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# Chemoselective hydrogenation of nitrobenzenes activated with tuned Au/h-BN

Qiuwen Liu<sup>a,b</sup>, Yan Xu<sup>a</sup>, Xiaoqing Qiu<sup>a,\*</sup>, Caijin Huang<sup>b,\*</sup>, Min Liu<sup>c,\*</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, Central South University, Changsha 41083, PR China

<sup>b</sup> State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350116, PR China <sup>c</sup> College of Physical Science and Electronics, Central South University, Changsha 41083, PR China

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# ABSTRACT

The azo- and hydrazo compounds are of great importance in pharmaceuticals, agrochemicals, and chemistry. The controlled reduction of nitroarenes to their coupled products such as aromatic azo and hydrazo compounds has been an interesting area of research synthetically and mechanistically. Herein, we report that the chemoselective catalytic hydrogenation of nitrobenzenes to hydrazobenzenes via azobenzenes can be achieved over gold nanoparticles supported by hexagonal boron nitride nanoplates. It is found that the catalytic process can be successfully conducted not only in N<sub>2</sub> but also in air with isopropanol alcohol/ KOH. Complete conversion of nitrobenzenes and high selectivity of azobenzenes and hydrazobenzenes have been achieved in one pot under N<sub>2</sub> or air atmosphere. Furthermore, as usual unstable intermediates in the reduction process of nitrobenzenes, azobenzenes and hydrazobenzenes can be alternatively harvested as the main product by controlling reaction time or atmosphere. This work shows promise for direct and chemoselective synthesis of azo- and hydrazo compounds under mild conditions in a controllable manner.

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## 1. Introduction

The yield of the target product is always a key topic for organic reactions and their industrial applications [1–3]. In particular, how to improve the selectivity of the aromatic azo- and hydrazocompounds from the hydrogenation of nitroarenes has long been a challenging issue, since the azo- and hydrazo-compounds play essential roles in the production of food additives, polymers, pharmaceuticals, herbicides and dyes [4,5]. Generally, azo- compounds are prepared by reducing nitroaromatics or oxidizing anilines through the azo coupling reaction using nitrite salts [6,7] or toxic oxidants [8]. On the other hand, as compared with azocompounds, the hydrazo-substrates are frequently obtained by reducing azo- or azoxybenzene with Zn or Al powder [9-11] or by electrochemical reduction of nitroarenes using Pb-containing electrodes [12,13]. Few synthetic methods threw the spotlight on the hydrazo-compounds in the process of hydrogenation of nitroarenes likely due to their instability and extremely low yield [14,15]. The aromatic hydrazo- as well as azoxy-compounds are commonly regarded as unwanted by-products in the most reduc-

\* Corresponding authors.

tion reactions of nitroaromatics to azo-derivatives, which brings the tedious product separation. Therefore, it will be extremely desirable to realize the conversion of nitrobenzenes to azobenzenes or hydrazobenzenes controllably in one pot with good selectivity and yield.

The conversion efficiency and selectivity of organic reactions can be controlled with the assistance of the suitable catalysts [2,4,16,17]. The Pt and Pd catalysts modified with harmful additives (e.g. Pb and V) have been found to improve the selectivity of the hydrogenation of nitrobenzenes under harsh reaction conditions of high temperature and high pressure [18]. Comparatively, gold (Au) has long been considered to be less catalytically active until Bond et al. reported the hydrogenation of olefins over supported Au catalysts [19]. Henceforth, the supported Au catalysts are actively pursued in the reduction of nitrogen oxides and the hydrogenation of organic compounds [4]. For instance, Corma and co-workers reported that the Au nanoparticles supported on TiO<sub>2</sub> exhibited up to 98% yield for the selective hydrogenation of nitroarenes into the corresponding aromatic azo- compounds [20]. Zhu et al. further proposed a photocatalytic pathway for the reduction of nitroaromatic compounds into aromatic azo- compounds over Au supported on ZrO2 utilizing isopropyl alcohol (IPA)/KOH as hydrogen source [21]. Moreover, the Au nanoparticles supported on meso-CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and other oxides, have also







*E-mail addresses:* xq-qiu@csu.edu.cn (X. Qiu), cjhuang@fzu.edu.cn (C. Huang), minliu@csu.edu.cn (M. Liu).

been demonstrated to be active in the reduction of nitro group of organic compounds [22,23]. As a matter of fact, the reaction pathways and yield of the nitrobenzenes hydrogenation are highly depend on the both Au particle size and the nature of the support [22,24]. The oxides supporters can generally activate the oxygen in the reaction system. Consequently, selectively catalytic reduction of nitrobenzene over the oxides supported Au catalysts is frequently performed under poor oxygen conditions, *i.e.* N<sub>2</sub>, H<sub>2</sub> or CO atmosphere, thereby increasing the cost and potential danger in industrial practice [14,25,26]. Thus, it is quite urgent to find novel materials to support Au nanoparticles and endow the catalysts with high selectivity for hydrogenation of nitrobenzene even under the air atmosphere. Unlike the conventional oxides, hexagonal boron nitride (h-BN) is a non-oxide compound constructed from lightweight and abundant elements. h-BN possesses outstanding physicochemical properties such as atomically smooth surfaces, nontoxicity, chemical and thermal stability, and thermal conductivity [27,28]. What's more, as a layered two-dimensional material structurally analogue to graphite/graphene, h-BN can provide a platform to support the metallic nanoparticles and offer the "naked" nanoparticle surfaces with highly active sites [29–31]. Our previous work demonstrated that h-BN serves as an excellent plane-like support for functional nanoparticles used as catalysts, rendering an improved catalytic performance [29,32].

Herein, we report that chemoselective hydrogenation of nitrobenzene to azobenzene and hydrazobenzene can be achieved catalytically in one pot under nitrogen or air atmospheres. The reaction was catalyzed over Au nanoparticles supported on h-BN nanoplates (noted as Au/BN) in the presence of IPA/KOH. We attempt to perform the reduction reaction in an industrial-favourable and controllable manner in order to directly harvest azobenzene or hydrazobenzene as the main final product with high selectivity.

## 2. Experimental

## 2.1. Preparation of Au/BN composites

A certain amount of HAuCl<sub>4</sub> (10 g/L) was added to the asobtained h-BN colloid (20.1 mg/mL, 5 mL). 2 mL of lysine (31 mg/ mL) was then added, and the mixture was stirred vigorously for 30 min. 10 mL of aqueous solution of NaBH<sub>4</sub> (3.8 mg/mL) was dropped into the mixture in 20 min. After keeping stirring for 1 h, the sample was left for 16 h in the dark without stirring. The precipitate was filtrated and washed with deionized water and ethanol, and then dried at 60 °C. The resulting sample was defined as x % Au/BN, where x was the Au content in the composites. The details for the sample characterization and catalytic activity test experiments are given as the Supporting Information.

## 2.2. Activity test

Nitrobenzene (0. 31 mmol) and 0.06 mmol KOH were dissolved in 3 mL isopropyl alcohol. 10 mg catalyst (Au/BN composites) was added to the mixture. The reaction was carried out in nitrogen or in air at 90 °C under stirring unless otherwise specified. The products were analyzed using an Agilent 7820A GC equipped with HP-FFAP column and a Varian Cary 500 Scan UV–Vis spectrometer.

## 2.3. Characterization

The actual contents of Au for the as-obtained Au/BN composites analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Powder X-ray diffraction (XRD) patterns were obtained at room temperature on a Bruker D8 Advance diffractometer with Cu kα1 radiation. Fourier transform infrared spectra (FTIR) were collected on a nicolet 670FTIR spectrometer using KBr as a transmission standard and a diluting reagent. UV–Vis spectra were recorded on a Varian Cary 500 Scan UV–Vis system. Raman spectra were acquired on a Renishawnin ViaReflex Raman Microphrobe with 633 nm excitation. The morphologies and microstructures of the samples were investigated by an Agilent SPM5500 Atomic Force Microscope (AFM), filed emission scanning electron microscopy (FESEM) on a Hitachi New Generation SU8100 apparatus and transition electron microscopy (TEM) on a TECNAIF30 instrument under an acceleration voltage of 200 kV. <sup>13</sup>C NMR spectra of final products were acquired using a Bruker Avance III 500 spectrometer equipped with an 11.7 T wide bore superconducting magnet, at Larmor frequencies of 500 MHz for <sup>13</sup>C.

# 3. Results and discussion

#### 3.1. Nanoparticle composition and morphology

The h-BN powder samples were prepared by thermal decomposition of the mixture of boron oxide and urea in the presence of copper nitrate according to the methods in our previous literatures [33,34]. The FESEM, TEM, and AFM images (Fig. S1 and Fig. S2) show that the h-BN samples exhibit a plate-like shape with the average diameter of 50-70 nm and ca. 2 nm in thickness. Au nanoparticles are loaded on h-BN nanoplates by reducing HAuCl<sub>4</sub> with NaBH<sub>4</sub> in the presence of lysine. The intensities of XRD peaks corresponding to Au increase with the increased amount of Au (Fig. 1a). The X-ray photoelectron spectroscopy (XPS) signals at 87.8 and 84.2 eV are attributed to Au  $4f_{5/2}$  and Au  $4f_{7/2}$  [21], respectively, suggesting Au exists in metallic state (Fig. 1b and Fig. S3). The diffusion reflectance spectra and Raman spectra of the samples are presented in Fig. S4. The optical absorption in the range 500-600 nm is owing to the localized surface plasmon resonance of Au nanoparticles [35] (Fig. S4a). A slight redshift of the B–N transverse stretching vibration (about 1380 cm<sup>-1</sup>) demonstrates the interaction of Au nanoparticles and the surface of h-BN nanoplates (Fig. S4b) [36,37]. As shown in Fig. 2 and Fig. S5, Au nanoparticles (average size of 5–6 nm) are well distributed on the h-BN surfaces. Clearly, no obvious difference in the size of Au nanoparticles was observed for 3.7% Au/BN and 20.9% Au/BN, but there is a higher dis-tribution density of nanoparticles for 20.9% Au/BN. As illustrated in Fig. 2b and d, the selected area electron diffraction (SAED) indicates Au nanoparticles have a face-centered cubic phase (FCC) which is consistent with the XRD results (Fig. 1a).

#### 3.2. Optimization of reaction conditions

To investigate the catalytic performance of the as-obtained catalysts in the reduction reaction, nitrobenzene was selected as the substrate to optimize reaction conditions including Au loading, reaction temperature, and atmosphere. As shown in Fig. S6 and Fig. 3, three main products have been observed in our experiments and appeared sequentially from azoxybenzene, azobenzene to hydrazobenzene, which obeys the condensation route of Haber model [38]. No other intermediates, such as nitrosobenzene and phenylhydroxylamine, were observed by GC-MS analyses, implying that conversion of these compounds to azoxybenzene is very fast. It can be clearly seen from Fig. 3 that the conversion of nitrobenzene is up to about ca. 100% within 30 min for the Au/ BN catalysts with Au contents >3.7 wt% in the composites. It should be mentioned that the BN and Au alone exhibited very limited activity for the conversion of nitrobenzene. Moreover, the selectivity for each product (azoxybenzene, azobenzene and hydrazobenzene) is different and varies with the Au content of the catalysts.



**Fig. 1.** (a) XRD patterns of Au/BN samples (the percentage is the mass ratio of Au with h-BN). From left to right, the (0 0 2), (1 0 0), (1 0 1) and (1 1 0) planes of h-BN (JCPDS card No. 34-0421) are marked by the sign ' $\blacklozenge$ ' and the '\*' represents the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of Au (JCPDS card No. 04-0784), respectively. (b) XPS Au core-level spectra of the sample 20.9% Au/BN.



Fig. 2. High-resolution TEM images and selected area electron diffraction of 20.9% Au/BN (a, b) and 3.7% Au/BN (c, d).

The catalyst with 20.9% Au content (noted as 20.9% Au/BN) is the most active for the catalytic complete reduction of nitrobenzene to the final product hydrazobenzene, and thus was selected for further study. The catalysts with Au content over 20.9% exhibit an aggregation of Au nanoparticles, lowering their effective exposed surface and active sites. In addition, we also investigated the effect of reaction temperature on hydrogenation of nitrobenzene using

the catalyst 20.9% Au/BN. The selectivity of the final product hydrazobenzene increases with the temperature and reaches 100% at 90 °C (Fig. S6). Considering the boiling point (82.45 °C) of isopropanol, other temperatures higher than 90 °C have not been attempted.

Fig. 3b shows the evolution for the reduction of nitrobenzene on 20.9% Au/BN at 90 °C. As the reaction proceeds, the selectivity of



**Fig. 3.** (a) Reduction of nitrobenzene over the as-prepared Au/BN samples with different Au contents within 30 min. (b) Reduction of nitrobenzene over the 20.9% Au/BN samples with different time. Top panel: photos of the transformation of nitrobenzene to hydrazobenzene. The reaction was conducted under nitrogen atmosphere at 90 °C for 30 min. Nitrobenzene: NB, azobenzene: AB, hydrazobenzene: AOB.

azoxybenzene decreases from 100% down to almost zero in 15 min. Meanwhile, the conversion of nitrobenzene and the selectivity of azobenzene increase up to 100%. The turnover frequency of 20.9% Au/BN catalyst is calculated to be 212 h<sup>-1</sup>, much higher than that of copper/graphene composites  $(24 h^{-1})$  in the similar experimental conditions [39]. Interestingly, although at the reaction time of 15 min azoxybenzene is completely converted to azobenzene, no formation of hydrazobenzene was observed. The transformation of azobenzene to hydrazobenzene appears to be blocked in the presence of nitrobenzene until all the nitrobenzenes are depleted [40]. For this reason, the conversion of azobenzene to hydrazobenzene could be a rate-determining step during the reduction reaction. Additionally, from the reaction profile, full consumption of nitrobenzene and azoxybenzene are occurred at 15 min without formation of hydrazobenzene, revealing that azoxybenzene is not directly hydrogenated to hydrazobenzene, which is different from the case of direct hydrogenation of azoxybenzene to hydrazobenzene [40]. Furthermore, after 15 min, the accumulated azobenzene tends to be reduced and almost completely converted to hydrazobenzene in 30 min while the solution colour turns from orange-red to colourless (Fig. 3b), showing that hydrazobenzene becomes the main final product at this stage. Therefore, from the product profile the main product azobenzene or hydrazobenzene varies with reaction time, providing a reliable way to harvest azobenzene and hydrazobenzene as expected with high selectivity by monitoring reaction time.

It is worth mentioning that hydrazobenzene cannot be directly detected by gas chromatograph (GC) equipped with FID detector. Fig. S7a gives the GC results of commercial hydrazobenzene (Ark Pharm Co., Ltd.), exhibiting two signals corresponding to aniline and azobenzene, respectively. This is likely due to the instability of hydrazobenzene under redox atmosphere and high temperature within FID detector [20]. Our colourless final product also has two similar signals corresponding to azobenzene and aniline on GC (Fig. S7b), leading to a misunderstanding for the production of aniline. Moreover, the evidence of <sup>13</sup>C NMR spectra proves that neither aniline nor azoxybenzene is formed in the final product but it is hydrazobenzene (Fig. S8), which is different from that reported by Zhu et al. over ZrO<sub>2</sub> supported Au under light illumination [21]. Therefore, the yield of hydrazobenzene presented in this work was evaluated by the Lambert-Beer law with a detection wavelength of 440 nm corresponding to its characteristic peak (Fig. S9). Most importantly, the Au/BN composite also shows high conversion activities in the highly selective reduction of other nitroaromatic compounds to produce the corresponding aromatic azo compounds and aromatic hydrazo compounds (Table 1). Meanwhile, the Au/BN catalyst shows excellent stability (Fig S10).

### 3.3. Mechanism of hydrogenation reaction on Au/BN

Furthermore, to explore the effect of air on the hydrazobenzene, we removed the catalyst and left the solution to be cooled down to room temperature and exposed to air. Interestingly, as seen in Fig. 4, the solution gradually turned from colourless to orangered and the product hydrazobenzene was oxidized to azobenzene in the presence of O<sub>2</sub>, but further oxidation does not proceed. This post-oxidation treatment is also an efficient way to convert hydrazobenzene to azobenzene just by introducing O<sub>2</sub>. Inspired by this case, an interesting question was raised that how the nitrobenzene hydrogenation reaction proceeds in O<sub>2</sub> which is different from that carried out under H<sub>2</sub> or N<sub>2</sub> atmosphere reported by the literature [20,21]. Fig. 5 shows the evolution of the products, demonstrating that the reduction of nitrobenzene to hydrazobenzene can also proceed in air. By comparing with the results depicted in Fig. 3, the existence of  $O_2$  obviously slows the reaction rate, such as a delay on the formation of hydrazobenzene, and lowers the final yield of hydrazobenzene. This is due to the presence of O<sub>2</sub> resulting in the consumption of activated Hydrogen (H-Au) and the oxidation of hydrazobenzene (Fig. 6). The main product azobenzene or hydrazobenzene can also be controlled by reaction time under O<sub>2</sub> atmosphere (Fig. 5). In addition, in our work the selectivity of the nitro reduction tuned in favor of azo- and hydrazo products might be due to the synergic effect between the metal and the support in the Au catalyst system [41-45].

For full understanding the reaction mechanism, we further collected and analysed the trace amount of by-products in the reaction system, and proposed a feasible mechanism (Fig. 6). As shown in Table S1, small amount of acetone and hydrogen was generated during the reaction, indicating that KOH abstracts hydrogen atoms from isopropyl alcohol, thereby producing the acetone and the activated H-donor [46,47], which could been confirmed by acetone generated in reaction (Fig. S11). This process could be facilitated over the surface of Au and generates H-Au species by binding hydrogen atoms on the Au surfaces [26,48] *i.e.* the Step I depicted in Fig. 6. Then, in II and III step, these H-Au species capture oxygen atoms from N-O bonds to yield azoxybenzene,

#### Table 1

Reduction of substituted nitro compounds to hydrazobenzene compounds. All reactions were carried out with 10 mg of 20.9% Au/BN catalyst, 0.31 mmol of reactant, 0.06 mmol of KOH, and 3 mL of IPA at 90 °C under N<sub>2</sub> atmosphere.

Reactant	Final product	Raction time	Yield (%)
		30 min	100 <sup>a</sup>
		30 min	>90 <sup>b</sup>
H <sub>2</sub> N-NO <sub>2</sub>		30 min	>90 <sup>b</sup>
	H <sub>3</sub> CNH HNCH <sub>3</sub>	30 min	>90 <sup>b</sup>
H <sub>3</sub> CO-NO <sub>2</sub>		60 min	>80 <sup>b</sup>

<sup>a</sup> Detection by UV–Vis spectrometer.

<sup>b</sup> NMR yield.



**Fig. 4.** Time-conversion plots for the transformation of hydrazobenzene to azobenzene in air after a complete reduction reaction of nitrobenzene (see text for details). Top panel: photos of the transformation of hydrazobenzene to azobenzene in air.

azobenzene, and HO-Au species that were consumed by isopropanol by evolving  $H_2O$  [49], as demonstrated by evaporating reaction solution which made the white anhydrous cupric sulfate turn into blue (Fig. S12). At the IV step, H-Au keeps away from nitrobenzene at last to reduce azobenzene to be hydrazobenzene due to itself reducing capacity [49].

With H-Au and HO-Au produced and consumed consequently, the catalytic reduction of nitrobenzene proceeds rapidly on the surface of Au under  $N_2$  atmosphere. It even still conducting after introduced  $O_2$ , which could remove the hydrogen from the Au surfaces [49], just lowering the catalytic activity and the reaction rate (Fig. 5). Meanwhile, the H atoms from the H-Au species could be collided with each other and thus produce  $H_2$  along with reaction



Fig. 5. Reduction of NB in air over the 20.9% Au/BN catalyst at 90 °C.



**Fig. 6.** Proposed mechanism for hydrogenation of nitrobenzene to hydrazobenzene over Au nanoparticles supported by h-BN nanoplates.

proceeding [50,51], this conjecture is based on a small quantity of  $H_2$  generated rather than that equivalent of  $H_2$  produced. By summing together, the reaction for the overall equation as following equation:

 $\begin{array}{l} 2PhNO_2+8CH_3CHOHCH_3+AuNP \xrightarrow{\Delta} PhNHNHPh+8CH_3COCH_3\\ +2H_2O+(8-x)H-AuNP+xH_2 \end{array}$ 

## 4. Conclusions

In summary, we demonstrated that the h-BN nanoplates supported Au nanoparticles can act as efficient catalyst for the reduction of nitrobenzenes in the presence of IPA/KOH without illumination. Unlike the conventional oxides supports, the h-BN nanoplates can refrain the activation of oxygen, thereby endowing that the catalytic hydrogenation of the nitrobenzene proceeds successfully in air. Moreover, high yield of azobenzene or hydrazobenzene can be harvested at different reaction time and their mutual transformation can be controlled simply by changing reaction atmosphere. This work enlarges the scope of direct catalytic reduction of nitroaromatics to azo- and hydrazo compounds in an industrial-friendly process, which is thus of tremendous fundamental as well as practical interest.

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### **Appendix A. Supplementary material**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2018.12.008.

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