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COMMUNICATION

Low-cost CuNi@MIL-101 as an excellent catalyst toward cascade reaction: integration of ammonia borane dehydrogenation with nitroarene hydrogenation

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Bimetallic CuNi nanoparticles (NPs) with low cost were rationally confined inside MIL-101 to give CuNi@MIL-101, which exhibits high efficiency and excellent recyclability toward the hydrogenation of nitroarenes under mild conditions, by coupling with ammonia borane dehydrogenation. This is the first report on MOF-stabilized base metal NPs for cascade reactions.

Aromatic amine and its derivatives are high-valued chemical raw materials for the intermediates of azo dyes, pigments, polyurethane, pharmaceuticals and agrochemicals.[1] The conventional synthetic route of aromatic amines is the catalytic hydrogenation of their corresponding nitroarenes under H_2 atmosphere in the presence of Pt, Pd, Au, or other noble metal-based nanoparticle catalysts,[2] but the widespread applications are limited by their low earth-abundance and high cost. Therefore, the design and synthesis of noble-metal-free catalysts with high and stable efficiency is highly desired.

As is known to all, tiny metal nanoparticles (NPs) with high catalytic activity usually possess high surface energies and are prone to aggregate, leading to deteriorated activity. One of the most effective solutions to avoid their aggregation is to confine metal NPs inside porous materials. As a class of crystalline porous materials, metal-organic frameworks (MOFs),[3] featuring tailorable structures and high surface area for potential applications in diverse fields,[4] have been well demonstrated to be ideal hosts providing a confinement effect to stabilize fine metal NPs for catalysis.[5]

On the other hand, the hydrogenation of nitroarenes under the participation of hydrogen gas usually requires high pressure and high temperature considering that hydrogen gas is hardly dissolvable in various solvents. Compared with hydrogen gas, the reducing agent of alcohol such as ethanol, isopropanol, and glycerol can guarantee sufficient contact between the reducing agent and nitroarenes. Nevertheless, the alcohol-engaged hydrogenation reactions tend to be slow and/or lack of reaction selectivity.[6] To meet these challenges, *in situ* hydrogen production coupled with the reduction of nitroarenes would be a suitable solution. The *in situ*-generated hydrogen gas throughout the reaction system will readily and immediately react with the nitro group, enhancing the reaction efficiency. In this regard, ammonia borane (NH_3BH_3) could be an ideal choice as the high-quality hydrogen source due to the advantages of high hydrogen capacity (19.6 wt %), non-toxicity, stability, and high solubility in polar solvents of water and methanol.[7] The hydrogen generated from NH_3BH_3 in water or/and methanol can be controllably released by the suitable metal NPs.[7c,8] The coupling of dehydrogenation of NH_3BH_3 and hydrogenation of nitroarenes in a cascade route is expected to achieve highly efficient reduction of nitroarenes.[9]

Recently, the first-row transition metal (for examples, Fe, Co and Ni) NPs have been recognized as efficient and low-cost catalysts for the dehydrogenation of NH_3BH_3.[7c] However, the preparation of the above metal NPs is generally carried out under harsh conditions, such as $NaBH_4$ or H_2 reduction under a high temperature or/and pressure owing to the negative electrode potential of M^{n+}/M. Unfortunately, many MOF hosts cannot sustain the harsh conditions. Therefore, it is desirable to obtain highly active noble-metal-free catalysts under mild conditions. It was reported that copper precursors could be readily reduced with moderate reductants, such as NH_3BH_3 and the M-H species produced during the NH_3BH_3 hydrolysis offers strong reducibility.[10] Therefore, it is possible to prepare noble-metal-free metal NPs under mild conditions by selecting Cu(II) as an initiator to induce the reduction of first-row transition metals. Moreover, the resultant bimetallic NPs are expected to possess superior catalytic activity to their monometallic counterparts, due to strong synergistic effects between different metals.[11]

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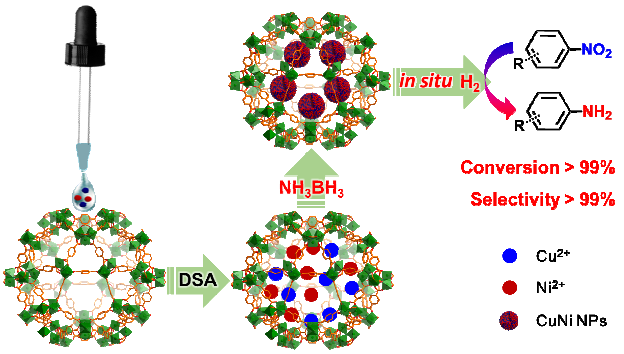

Scheme 1 Schematic illustration depicting introduction and *in situ* reduction of Cu^{2+} and Ni^{2+} encapsulated into MIL-101 for cascade catalysis involving dehydrogenation of NH_3BH_3 and hydrogenation of nitroarenes.

Bearing the above points in mind, the Cu(II) and Ni(II) were rationally incorporated into a mesoporous Cr(III)-based MOF, MIL-101, by a double solvent approach (DSA) followed by *in situ* reduction by NH_3BH_3 to achieve CuNi NPs with the average diameter of *ca.* 3 nm mainly encapsulated inside MIL-101. The obtained CuNi@MIL-101 exhibits excellent catalytic performance in cascade reactions of NH_3BH_3 dehydrogenation and nitroarene reduction (Scheme 1). Especially, the turnover frequency (TOF) for the hydrogenation of nitrobenzene is as high as 99.2 $mol_{nitrobenzene}{\cdot}mol_{Ni}^{-1}{\cdot}h^{-1}$. The non-noble metal NPs@MOF has been rarely reported and all reported cascade catalysis on the basis of metal NPs@MOFs involves noble metals.[2b, 12] To our knowledge, this is the first work of noble-metal-free bimetallic NPs@MOF catalyzing a cascade reaction.

The mesoporous MOF, MIL-101 with the chemical formula $Cr_3F(H_2O)_2O(BDC)_3{\cdot}nH_2O$ (BDC= benzene-1,4-dicarboxylate, n ≈ 25), was selected as a host matrix to incorporate metal NPs, due to its two giant cavities with diameters of 2.9 and 3.4 nm, large surface area and high stability in water and alcohol.[13] An aqueous solution of $Ni(NO_3)_2$ and $Cu(NO_3)_2$ was dropwise pumped into the hexane containing the suspended MIL-101, with the volume of aqueous solution slightly less than the pore volume of MIL-101. To avoid a large deposition of CuNi NPs onto the external surface of MIL-101 and their possible aggregation, the double solvents approach was employed for the incorporation of the guest NPs herein. Since MIL-101 with the hydrophilic inner pore surface was suspended in the hydrophobic hexane, the aqueous solution of metal salt was readily absorbed into MIL-101 pores by capillary force during the impregnation process.[8a, 12b] The Cu^{2+} and Ni^{2+} loaded into MIL-101 are subsequently reduced by NH_3BH_3 to give CuNi@MIL-101, where Cu NPs would be formed first and behaved as seeds to induce the subsequent Ni^{2+} reduction to give CuNi NPs.

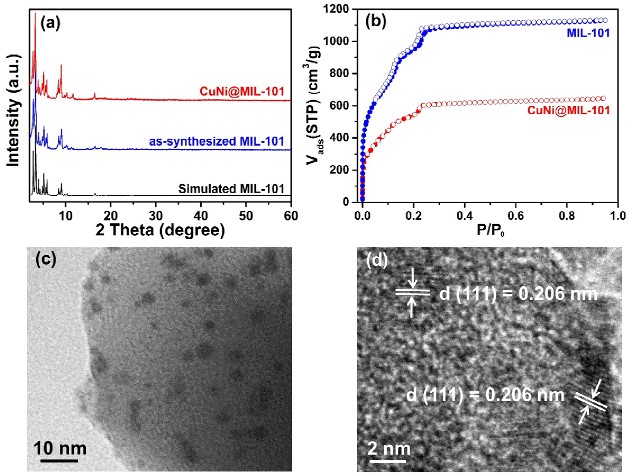

Fig. 1 (a) PXRD patterns of simulated MIL-101, as-synthesized MIL-101, and CuNi@MIL-101. (b) N_2 sorption isotherms of MIL-101 and CuNi@MIL-101 at 77 K. (c) transmission electron microscopy (TEM) and (d) high-resolution TEM (HRTEM) images of CuNi@MIL-101.

As shown in Fig. 1a, there was no apparent loss of crystallinity and structure based on powder X-ray diffraction (PXRD) patterns for MIL-101 after loading CuNi NPs. The PXRD patterns of CuNi@MIL-101 did not exhibit the identifiable diffraction peaks for CuNi NPs, implying that they are very small or/and of low contents. Moreover, N_2 sorption isotherms were measured at 77 K (Fig. 1b). The Brunauer-Emmett-Teller (BET) surface areas of as-synthesized MIL-101 and CuNi@MIL-101 are 3660 and 1983 m^2/g, respectively. The appreciable decrease in the amount of N_2 sorption indicated that CuNi NPs were dispersed to the cavities of MIL-101. In addition, TEM observation shows that CuNi NPs are in ~3 nm size and HRTEM image with 0.206 nm of lattice fringe distance indicates that CuNi NPs might have an alloyed structure (Figure 1c-d, S1). The actual content of Cu and Ni are determined as 1.09 wt% and 2.65 wt%, respectively, by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

To investigate the catalytic behavior, the as-synthesized CuNi@MIL-101 has been applied as the catalyst for the cascade reaction of NH_3BH_3 dehydrogenation and nitroarene hydrogenation. The reaction was initiated by adding NH_3BH_3 into the reaction flask containing Cu^{2+}/Ni^{2+}@MIL-101 and nitroarene with vigorous stirring at room temperature. To explore the optimization of reaction conditions, nitrobenzene was first studied as the model substrate in the cascade catalysis over CuNi@MIL-101. Due to the poor solubility of nitroarene in water whereas great solubility in methanol, a mixture solvent of methanol and water (*v*: *v* = 2: 3) was employed to dissolve nitroarene and NH_3BH_3 to achieve the homogeneous solution. The reaction proceeded rapidly and nitrobenzene was converted to the target product of aniline within 4 min with a real Ni / nitroarene molar ratio of ~ 0.15 : 1 at 298 K (Table 1, entry 1). It is noteworthy that the TOF is calculated to be 99.2 $mol_{nitrobenzene}\ mol_{Ni}^{-1}\ h^{-1}$ for CuNi@MIL-101, which is the highest value among the Ni-based catalysts ever reported for this reaction (Table S1, ESI†).

With the optimized reaction parameters, a series of substrates were applied to expand the scope of the cascade reaction over CuNi@MIL-101. Different nitroarenes investigated were converted into the corresponding anilines with excellent yields (> 99%) at room temperature (Table 1). Various nitroarenes with electron-donating substituents connected to aromatic backbone were able to be reduced to the related amine products in excellent yields within 4 min,

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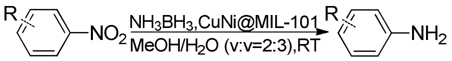
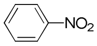
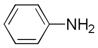
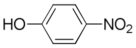
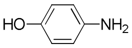
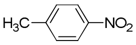
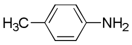
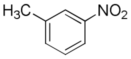
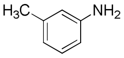
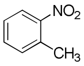
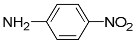
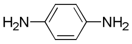
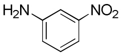
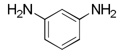
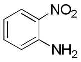
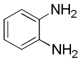
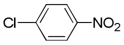
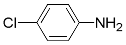
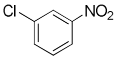
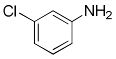
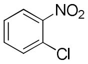
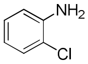
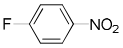
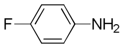
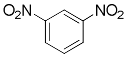
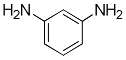
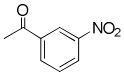
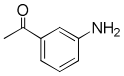
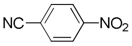
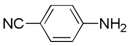
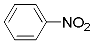
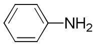
Table 1 Cascade reactions of NH_3BH_3 dehydrogenation and nitroarene hydrogenation over CuNi@MIL-101.[a]



Entry	Substrate	Product	Yield [c]	Time
1			>99 %	4 min
2			>99 %	4 min
3			>99 %	4 min
4			>99 %	4 min
5			>99 %	4 min
6			>99 %	4 min
7			>99 %	4 min
8			>99 %	4 min
9			>99 %	4 min
10			>99 %	4 min
11			>99 %	4 min
12			>99 %	6 min
13			>99 %	8 min
14			>99 %	5 min
15			>99 %	6 min
16[b]			2 %	19 h

[a] Reaction conditions: 0.1 mmol nitroarene, 0.875 mmol NH_3BH_3, 33.5 mg Cu^{2+}/Ni^{2+}@MIL-101 (Cu: 1.09 wt%; Ni, 2.65 wt%), 4 mL MeOH, 6 mL H_2O, 25 °C. [b] NH_3BH_3 was replaced by 1 bar hydrogen. [c] Catalytic reaction products were analyzed and identified by gas chromatography.

such as nitrobenzenes bearing *p*-hydroxyl, *o*-methyl, *m*-methyl, *p*-methyl, *o*-amino, *m*-amino and *p*-amino groups (entries 2-8).Additionally, the slight steric hindrance can be tolerated during the reduction of nitroarenes (entries 3-11). However, the electron-withdrawing substituents of the fluoro- and nitro-groups would make the nitroarene reduction a little bit slower (entries 12 and 13). It should be noted that the nitroarenes containing other reducible groups of ketone and nitrile were successfully reduced to the targeted aniline products with absolute selectivity (entries 14 and 15). The strong electronic/conjugation interaction between the substituent (such as cyano-, keto- group) and the benzene backbone would account for the catalytic selectivity.[9c] These results demonstrate that, when coupling with NH_3BH_3 dehydrogenation, CuNi@MIL-101 is highly efficient and chemoselective toward the reduction of various nitroarenes to the corresponding anilines.

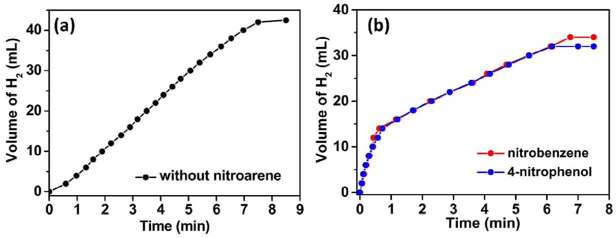


Fig. 2 (a) Plot of time versus the volume of hydrogen generated from by the hydrolysis of 0.583 mmol NH_3BH_3 over CuNi@MIL-101 in the mixed solvent of methanol/water in the absence of nitroarene, and (b) in the mixed solvent of methanol/water containing different nitro compounds. (33.5 mg Cu^{2+}/Ni^{2+}@MIL-101, R-NO_2 = 0.1 mmol, MeOH = 4 mL, H_2O = 6 mL, T = 25 °C).

To explore the possible reason behind the efficient cascade reaction, the kinetic experiments for the hydrolytic dehydrogenation of NH_3BH_3 were carried out. Under the above conditions in the absence of nitroarene substrates, the dehydrogenation of NH_3BH_3 over CuNi@MIL-101 was rapidly proceeded, and the amount of hydrogen generated from NH_3BH_3 approached to the theoretical maximal molar equivalents [n(H_2): n(NH_3BH_3) ≈ 3: 1] within 8 min (Fig. 2a). Interestingly, when nitrobenzene was added into the reaction system, the hydrogen generation rate was further accelerated, especially in the initiation stage (Fig. 2b). The phenomena would be attributed to the synergistic effect when the reactions of NH_3BH_3 dehydrogenation and the nitroarene reduction were coupled. For comparison study, the hydrogen source generated by NH_3BH_3 dehydrogenation for the nitroarene reduction was replaced by hydrogen flow from an external hydrogen supply, while other reaction parameters remain unaltered. However, the reaction yield was as slow as ~2 % even after 19 hours (entry 16), indicating that the limited hydrogen gas dissolved in the solution significantly affects the molecular contact between hydrogen and substrate. Therefore, the coupling strategy of NH_3BH_3 dehydrogenation and nitroarene reduction would be an ideal way to efficient hydrogenation reaction.

The stability and recyclability of catalysts are important to their practical application. It can be found that the catalytic performance and framework integrity of CuNi@MIL-101 are well retained after 20 consecutive runs without any treatment or activation of the catalyst (Table 2 and Fig. S2), clearly demonstrating the reusability and durability of the catalyst.

Table 2 Catalytic recyclability of CuNi@MIL-101 toward the cascade reaction of the dehydrogenation of NH_3BH_3 and hydrogenation of nitroarenes.

Num.[a]	Yield	Num.	Yield	Num.	Yield	Num.	Yield
1	>99%	6	>99%	11	>99%	16	>99%
2	>99%	7	>99%	12	>99%	17	>99%
3	>99%	8	>99%	13	>99%	18	>99%
4	>99%	9	>99%	14	>99%	19	>99%
5	>99%	10	>99%	15	>99%	20	>99%

[a] Num.= number of cycles. Reaction conditions: 0.1 mmol nitrobenzene, 0.875 mmol NH_3BH_3, 33.5 mg Cu^{2+}/Ni^{2+}@MIL-101, 4 mL MeOH, 6 mL H_2O, 25 °C; the yield was evaluated at 4 min for each run.

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Moreover, the size and morphology of CuNi NPs have no significant change after 5 and even 20 runs , verifying the favorable confinement effect of the porous MIL-101 (Fig. S3).

In reference to the previously reported CuNi/graphene catalyst,[9d] the CuNi@MIL-101 with smaller CuNi NPs by a facile synthesis exhibits significant improvement in both catalytic activity and recyclability, probably due to the great pore confinement effect in MIL-101. Moreover, CuNi/MIL-101 prepared by wet impregnation method instead of DSA can maintain its activity in 4 consecutive cycles, and its activity gradually decreases to 85%, 81% and 79% in the subsequent 5th-7th cycles, respectively, which might be explained by the unstable CuNi NPs mainly stayed on MIL-101 (Fig. S4).

In summary, a cascade process has been successfully developed to enhance the catalytic reduction of nitroarene by coupling with NH_3BH_3 dehydrogenation. CuNi@MIL-101 catalyst was facilely synthesized by rational incorporation of Cu^{2+}/Ni^{2+} ions into MIL-101 *via* DSA accompanied by *in situ* reduction with NH_3BH_3. The resultant CuNi@MIL-101 exhibits a superior catalytic activity for the cascade reaction of NH_3BH_3 dehydrogenation and the subsequent selective reduction of nitroarenes. The excellent activity would be attributed that the hydrogen, *in situ* generated from NH_3BH_3, is beneficial to its sufficient contact with substrate, and thus accelerates the nitroarene reduction. Various nitroarenes with different substituents can be reduced to into the corresponding anlines in 4-8 min with >99% yields. Moreover, the great stability and recyclability of CuNi@MIL-101 catalyst can be unambiguously demonstrated by five consecutive runs of the cascade reaction. We believe the obtained cost-effective catalyst is very promising for the nitroarene hydrogenation in the presence of *in situ* generated hydrogen from ammonia borane, and relative cascade reactions for industrial applications. Research along this line is ongoing in our laboratory.

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