



## Review

## Review on selective hydrogenation of nitroarene by catalytic, photocatalytic and electrocatalytic reactions

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## ABSTRACT

Selective catalytic hydrogenation of nitroarenes is of great importance for dyestuff and pharmaceutical industry. A critical step toward the rational design of targeted catalysts is to determine their electronic structures and related reaction mechanism. In this review, we summarize the breakthroughs on the development of multiple catalytic technologies in the past decade, including direct hydrogenation using high-pressure hydrogen; transfer hydrogenation using reductive compounds; photocatalytic hydrogenation using hole scavenger; electrocatalytic hydrogenation accompanied with water oxidation. We focus on how to understand the two key element steps including hydrogen dissociation and the activation of nitro group in the process of hydrogenation, and design and fabricate nanostructured catalysts with desired activity and selectivity. For direct catalytic hydrogenation, representative catalysts include metal, metal oxide/sulfide/carbides/nitrides/boride, and functional carbon material, and the crucial factors to tune their activity and selectivity are discussed such as metal-support interaction, size effect, alloy effect, defect engineering, and so on. Catalytic transfer hydrogenation, photocatalytic and electrocatalytic hydrogenation, in which these catalysts abstracts hydrogen species from the hydrogen donor and stabilizes it on the catalyst surface, restricting active H<sup>\*</sup> recombination, and then the active hydrogen species can be promptly transferred to nitroarenes for the hydrogenation. It is worth mentioning that the light harvesting and charge separation of photocatalyst and the conductivity of electrocatalyst should also be considered together for the overall performance. All these experiences lay the foundation for large scale production of anilines and guide the rational design of catalysts for other organic transformation reactions.

## 1. Introduction

The transformation of nitroarenes to anilines is of great importance because anilines are among the most important intermediates necessary for dyestuffs and pharmaceuticals in chemical industry [1–5]. Currently, the commercial production of functionalized anilines mainly depends on non-catalytic reduction of nitroarenes using stoichiometric reducing agents such as sodium hydrosulfite, iron, tin or zinc in ammonium hydroxide [6]. Such processes, however, have serious environmental issues and suffer from poor selectivity. Therefore, the development of more efficient, selective and environmentally friendly process to produce anilines is important for both fundamental studies and industrial applications.

Catalytic hydrogenation using high-pressure hydrogen with supported precious metal such as Pt as catalyst is a preferred choice [1]. Nevertheless, the selective hydrogenation of nitro groups but not functional groups (e.g., –OH, –Cl, –C=O, –C=C) remains a great

challenge. Corma et al. reported a breakthrough with regard to functional-group tolerance using Au/TiO<sub>2</sub> as catalyst, exhibiting selectivity of over 95% for hydrogenation of nitro group in 3-nitrostyrene, 4-nitrobenzaldehyde, 4-nitrobenzotrile, and 4-nitrobenzamide [2–5]. They attributed the high selectivity to the metal/support interface of catalyst that regulates the adsorption to preferentially activate –NO<sub>2</sub> group. Still the high-cost and limited availability for Au also stimulate numerous efforts in seeking earth-abundant, highly active and stable catalyst with excellent selectivity. In the past decade, many significant and encouraging breakthroughs on non-noble metal catalysts have been made for highly-efficient selective hydrogenation of nitroarenes to anilines. For example, Beller et al. reported catalysts based on abundantly available transition metals, such as Fe, Co and Ni, can mediate selective hydrogenation of nitroarenes efficiently [7–9]. Also, Zhang et al. found atomically dispersed single-atom Co in form of Co–N–C is very active and selective for this reaction. DFT calculations have conducted to explain and predict the reactivity and selectivity of the catalysts, mainly

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by estimating the adsorption and dissociation energy of reactant on catalyst surface [10–15]. Besides, some analytical and characterization techniques including Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray absorption/diffraction, Mössbauer spectroscopy and so on, allow us to monitor the reaction pathway in situ and confirm the actual active phase/intermediates during the catalytic process [16–19].

Catalytic transfer hydrogenation using hydrogen donors like hydrazine, formic acid, or  $\text{NaBH}_4$  are also very attractive, because it can be performed in a convenient manner without the requirement of high-pressure equipment and avoid sluggish  $\text{H}_2$  activation dynamics. Similarly, photocatalytic and electrocatalytic hydrogenation of nitroarenes under room temperature and atmosphere have recently attracted increasing attentions, which can be driven by solar energy, or solar-, wind- and other renewable resources-derived electricity. In these processes, catalysts are also very necessary to adsorb and activate the nitro groups for proton-coupled electron transfer.

This review describes recent progress on the development of multiple catalytic technologies and design and synthesis of corresponding nanostructured catalytic materials towards selective catalytic hydrogenation of nitroarene. The fundamentals of direct catalytic hydrogenation of nitroarene to aniline including reaction mechanism are first introduced. Then we summarize various types of nanostructured catalysts for catalytic and selective hydrogenation of nitroarenes including metal, metal oxide, sulfide/carbides, nitrides and boride, and functional carbon material. The crucial factors determining the activity and selectivity are discussed, including (1) metal-support interaction, size effect, single-atom catalyst, alloy effect, shape-selective catalysis, strain effect, and interfacial adsorbent-metal interaction of metal; (2) defect engineering and metal oxide/N-doped carbon interaction of metal oxide; (3) interfacial electronic effect of carbon material. All these strategies can tune and optimize the production of reactive hydrogen species and preferential adsorption of nitro group of nitroarenes. In addition, catalytic transfer hydrogenation using reductive compounds such as hydrazine,  $\text{NaBH}_4$ , alcohols and formic acid, photocatalytic hydrogenation using hole scavenger and electrocatalytic hydrogenation accompanied with water oxidation are also reviewed from the aspects of reaction mechanism, design and performance of catalysts.

## 2. Fundamentals of catalytic hydrogenation of nitroarene

### 2.1. Reaction mechanism

More than 100 years ago, Haber et al. proposed a reaction network (Fig. 1a) for the hydrogenation of nitrobenzene and substituted nitrobenzene [20], in which nitrosobenzene, phenylhydroxylamine,

azobenzene, azoxybenzene, and hydrazobenzene are potential intermediates. They assumed there are equilibria between these species in solution and reversibly adsorbed on the surface of solid catalysts (both the active phase and the support). This mechanistic scheme is an excellent basis to describe how the catalytic hydrogenation proceeds. Usually, only the starting nitroarene, nitroso, hydroxylamine, and aniline products are detected in solution, which is recently confirmed by several kinetic studies by applying online Raman and IR spectroscopic techniques [20]. The nitroso intermediate typically presents in very trace concentration, and hydroxylamine concentration varies considerably depending on such factors as substrate structure, reaction temperature, hydrogen pressure, solvents, catalysts, and pH value. The reaction profile indicates a fast reduction of nitro group to nitroso intermediate that are adsorbed very strongly on metal surface and hydrogenated to hydroxylamine very quickly, and the hydrogenation of hydroxylamine to aniline is the rate-determining step. Condensation to azo and azoxy products does not occur usually, except when a strong base is present, via the intermolecular dehydration between nitrosoarenes and hydroxylamine (Fig. 1a).

In addition to the Haber mechanism, Jackson et al. found that the reaction profiles are different when nitrosobenzene is used as a starting substrate, indicating the nitroso species is not an obligatory intermediate and there might be a direct pathway from nitro group to hydroxylamine [2,21–23]. However, the evidence is rather circumstantial, and no proposal has been made as to how the addition of four H atoms to the nitro group and the loss of one  $\text{H}_2\text{O}$  could proceed in one step. They considered  $\text{Ph-N(OH)}$  as a common intermediate (Fig. 1b) in nitrobenzene hydrogenation, and then it directly reacts with adsorbed H to produce  $\text{Ph-NH}$  (accompanied by dehydration) and final  $\text{PhNH}_2$ . However, the  $\text{Ph-N(OH)}$  intermediate reacts with itself to eliminate water and mainly produce azoxybenzene in nitrosobenzene hydrogenation. As a result, nitrosobenzene as starting substrate has a slower rate of aniline formation.

### 2.2. Advantages and challenges

Noncatalytic reduction of nitroarenes with stoichiometric reducing agents, such as sulfides, Fe, and Zn, is widely used to produce functionalized anilines in industry [20]. However, these processes generate large amount of waste acids and residues, leading to serious environmental problems. In contrast, catalytic hydrogenation with the supported catalysts is environmentally benign and highly efficient [5,9,24]. Due to the enormous potential rewards, extensive studies have been done for nitroarenes hydrogenation. However, up till now, few catalysts have met the requirements for practical use. Several scientific challenges still remain, such as:

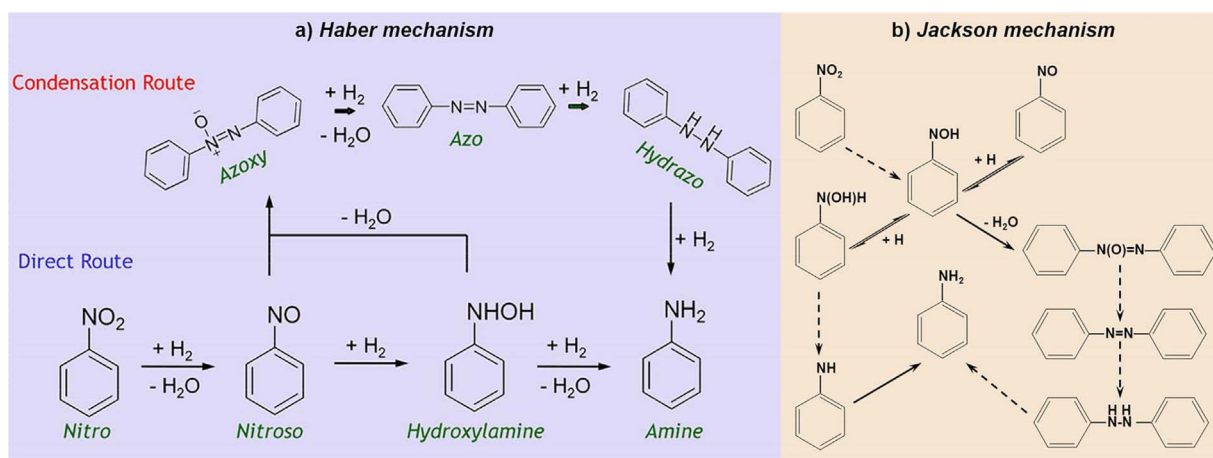


Fig. 1. (a) Haber mechanism for hydrogenation of nitrobenzene. (a reproduced from Ref. [20] with permission. Copyright 2015, American Chemical Society) (b) Jackson mechanism for hydrogenation of nitrobenzene. (b reproduced from Ref. [21] with permission. Copyright 2005, Royal Society of Chemistry).

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