, Table 3) could also be generally reduced to the corresponding alkanes with good conversions (26–65%) and excellent selectivity (>99%). For internal olefins a *cis* geometry (Entry 6, Table 3), appears to be necessary to facilitate transfer hydrogenation for full conversion to target product within 5 min, as demonstrated by the high conversion of *cis*-stilbene whilst

Table 4 Hydrogenation of aldehydes and ketones using Co/CN and AB[a]

Entry	Substrate	*t* [min]	*C* [%]	*S* [%]
1		15	>99	>99
2		5	>99	>99
3		5	>99	>99
4		10	>99	>99
5		30	80	>99
6		10	>99	>99
7		10	64	>99
8		15	44	>99

[a] Standard reaction conditions as described in Table 1.

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trans-stilbene was totally unreactive. The significant difference between the conversions of *cis*- and *trans*-stilbene may be due to steric constraints or to the orientation of the interaction involved between the olefins and the surface of the catalyst.[14]

We also investigated the hydrogenation of aromatic aldehydes and ketones in our catalytic system. Benzaldehyde and substituents (Entries 1–4, Table 4) were completely reduced to alcohols within short time. 2-Furaldehyde was found to reach a yield of 99% for furfuryl alcohol (Entry 6, Table 4). Note that such hydrogenation reactions were usually conducted at high temperature in high-pressure hydrogen gas.[7] Moreover, both non-activated (Entry 7, Table 4) and activated ketones (Entry 8, Table 4) were reduced to alcohols with high selectivity.

Benzimidazole with C=N bond and cyanobenzene with C≡N bond could be transferred to secondary amine (yield: 99%) and benzylamine (yield: 82%, byproduct: 18% phenylmethanimine) respectively under standard conditions (Scheme S1†). All these results revealed the generality of our catalytic system for hydrogenation of unsaturated compounds. The transfer hydrogenation reactions could be scaled up facilely with constant yields for typical substrates (Table S3†), promising the great potential of Co/CN as sustainable catalysts for practical use.

In order to demonstrate the reaction path of AB and various substrate over Co/CN, a series of control reactions were conducted. Taking the transfer hydrogenation of nitrobenzene as an example, complete conversion of substrate could be achieved within 2 minutes under standard conditions with a conversion of AB of 25% (Fig. 2a and S8†). When substrate was not involved, 10 mL of H_2 forms in our catalytic system *via* the decomposition of AB with a conversion of AB to be 14%. No obvious conversion of nitrobenzene (Entry 8, Table 1) could be observed over Co/CN when hydrogen gas (1 bar) was used for the hydrogen reaction at room temperature for 12 h, excluding the possible role of as-formed hydrogen gas as reductant here. The fact that possible intermediates between AB and substrate were not detected in the ^{11}BNMR spectra of byproducts from AB (Fig. 2b) further demonstrated a direct hydrogen transfer from AB to substrate on the surface of Co/CN. AB was finally split into H_3BO_3, BO^{2-} and other borate species in water solution,[15] no matter whether organic substrates were involved. Combining these results with the Co^{2+}/Co^0 directed hydrogenation process of various substrates, we propose a direct hydrogen transfer path (Scheme 1) from AB to substrate over Co/CN. Co^{2+}/Co^0 pairs in Co/CN were believed to be active centers in our catalytic system, although more detailed investigations of the reaction mechanism and the possibility of formation of CoHx or Co-amidoborane intermediates are still in progress.[16]

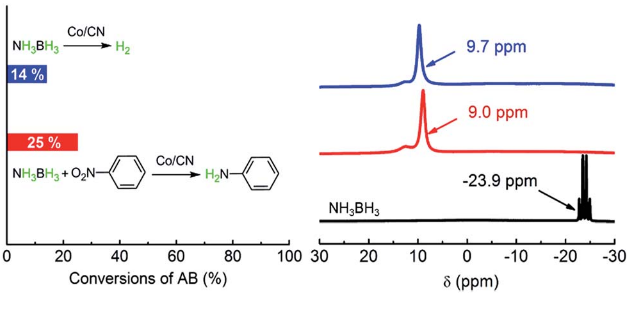
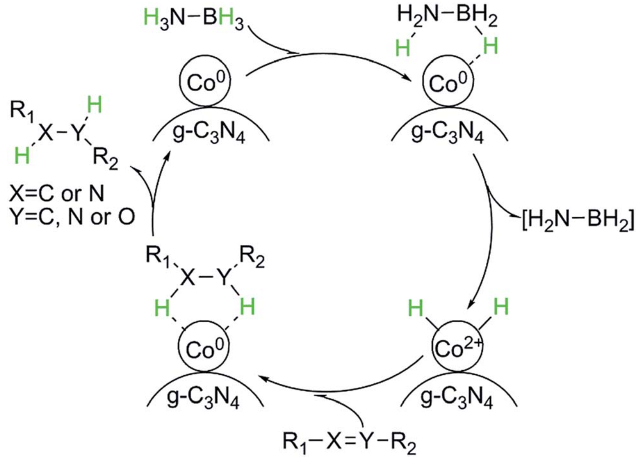


Fig. 2 Conversions of AB (b) over Co/CN with (red) or without (blue) the presence of substrate and the ^{11}BNMR spectra of corresponding decomposition products of AB. Standard reaction conditions were applied except a shorter reaction time (2 minutes). The ^{11}BNMR spectra of pure AB (black) was also tested and an external reference $BF_3\cdot(C_2H_5)_2O$ was set as 0 ppm.



Scheme 1 Proposed reaction mechanism for transfer hydrogenation reactions from AB over Co/CN.

Heterogeneous catalysts are preferred due to their stability and reusability. The catalytic transfer hydrogenation of nitrobenzene under ambient conditions was studied as a model reaction to investigate the stability and reusability of the Co/CN catalyst. Co/CN catalyst was reused for 9 times without any significant loss of catalytic activity (Fig. S9†). After multiple use, a slight decrease in the crystallinity of Co saturated substrates was observed, whilst the decrease in the amount of metallic Co nanoparticles didn't disturb the final activity of Co/CN at all (Fig. S10 and 11†).

Moreover, the excellent chemoselectivity of the Co catalysts is highly impressive here. In contrast, noble metal nanoparticle based catalyst could also trigger the reduction of these substrates but offer worse selectivity.[6] For example, halogenated compounds shown here could be hydrogenated with high selectivity (>99%) over Co/CN (Entry 10 of Table 2, Entry 5 of Table 3 and Entry 4–5 of Table 4). As shown in Table S4,† complete or partial dehalogenation occurred in all these reactions when tested over Pd/CN catalysts. Note that such a dehalogenation reaction was general for noble metal-based nanocatalysts.

Conclusions

In summary, noble metal-free Co/CN catalysts were successfully applied as heterogeneous catalyst for the highly effective and selective transfer hydrogenation of a series of organic compounds in aqueous AB solution. The transfer hydrogenation of nitroarenes, olefins, imines, aldehydes, ketones and cyanobenzene generally proceeded under mild conditions

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(ambient atmosphere and room temperature) and afforded the desired products in good to excellent yields in water. To the best of our knowledge, these results constitute the first example of using non-noble metal heterogeneous catalyst to extract the hydrogen of AB for organic synthesis at room temperature. Further extending the application of first-row transition metal based nanocatalysts for facilitating synthetically useful transformations is promising and will be tried in the near future.

Acknowledgements

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