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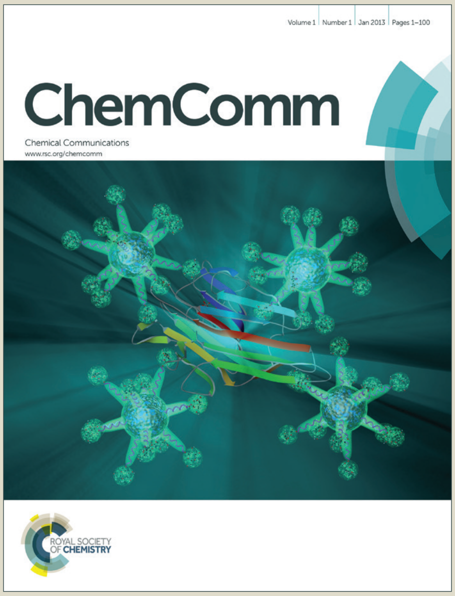

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One-Pot Tandem Catalysis over Pd@MIL-101: Boosting Efficiency of Nitro Compound Hydrogenation by Coupling with Ammonia Borane Dehydrogenation

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The hydrogenation efficiency of nitro compounds was found to be greatly boosted by coupling with dehydrogenation of ammonia borane. The Pd@MIL-101 with tiny Pd NPs is exceptionally efficient and recyclable in the tandem reactions and diverse nitro compounds can be selectively reduced to the corresponding amines in 1.5-5 min with quantitative yields.

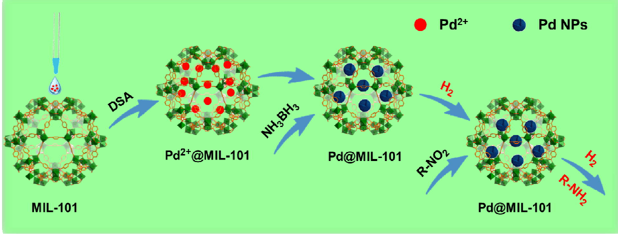
Aniline and its derivatives are important chemical raw materials with production of more than 4,000,000 tons every year. They are used widely for the synthesis of dyes, polymers, agro-chemicals, pharmaceuticals, and various fine chemicals.[1] One common route for their preparation is the reduction of the corresponding nitro derivatives. The reduction of nitro compounds is generally achieved in the presence of noble metal catalysts under hydrogen atmosphere.[2] However, hydrogen gas is hardly dissolvable in the solution of nitro compounds, thus making the reduction of nitro compounds by hydrogenation relatively slow. To improve the efficiency of the reaction, it is crucial to enable sufficient contact between hydrogen gas and the substrate (nitro compounds). In this regard, a system where in situ hydrogen generation is coupled with nitro group reduction could provide an effective solution, since the hydrogen produced throughout the reaction system will be able to well contact and react with nitro group immediately, thus to greatly boost the reaction rate.

Ammonia borane (NH_3BH_3, AB) is a versatile reducing agent due to its high hydrogen content of 19.6 wt%, stability, non-toxicity, and high solubility in water and methanol.[3,4] As a high quality of hydrogen source, dehydrogenation of ammonia borane in water or/and methanol can be effectively catalyzed over fine metal nanoparticles (NPs).[4,5] Therefore, it is possible to achieve highly efficient reduction of nitro compounds by taking advantage of in situ generated hydrogen from NH_3BH_3 in the presence of a suitable catalyst.

Palladium NPs have been previously demonstrated to be effective catalysts for both NH_3BH_3 dehydrogenation and hydrogenation of $R\text{-}NO_2$ to $R\text{-}NH_2$.[5,6] It is well known that the catalytic activity of noble metal NPs is closely relevant to their sizes. While small size typically corresponds to enhanced catalytic activity of metal NPs, it also results in high surface energies. Thus small-size metal NPs tend to aggregate/fuse, resulting in the reduction of their catalytic activity. To solve this problem, the encapsulation/confinement of tiny metal NPs inside porous materials has been recognized as an effective way.[7]

As a relatively new class of porous material, metal-organic frameworks (MOFs),[8] possess exceptionally high porosity and exhibit promising applications in diverse fields including gas storage and separation, sensing, catalysis, etc.[9] Porous MOFs have been demonstrated to be ideal candidates to stabilize fine metal NPs for catalysis.[10] However, the metal NPs@MOF has been rarely reported for tandem catalysis,[11] particularly, among which almost all are based on synergistic effect between MOF acidity/basicity and metal NPs, while tandem catalysis over metal NPs alone remains unexplored thus far.

In this work, a Pd precursor was rationally introduced into a mesoporous MOF, MIL-101, via a double solvents approach (DSA) followed by in situ reduction by NH_3BH_3 to afford tiny Pd NPs of ~3 nm in diameter mainly confined inside the cavities of MIL-101. The obtained Pd@MIL-101 exhibits excellent catalytic performance in tandem dehydrogenation of ammonia borane and reduction of nitro compounds (Scheme 1). Especially, the turnover frequency (TOF) value for the hydrogenation of nitrobenzene is as high as 97 $mol_{nitrobenzene} \cdot mol_{Pd}^{-1} \cdot min^{-1}$, to the best of our knowledge, which surpasses all previously reported Pd catalytic activity in this conversion. In addition, this is the first work of metal NPs@MOF catalyzing a tandem reaction with monometallic NPs as the sole active sites.



Scheme 1 Schematic illustration showing the in situ reduction of Pd^{2+} incorporated into MIL-101 and the subsequent tandem catalysis of the dehydrogenation of ammonia borane and hydrogenation of nitro compounds.

The mesoporous MOF, MIL-101, a chromium-based MOF with the molecular formula $Cr_3F(H_2O)_2O[(O_2C)C_6H_4(CO_2)]_3 \cdot nH_2O$

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(where n is ∼25), is chosen due to its high stability in water and methanol, large surface area (BET, >3600 m^2/g), and two giant cavities (2.9 and 3.4 nm) accessible through pore windows of *ca.* 1.2 and 1.6 nm.[12] To avoid the deposition of Pd NPs onto the external surface of the MOF and their possible aggregation, double solvents approach (DSA) was adopted herein. An aqueous Pd(NO$_3$)$_2$ solution with a volume slightly less than MIL-101 pore volume was pumped dropwise into the MIL-101 suspension in the hydrophobic solvent *n*-hexane. Given the hydrophilic nature of the inner pore environment of MIL-101, the aqueous Pd(NO$_3$)$_2$ solution was readily absorbed into the pores of activated MIL-101 by capillary force during the impregnation process.[10k,11f,13] The Pd^{2+} loaded MIL-101 was subsequently reduced in situ by NH$_3$BH$_3$ to give Pd@MIL-101.

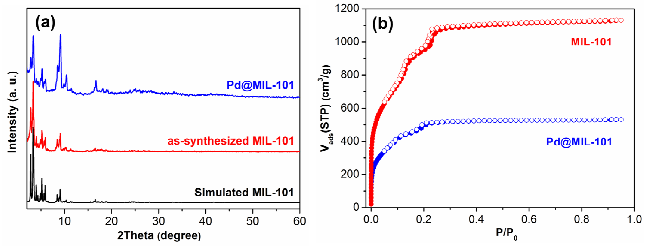


Fig. 1 (a) Powder XRD patterns of simulated MIL-101, as-synthesized MIL-101 and Pd@MIL-101. (b) N$_2$ sorption isotherms for MIL-101 and Pd@MIL-101 at 77 K. Filled and open symbols represent adsorption and desorption branches, respectively.

The powder X-ray diffraction (PXRD) pattern for Pd@MIL-101 shows that the crystallinity and structure of MIL-101 remain well upon loading Pd NPs (Fig. 1a). The absence of identifiable diffraction peak of Pd NPs implies that the Pd NPs are tiny. The impact of metal loading on the porosity of MIL-101 (BET: 3660 m^2/g) has been established by measuring N$_2$ sorption at 77 K, which reveals that Pd@MIL-101 still remains highly porous with a BET surface area of 1597 m^2/g. The appreciable decrease in N$_2$ sorption amount and surface area indicates that the cavities of the host framework are occupied by dispersed NPs or/and blocked by the NPs located on the surface (Fig. 1b). Transmission electron microscopy (TEM) image demonstrates that the Pd NPs are well dispersed with average sizes of ∼2.5 nm (Fig. 2). The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) indicates the actual Pd content (0.86 wt%) is close to the nominal value (1.00 wt%).

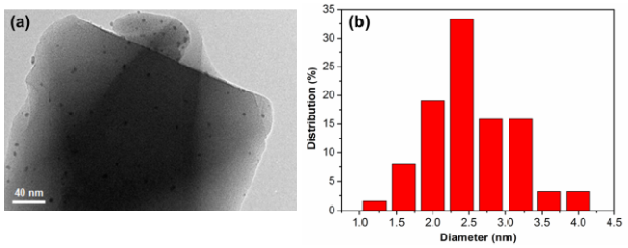


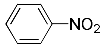
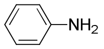
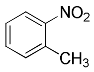
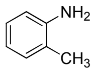
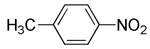
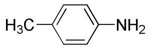
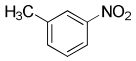
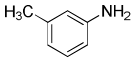
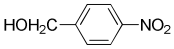
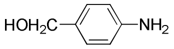
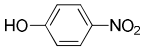
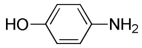
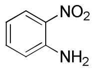
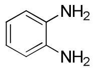
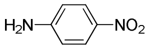
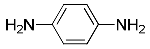
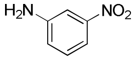
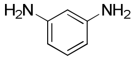
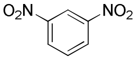
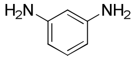
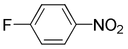
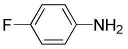
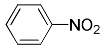
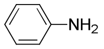
Fig. 2 (a) TEM image of Pd@MIL-101 and (b) size distribution for Pd NPs.

With Pd@MIL-101 in hands, we proceeded to investigate the catalytic performance of Pd NPs for the tandem reaction of ammonia borane dehydrogenation and nitro compound hydrogenation. The reaction was initiated by adding NH$_3$BH$_3$ to the solution in flask containing Pd^{2+}@MIL-101 and nitro compounds under magnetic stirring. Nitrobenzene was first employed as a model compound in the tandem catalysis over Pd@MIL-101 to explore the optimized reaction parameters. Given the great solubility of R-NO$_2$ in methanol but not in water, a mixture of methanol and water (v:v = 2:3) was adopted to dissolve the nitro compounds and ammonia borane to give a homogeneous solution. The reaction proceeded smoothly and nitrobenzene was converted to aniline very rapidly as short as 1.5 min with real Pd/nitro compound molar ratio of ~0.007:1 at room temperature (Table 1, entry 1). The turnover frequency (TOF) was calculated to be 97 mol$_{nitrobenzene}$·mol$_{Pd}^{-1}$·min^{-1}. As far as we know, this is the highest value for the reduction of nitrobenzene over diverse Pd catalysts reported thus far (Table S1).

With the optimized conditions, the catalytic results for the tandem reaction with diverse R-NO$_2$ substrates over Pd@MIL-101 are summarized in Table 1. All aromatic or aliphatic nitro compounds examined were converted into the corresponding primary amines with excellent conversion yields (>99%) at room temperature. Aliphatic nitro compounds such as nitro-methane and nitro-ethane were reduced in excellent yields in 1.5 min (entries 2, 3). A variety of aromatic nitro compounds with electron-rich groups can be efficiently reduced in the same fashion. For example, nitrobenzenes bearing the *o*-methyl, *m*-methyl, *p*-methyl, *p*-methylol, *p*-hydroxyl, *o*-amino, *m*-amino and *p*-amino were reduced to the corresponding amine products in 1.5 min (entries 4-11). Moreover, the slight space steric hindrance was tolerated well to the hydrogenation of nitro compounds (entries 4-6 and 9-11). Electron-deficient substituents, such as fluoro- and nitro groups slow down the reduction a little bit (entries 12, 13), but the reaction are still very fast from the practical point of view.

Table 1 Tandem Reaction Results for Dehydrogenation of NH$_3$BH$_3$ and Hydrogenation of Various R-NO$_2$ Compounds over Pd@MIL-101.[a]

$$R\text{-}NO_2 \xrightarrow[\text{MeOH/H}_2\text{O (v:v/2:3), RT}]{\text{NH}_3\text{BH}_3\text{, Pd@MIL-101}} R\text{-}NH_2$$

Entry	Substrate	Product	Yield (%)[c]	Time (min)
1			>99	1.5
2	CH$_3$NO$_2$	CH$_3$NH$_2$	>99	1.5
3	CH$_3$CH$_2$NO$_2$	CH$_3$CH$_2$NH$_2$	>99	1.5
4			>99	1.5
5			>99	1.5
6			>99	1.5
7			>99	1.5
8			>99	1.5
9			>99	1.5
10			>99	1.5
11			>99	1.5
12			>99	3
13			>99	5
14[b]			>99	30

[a] Reaction conditions: 0.4 mmol nitro compound, 0.875 mmol NH$_3$BH$_3$, 34 mg 0.86 wt% Pd@MIL-101, 8 mL MeOH, 12 mL H$_2$O, 25 ºC. [b] NH$_3$BH$_3$ was replaced by 1 bar hydrogen. [c] Catalytic reaction products were analyzed and identified by gas chromatography.

To explore the possible reason for this extremely efficient reduction of nitro compounds, the uncoupled dehydrogenation of NH_3BH_3 in a mixture of methanol and water (v:v = 2:3) over Pd@MIL-101 was conducted and the reaction was completed in 27 min (Pd/NH_3BH_3 molar ratio of ~0.003:1) (Fig. S1), where theoretical maximal amount of hydrogen was generated ($H_2/NH_3BH_3 \approx 3$). When additional nitro compounds were introduced into the reaction system, unexpectedly, the generation of H_2 was greatly accelerated, especially in the initiation stage (Fig. S2). Although the reason behind this phenomenon currently remains unclear, we believe the extremely rapid hydrogen generation kinetics certainly contributes to the boosting reduction of nitro compounds. Moreover, there is clearly a synergistic effect when both the NH_3BH_3 dehydrogenation and nitro compounds reduction are coupled. We also attempted to change the hydrogen source for the reduction of nitro compounds. Strikingly, when ammonia borane was replaced with hydrogen flow while other conditions remained unaltered (with Pd@MIL-101 catalyst pre-reduced by ammonia borane), the reaction was completed after 30 min (entry 14), 20 times slower than that of the above NH_3BH_3-engaged tandem process. Our experiments support that the content of dissolved hydrogen in the reaction solution as well as sufficient contact between hydrogen and nitro compounds jointly control the reduction rate of the nitro group, for which the coupling of in situ dehydrogenation and reduction reactions has been proved to be a very effective approach.

The stability and reusability of catalysts are of great importance for their practical application. It can be seen that the activity, selectivity and framework integrity of Pd@MIL-101 were well retained during six consecutive runs without any treatment or activation for the catalyst (Fig. 3a, S3), clearly demonstrating the recyclability and reusability of the catalyst. In addition, the Pd NPs remain high dispersion and their sizes are almost retained even after 6 runs, revealing the good confinement effect of MIL-101 based on its porous structure (Fig. 3b). The ICP-AES result shows negligible Pd species can be detected in the reacted solution, which reveals the leaching of active sites almost does not occur during the reaction.

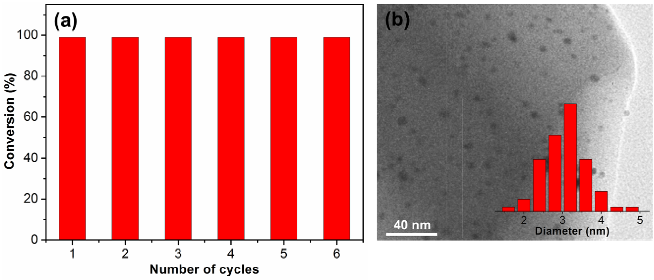


Fig. 3 (a) Catalytic recyclability of Pd@MIL-101 for tandem reactions of ammonia borane dehydrogenation and nitrobenzene hydrogenation. Reaction conditions: 0.4 mmol nitrobenzene, 0.875 mmol NH_3BH_3, 34 mg 0.86 wt% Pd@MIL-101, 8 mL MeOH, 12 mL H_2O, 25 ^oC; only 1.5 min for each in all 6 cycles. (b) TEM image for Pd@MIL-101 catalyst after 6 catalytic runs. Inset: size distribution for Pd NPs in Pd@MIL-10 after 6 cycles of tandem reactions.

In summary, a tandem process has been developed to successfully improve the reaction rate of the hydrogenation of nitro compounds by coupling with the hydrogen generation from NH_3BH_3. The tandem reaction exhibits exceptionally high activity, selectivity and recyclability. The key to the success are ascribed to: 1) the presence of fine and highly active Pd NPs, which were obtained by rational incorporation of Pd^{2+} into MIL-101 via DSA followed by in situ reduction with NH_3BH_3; 2) the extremely rapid kinetics of hydrogen generation from NH_3BH_3 enables the generation of local high-concentration hydrogen dispersed throughout the reaction system, which greatly facilitates the contact between hydrogen and nitro compounds, thus boosting the reaction rate. A variety of aliphatic and aromatic nitro compounds with different groups were able to be reduced to the respective primary amines with excellent conversion yields (>99%) in very short reaction time (1.5-5 min). Six consecutive runs of the tandem catalysis unambiguously demonstrate the great stability and recyclability of Pd@MIL-101 catalyst. Compared to other reported reduction systems for nitro compounds, the current tandem manner does not require stored/pressurized hydrogen and it is therefore not only more efficient but also much safer. We envision the strategy with tandem catalysis in this work opens an avenue to the improvement of catalytic efficiency for other related reactions.

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Notes and references

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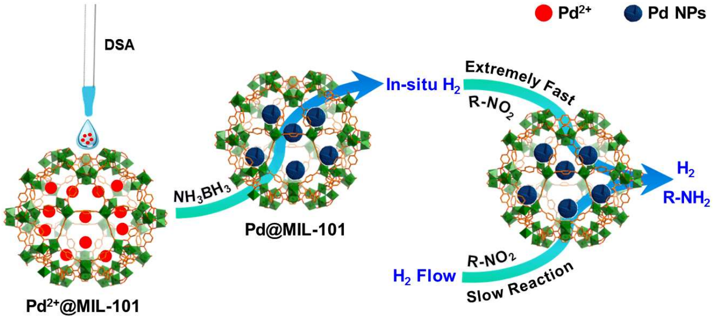
Graphical Abstract



The hydrogenation efficiency of nitro compounds is greatly boosted by coupling with ammonia borane dehydrogenation over rationally synthesized Pd@MIL-101 with Pd NPs in ~3 nm.