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ARTICLE

Maximizing Hydrogen Utilization Efficiency in Tandem Hydrogenation of Nitroarenes with Ammonia Borane

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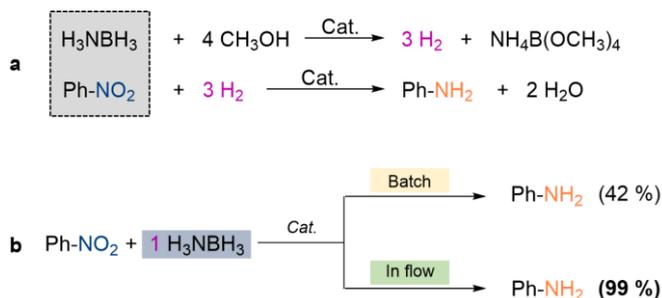
Tandem catalysis involving simultaneous dihydrogen generation from a hydrogen carrier and substrate reduction on a heterogeneous catalyst provides unique opportunities for green chemistry synthesis under mild reaction conditions. However, in traditional batch conditions for nitro reductions, excess hydrogen is often necessary to achieve full conversion and thermal management on scale-up is a safety issue due to large heats of reaction and adiabatic temperature rise. Herein, we report a continuous-flow strategy to maximize hydrogen utilization efficiency (HUE) and improve reaction safety in tandem nitro-reduction reactions, using stoichiometric amounts of ammonia borane (AB) in methanol as the hydrogen source with Pd/C catalyst. This strategy provides a full conversion of nitrobenzene to highly pure aniline in 15 s, with only air cooling needed. In comparison, a batch reaction with stoichiometric AB only reaches a 42 % yield of aniline over Pd/C after 30 min. The space-time yield of aniline in a flow system ($92.07 \text{ g}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$) is substantially higher than that in a batch reaction ($0.13 \text{ g}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$). The tandem reaction set in a flow configuration was simulated with commercial software (Aspen Plus v8.8) enabling scale-up, safe operation, and optimization of energy use. Our tandem flow system with a full HUE, good thermal management, and excellent catalytic efficiency provides a practical way for the green chemistry synthesis of anilines.

Introduction

Ammonia borane (AB, NH_3BH_3) is attractive for hydrogen storage and transport because it is not toxic, has a high hydrogen content (19.6 wt %), and is a solid at room temperature.¹⁻³ AB is readily soluble in polar solvents and has been explored as an energy carrier.^{4, 5} Hydrogen (H_2) can be easily generated from AB by hydrolysis or alcoholysis (**Scheme 1a**) in solution, or thermal decomposition in the solid state.⁵⁻¹³ Moreover, AB can be regenerated from the dehydrogenated product.¹⁴⁻¹⁷ Transition-metal catalysts, such as Pd, Pt, and Ni nanoparticles (NPs), are active in catalyzing not only AB hydrolysis/alcoholysis but also the hydrogenation of organic compounds. Thus, combining AB dehydrogenation with organic hydrogenation using heterogeneous catalysts has sparked enormous interest for green chemistry synthesis because the usage of pure H_2 and harsh reaction conditions can be avoided.¹⁸⁻³⁰ Generating H_2 in-situ during the reaction avoids H_2 transportation, handling, and storage, allowing for reduced capital cost and enhanced safety. In addition, it avoids the gas-

liquid mass transfer with associated coefficient k_{La} [1/s] from the headspace of a traditional vessel,³¹ as the H_2 is generated at the reactive site of the catalyst exactly where it is needed.

Hydrogenation of aryl nitro compounds is an important step in producing aromatic amines in the synthesis of pharmaceuticals, dyes, polymers, and fine chemicals.³²⁻³⁴ Tandem nitro-reduction with AB is widely used for amine synthesis, typically under ambient conditions.^{18, 19, 21} Theoretically, one equivalent (equiv) of the nitro group only requires one equiv of AB to achieve full conversion to the amine group (**Scheme 1a**). In practice, however, due to the speed of AB dehydrogenation and the low solubility of H_2 in water/alcohol,³⁵ the in-situ generated H_2 will quickly escape from the solution into the headspace of the reactor.³⁶ Thus, AB-catalyzed hydrogenation reactions generally require excess AB (*ca.* three equiv) to achieve a high conversion of the substrates,



Scheme 1. (a) Tandem hydrogenation of nitrobenzene with AB (b) under batch and flow conditions.

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Table 1. Tandem hydrogenation of nitrobenzene to aniline under different conditions.

Entry	Cat.	Method	AB (equiv.)	Concentration (mmol)	Inlet flow rate (mL/min)	Time	Yield (%)
1		Batch	1	100	/	30 min	42
2			3	100	/	30 min	91
3	Pd/C	Flow	1	100	1	15 s	99
4			1	250	1	15 s	99
5		Flow	1	250	2	7.5 s	92
6			1	500	1	15 s	87
7*		Batch	3	100	/	30 min	97
8	CuNi NPs		1	100	/	30 min	38
9		Flow	1	100	0.1	2.5 min	90

Reaction conditions: 298 K, ambient pressure. For the batch reaction: nitrobenzene (1 mmol), metal catalyst (1 mole % metal), methanol (10 mL). Yields were determined by GC-MS using 1,3,5-trimethoxybenzene as an internal standard.

which leads to inefficient use of AB (see **Table S1**).^{18-20, 28, 29} For example, when Sun *et al.* studied the effect of AB/nitrobenzene ratio on tandem nitro-reduction with NiPd NPs as the catalyst,¹⁸ the yield of aniline was poor (~10%) with one equiv of AB, but increased to 99% with three equiv of AB. Tandem hydrogenation with AB has attracted great interest as a methodology, yet the waste of the excess AB is a concern due to its high cost (~\$1000/kg estimated from Boron Specialties, Ambridge, PA). Thus, finding a new strategy to maximize the AB utilization is economically desirable for developing technology surrounding AB as a hydrogen carrier.

Xu *et al.* developed a system where hydrogen loss was minimized via the usage of emulsion microreactors, reaching almost full hydrogen utilization efficiency (HUE) in the tandem hydrogenation of alkenes with AB.³⁶ Nevertheless, this approach is synthetically complex, requires long reaction times (up to 18 hours), and excess of styrene in relation to AB, hindering its viability for an easy scale-up.

For nitro-reduction under batch conditions, heat management is an important safety concern, especially in large-scale and high-concentration synthesis.^{37, 38} The heat of the nitrobenzene hydrogenation to aniline is 560 kJ/mol,³⁸ which can raise the reaction temperature quickly, cause safety issues, and lead to undesired side reactions like nitrobenzene decomposition.^{38, 39} AB dehydrogenation is also exothermic,^{2, 40} so, well-regulated heat transfer is essential for safety management in the tandem hydrogenation of nitroarenes.

Here, we report a green strategy that maximizes HUE and improves reaction safety in the tandem hydrogenation of nitroarenes (-NO₂) with a stoichiometric amount of AB in a continuous-flow fashion over Pd/C (**Scheme 1b**). The reactions

are completed within 15 s and give high conversions (99%) to anilines under ambient temperature and pressure. In comparison, the batch hydrogenation of nitrobenzene with one equiv of AB only achieves a 42% conversion after 30 min. With its easily transportable and storable hydrogen source AB, mild reaction conditions, enhanced reaction safety, and reduced waste of AB, the method fulfills the essential pillars of the 12 principles of Green Chemistry devised by Anastas and Warner and is a promising addition to the catalytic portfolio of AB.⁴¹

Results and discussion

We first investigated the tandem nitro-reduction with AB on Pd/C (10 wt %) catalyst under both batch and flow conditions. Methanol, which dissolves both AB and the substrates, was chosen as a solvent due to its lower boiling point for easy and energy-efficient separation. Also, methanol combines a favourable EHS indicator score with a low cumulative energy demand (CED),⁴² and will also be industrially available from direct CO₂ reduction in the near future.⁴³ Nitrobenzene was selected as a model to optimize the reaction conditions. In the batch reactions, the catalyst loading was usually around 0.5 – 5 mol % of the substrates.^{18-21, 24, 25} As shown in **Table 1 (entry 1)**, commercial Pd/C (1 mol %) gave only a 42% yield of aniline with one equiv of AB after 30 min at ambient conditions. Increasing the amount of AB to three equiv increased the yield to 91% (**Table 1, entry 2**).

To conduct the reaction in a continuous flow, a Pd/C catalyst was packed into the reaction column (see **Fig. S1a**), preventing the H₂ from being released into the atmosphere, and ensuring full H₂ consumption. Solutions containing PhNO₂, AB, and an

reactor column (H-Cube Mini Plus) is 22 mm in length and has a 3.8 mm internal diameter. The column was charged with 80 mg of catalyst, which filled the reactor volume. Under the conditions tested, the flow was creeping and laminar at 1.0 mL/min ($Re=7.9$) and the mass transfer approached a lower limit relative to the molecular diffusivity. The low superficial velocity (0.14 cm/s) is a unique feature of this flow reactor profile which may improve the observed reaction reproducibility by suppressing turbulence and limiting dispersion, with an advection mechanism being prominent in the direction of flow. The high surface-to-volume of this reactor as well as its steel construction allows it to dissipate heat well. Notably, for the reaction conditions in **Table 1, entry 4**, the adiabatic temperature rise predicted for complete conversion is 70 K, which would raise the reaction temperature above the boiling point of methanol; heating was well mitigated through the heat sink of the metal reactor. Running a reaction under the same conditions in a large batch reactor could be dangerous (70K in 15 sec), whereas, in the miniature flow reactor, the heat was dissipated with air-cooling. Not only is safer, it saves energy costs.

To study the reaction kinetics of the flow tandem reduction of nitrobenzene, we reduced the amount of the Pd/C catalyst to 10 mg and increased the concentration of nitrobenzene to 1000 mM to lower the conversion of nitrobenzene. We ran the flow reaction at different flow rates to control the residence (reaction) time (**Fig. 2**). For example, the residence time was 5 s when the flow rate was 3.0 mL·min⁻¹, and increased to 30 s when the flow rate was decreased to 0.5 mL·min⁻¹. **Fig. 2a** shows a linear increase in the conversion of nitrobenzene with an increase in the reaction time, indicating that the reaction is of zero order in nitrobenzene under our standard conditions, suggesting that the surface of the Pd/C is saturated with in-situ generated H₂ molecules. The observed zero-order kinetics implies that the reactions are limited by the amount of available catalysts surface. Besides aniline, azoxybenzene (5 %) was detected as another product at 7.5 min (flow rate: 2.0 mL·min⁻¹) and then disappeared at 15 min (flow rate: 1.0 mL·min⁻¹).

For a better understanding of the reaction kinetics, the reaction was modeled in Aspen+ v8.8 simulation software using a plug flow reactor model. The kinetic parameters were estimated based on a best fit to the experimental data, assuming that the primary reaction rates are surface limited reactions using Langmuir Hinshelwood kinetics (**Fig. 2a**). Compared with the experimental data indicating apparent zero order kinetics, the simulation result shows a slight curvature due to adsorption term in the denominator of the rate expression. This kinetic framework can be used to scale up the reactor to industrial production scenarios, and was used to calculate the adiabatic temperature rise of 70K for a reactor with no cooling. This model can be used for reactor design, scale-up, process safety analysis, and also energy minimization vis a vis cooling requirements. The details of the equations and model framework are provided in the supplemental information. As AB enters the reactor, an initial burst of hydrogen production is expected, followed by a decay in hydrogen quantity as it is consumed. High conversions at

stoichiometric hydrogen indicate that both reactions are essentially irreversible, with the reduction of the nitrobenzene to aniline being driven by hydrogen saturation in the liquid phase for the majority of the reaction progress. A reaction profile of the overall mole fractions of the components, including liquid and gas phases, vs. reactor path length is provided in **Fig. 2b**.

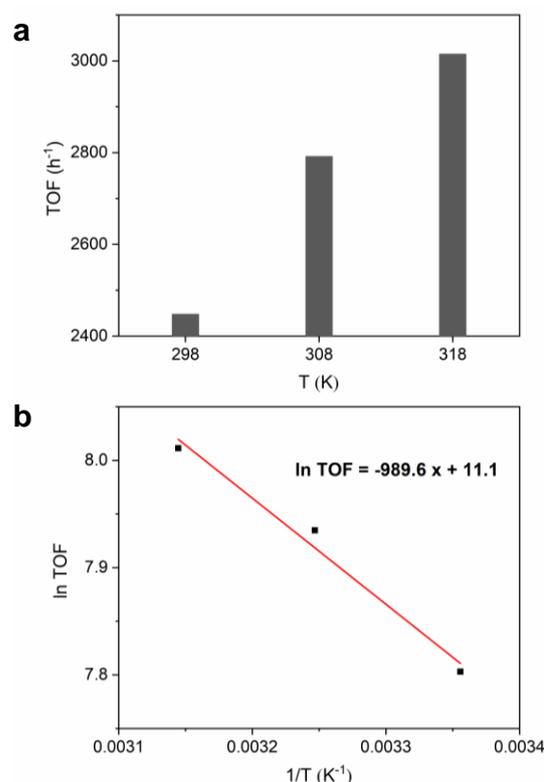


Fig. 3 (a) TOF values for tandem nitrobenzene hydrogenation at different reaction temperatures (b) The related Arrhenius plot, $E_{app}=8.2$ kJ/mol. Nitrobenzene: 1000 mM, Pd/C: 10 mg.

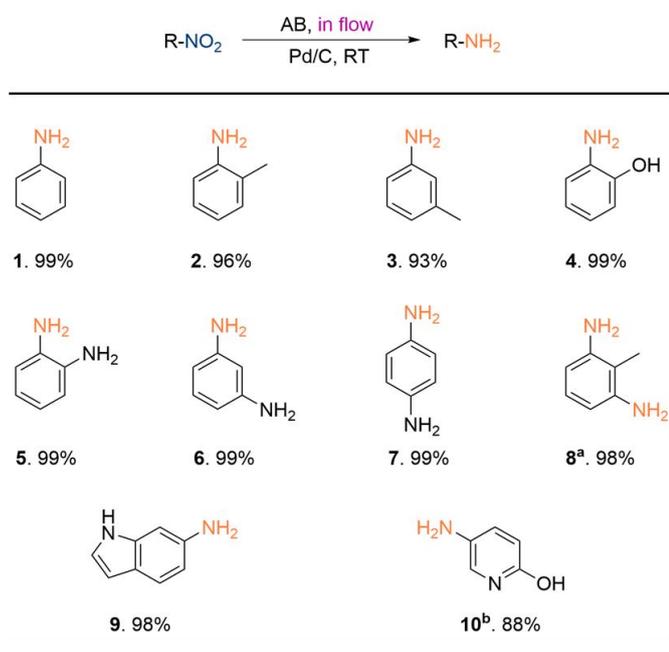
Reaction kinetics at different reaction temperatures were further studied. **Fig. 3a** shows the turnover frequency (TOF) values calculated at different reaction temperatures (298 K, 308 K, and 318 K). The TOF values increased with the temperature. A linear Arrhenius plot was observed, yielding an activation energy of 8.2 kJ/mol in the range of 298 – 318 K (**Fig. 3b**).

Besides noble metal catalysts, several first-row elements, such as Ni, Cu, and Co, can heterogeneously catalyze AB dehydrogenation and organic hydrogenation reactions.^{9, 11, 21} We reasoned that the stoichiometric tandem hydrogenation in a flow system could be extended to non-noble catalysts. Yu *et al.* found that CuNi NPs exhibited high catalytic activity for both AB methanolysis and nitro-reduction in batch reactions with three equiv of AB (**Table 1, entry 7**).¹⁹ We synthesized the same CuNi catalyst¹⁹ (see **Fig. S2**) and tested its ability to catalyze the reaction with only one equiv of AB. It exhibited a low yield of aniline (38 %) in the batch reaction (**Table 1, entry 8**), but the yield increased to 90 % in a flow system, suggesting

stoichiometric tandem hydrogenations have great potential with other non-noble metal catalysts.

To explore the substrate scope for this reaction, other nitro aromatics were hydrogenated using stoichiometric AB with Pd/C in our flow system (**Scheme 2**). All these compounds were converted into their respective primary amines in high yields within 15 s at ambient conditions (**Scheme 2, products 1-10**). In the case of 2,6-dinitrotoluene, both nitro groups were fully reduced to NH₂ groups (**8**) with only two equiv of AB. Good yields were obtained with heteroaromatic compounds such as indole (**9**) and pyridine (**10**). Although there have been many reports of nitrobenzene hydrogenation in a continuous-flow reactor,⁵⁴⁻⁵⁷ our reaction occurs in quantitative yield with stoichiometric reductant for the first time, maximizing the effectiveness of AB by carefully controlling the catalytic conditions. To further improve the overall HUE of our system, we propose a green chemistry route for facile product separation and starting materials recovery, shown in **Scheme S1**. After the tandem hydrogenation, methanol can easily be recovered and recycled by distillation. Anilines can be separated from the AB methanolysis product by extraction, and AB can be regenerated from the methanolysis product.^{14, 15} Aniline can be produced on a gram scale within an hour and is easily purified via extraction. In all, our flow catalysis provides a general way to maximize the HUE in the tandem hydrogenation of nitro compounds with AB. Both TEM and XRD results show that the Pd/C catalyst is stable and reusable under the flow reaction

Scheme 2. Stoichiometric hydrogenation of nitroarenes with AB in flow.



Reaction conditions: Substrate (250 mM in methanol), AB (1 equiv), inlet flow rate (1 mL·min⁻¹), 298 K, ambient pressure. ^aConcentration (125 mM), AB (2 equiv) ^bConcentration (125 mM), AB (1 equiv). Yields were determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard.

conditions, without any noticeable structural and morphological changes after the reactions (**Fig. S3-S4**).

Conclusions

In summary, a highly efficient continuous-flow green synthesis of anilines has been developed to maximize the catalytic efficiency and HUE of the tandem hydrogenation of nitro compounds with AB. A series of nitro compounds can be reduced to primary amines with one equiv of AB in 15 seconds, using a commercial Pd/C catalyst under ambient conditions. In contrast, 3 times the amount of AB is required to achieve quantitative conversion in the batch reaction after 30 min. The space-time yield in the flow reaction is over 700 times higher than that in the batch reaction. A plug flow reactor model was created and fit to experimental data in commercial software (Aspen+ v8.8) enabling reactor design, thermal management, scale-up, and safer and more efficient operations. Our new “green” route is not limited to Pd/C but extends to other transition-metal catalysts, such as Cu, Ni, Co, and their alloys, that are active for both AB dehydrogenation and nitro compound hydrogenation reactions.

Author Contributions

M.S.[‡] and C.B.[‡] contributed equally to this study. M.S. and C.B. conceived the project. A.J.M. and J.R.N. supervised the research. M.S. and C.B. designed and carried out all the experiments on the main manuscript. M.S., C.B., and H.B.V. analyzed the experimental results. P.T.K. contributed to the Aspen+ modelling. M.S. and C.B. composed the manuscript and the Supplementary Information Section. All authors discussed the results and commented on the manuscript. All authors have approved the final version of the manuscript.

Conflicts of interest

The authors declare no conflicts of interest.

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