



# Rh Catalyzed Selective Hydrogenation of Nitroarenes under Mild Conditions: Understanding the Functional Groups Attached to the Nanoparticles

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Modifying the surface of metal catalyst is a crucial subject for improving the heterogeneous metal catalysts. It is still a great challenge to understand the structure-activity relationship (SAR) between the surface supporting groups and the metal particles. Herein, Rh NPs supported on the magnetic silica sphere with various functional groups ( $-NH_2$ , -SH,  $-SO_3H$ ,  $-N=CH_2$ , -CI,  $-NHCOCH_3$  and  $-NHCH_2Ph$ ) have been prepared for catalytic hydrogenation of nitroarenes under atmospheric pressure at room temperature. We discover that the chemical state of Rh NPs depends on the supporting groups significantly. The

## Introduction

Heterogeneous catalysts hold a great situation in the hydrogenation reactions due to their unparalleled advantages of reusability and environment friendliness.<sup>[1]</sup> For the reduction of nitro-compounds (-NO<sub>2</sub>) especially the catalytic hydrogenation, the metal based heterogeneous catalysts have contributed prominent progresses, which have been applied in the presence of coexisting reducible groups, such as -C=O, -C=C, -CI and -CO-NH-.<sup>[2]</sup> Nevertheless, it still remains a great challenge for directional adjustment of the structure and function of heterogeneous catalysts. In the early research, the effect of metal centers on the activity of catalysts was firstly explored. The catalysts containing metallic active sites such as gold, nickel, platinum and palladium nanoparticles have unsatisfied performance in terms of activity or selectivity due to the

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.201901491

electron-donating functionalities can effectively elevate the Rh<sup>0</sup>/Rh<sup>3+</sup> ratio, which increase the catalytic performance both in conversion and selectivity. The amino group decorated catalyst has such a good selectivity that no dechlorination reaction is observable in the hydrogenation of 2-chloro-3-nitropyridine. What's more, by introducing magnetic Fe<sub>3</sub>O<sub>4</sub> nuclei and mesoporous silica encapsulating layer, the catalyst can be recovered conveniently by an external magnet, and can be reused 10 cycles without any loss of activity.

competitive adsorption between H<sub>2</sub> and substrates.<sup>[3]</sup> Accordingly, specializing the SAR is instructive in the fabrication and application of catalysts.<sup>[4]</sup> Various strategies have been adopted to improve performance such as alloying synergy,<sup>[5]</sup> strong metal support interaction (SMSI)<sup>[6]</sup> and phase interfacial effect.<sup>[7]</sup> By adjusting the arrangement of atoms on the active surface through alloying, both adsorption and activation energy changed in favorable directions and even for hydrogen passivation metal such as gold.<sup>[8]</sup> Li and co-workers fabricated highly dispersed CeO2-supported Ni catalyst with SMSI, which favors the H<sub>2</sub> dissociation and adsorption of nitroarenes.<sup>[9]</sup> While the Pt-Fe<sup>3+</sup>-OH interface could suppress the further hydrogenation of imine to amine.<sup>[10]</sup> There are also methodologies that provide various protocols for the selective reduction of nitro compounds through special pathway, such as space confined sterically absorption,<sup>[11]</sup> surface diversities of coordination sites,<sup>[12]</sup> special location of active metal sites<sup>[13]</sup> and modifying surface hydrophobic properties.<sup>[14]</sup> For humble metalbased catalysts, it has been proposed that the partial surface oxidization benefits the vertical adsorption of nitroarenes or reduction intermediates, which favor the selectivity at the cost of activity.<sup>[15]</sup> With the development of modern characterization techniques, the single atom catalyst has been regarded as a better model to shed light the precise construction of the SAR.<sup>[16]</sup> An example is that the single atomic Pt on the four-fold hollow sites on phosphomolybdic acid, each single Pt atom is stabilized by four oxygen atoms with positive charge. It exhibits excellent performance in the hydrogenation of nitrobenzene and cyclohexanone.<sup>[17]</sup>

Modifying the electron density of the nanoparticles via the corresponding supports is an alternative strategy.<sup>[18]</sup> In a recent report, Xiao and co-workers introduced Au, Pt or Ni nano particles on the support of  $TiO_2$  with the single atom dispersed



Sn, and the Sn–O–Ti provide oxygen vacancies to enhance the selectivity.<sup>[19]</sup> Su et al. reported that the platinum nanoparticles loaded on diverse functionalized carbon nanotubes exhibited different activity.<sup>[20]</sup> By doping with oxygen and nitrogen into carbon nanotubes, the catalysts were increased by two and four times, respectively. Triphenylphosphine is verified positive for Pd-based hydrogenation catalyst, both on enhancing surface electron density and splitting Pd–H bonds.<sup>[21]</sup> It was also reported that the electron density of ultrathin platinum nanowires can be promoted by ethylenediamine coating. This favors the adsorption of electron-deficient reactants over electron-rich products, then the selectivity could be effectively improved.<sup>[22]</sup>

It is noticeable that dechlorination usually occurs in the catalytic hydrogenation of chloro-containing nitro arenes, which brings the problem of chemical selectivity.<sup>[23]</sup> Rhodium nanoparticles have shown excellent performance in catalytic transfer hydrogenation of nitroarenes using hydrazine hydrate,<sup>[24]</sup> sodium borohydride<sup>[25]</sup> and alcohols<sup>[26]</sup> as hydrogen source. The leaching of Rh particles that leads the reduced lifetime can be resolved by covering another layer of mesoporous silica.<sup>[27]</sup> Thus, it is of great significance for improving catalytic performance by investigating the influence of electronic properties on the catalyst. Based on these considerations, we fabricated a series of Rh-based catalysts, which are the functionalized magnetic silica spheres supported Rh nanoparticles. The typical structure and synthesis strategy to fabricate the amino group decorated catalyst Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>-RhNPs@mSiO<sub>2</sub> is shown in Scheme 1. The  $Fe_3O_4$  core endow the catalyst with favorable



Scheme 1. Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>-RhNPs@mSiO<sub>2</sub>.

recoverability. The inner silica shell is produced through hydrolysis of TEOS to provide sufficient space for linking the functional groups with silica coupling reagent, e.g. amino propyl tri-ethoxyl silicane (APTES) for  $-NH_2$ . After the active metals are embedded in the silica shell, another mesoporous silica shell is encapsulated. The pores are made through extracting the Cetyltrimethyl Ammonium Bromide (CTAB) that are embedded in the silica shell. As a benchmark, the  $-NH_2$  group decorated catalyst showed the best performance for the selective catalytic hydrogenation of nitroarenes. Based on the in-depth study of XPS, the SAR between the catalysts and

ChemCatChem 2019, 11, 1–11 www.chemcatchem.org 2 These are not the final page numbers!

supported surface groups is thoroughly investigated. We discovered that the different groups act not only as the anchor site,<sup>[28]</sup> but also the surface groups have a great influence on the electron properties of the rhodium nanoparticles. It can be systematically summarized that catalysts with electron-rich groups, especially for  $-NH_2$ , are superior to those electron-withdrawing opposites.

### **Results and Discussion**

To further illustrate the morphological properties, the shape and size distribution of these catalysts were surveyed by high resolution transmission electron microscopy (HR-TEM). As shown in Figure 1 and Figure S1–S2, both



 $\begin{array}{l} \label{eq:Figure 1. HR-TEM images: (a) $Fe_3O_4@SiO_2-NH_2-RhNPs; (b-d) $Fe_3O_4@SiO_2-NH_2-RhNPs@mSiO_2; EDS mapping of (e) $Fe_3O_4@SiO_2-NH_2-RhNPs, (f) $Fe, (g) $Si, (h) $N$ and (i) $Rh$. \end{array}$ 

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs@mSiO<sub>2</sub> have a spherical shape with an average diameter of 260 nm and 400 nm, respectively. It is clear that the Fe<sub>3</sub>O<sub>4</sub> nanospheres in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs are covered by a layer of silica shell, which provides the location for binding amino groups and Rh nanoparticles, as shown in Figure 1a. What's more, it can effectively prevent the agglomeration of the particles.<sup>[29]</sup> When another layer of silica shell is encapsulated on the nanospheres, the interface of the layered structure can be easily distinguished (Figure 1c), where the Rh nanoparticles with an average diameter of about 3 nm are evenly dispersed. The Rh loading on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs@mSiO<sub>2</sub> are 1.187 wt% and 0.5863 wt% detected by ICP respectively. The existence of metallic Rh can be further confirmed due to the lattice fringe on the catalysts





Figure 2. (a) XRD patterns of  $Fe_3O_4@SiO_2-NH_2-RhNPs@mSiO_2$  compared with standard spectrum card of  $Fe_3O_4$ . (b) Nitrogen adsorption-desorption isotherm of  $Fe_3O_4@SiO_2-NH_2-RhNPs@mSiO_2$ .

<b>Table 1.</b> Rh <sup>0</sup> /Rh <sup>3+</sup> ratio and Rh binding energies of different catalysts. <sup>[a]</sup>								
			Rh 3d <sub>5/2</sub> (eV)			Rh 3d <sub>3/2</sub> (eV)		
-	Entry	Catalyst	Rh <sup>0</sup> /Rh <sup>3+</sup>	$Rh^0$	$Rh^{3+}$	Rh <sup>0</sup> /Rh <sup>3+</sup>	$Rh^0$	$Rh^{3+}$
	1	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub> -RhNPs	3.458	307.24	308.7	2.879	311.86	313.75
	2	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -N=CH <sub>2</sub> -RhNPs	3.037	307.06	308.37	2.734	311.97	314.39
	3	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SH-RhNPs	2.002	307.12	308.36	2.243	311.57	313.40
	4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SO <sub>3</sub> H-RhNPs	2.077	306.96	308.69	1.976	311.67	313.93
	5	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH-Ph-RhNPs	0.371	307.98	309.28	0.373	312.91	313.89
[a] The data was obtained from XPS results.								

measured to be 0.221 nm, assigned to the (111) of metallic Rh, respectively, as shown in Figure 1d.

The EDS layered images and the distribution of Fe, Si, N and Rh are shown in Figure 1e–1i. The  $Fe_3O_4$  solid cores are encapsulated by  $SiO_2$ , which shows a bigger hollow spherical structure in Figure 1g, and can be distinguished easily in Figure 1f. The presence of highly dispersed Rh confirms the fact that the Rh nanoparticles have been loaded successfully between the two silica layers of the catalysts as shown in Figure 1i.

In order to discuss the characteristic of  $Fe_3O_4@SiO_2-NH_2-RhNPs@mSiO_2$ , a powder X-ray diffraction pattern analysis (PXRD) was shown in Figure 2a. The characteristic diffraction peaks of the catalyst can be assigned to the planes of  $Fe_3O_4$  accurately. A short and wide peak is observed in the range of  $2\theta = 19-23^{\circ}$ , which is considered as the characteristic peak of amorphous silica.<sup>[30]</sup> Nevertheless, there is no obvious diffraction peaks of rhodium that can be observed due to the low loading and small size of the metal nanoparticles.

The nitrogen adsorption/desorption isotherms and the pore size distribution of the catalysts are presented in Figure 2b. It is clearly that the type IV hysteresis loop can be observed in Figure 2b, from which we can conclude that a large number of mesoporous have been created by CTAB in solid-liquid extraction processing with boiling ethanol, and the average pore diameter of the catalysts is measured to be 2.6 nm by BJH (Barrett-Joyner-Halenda) model. Moreover, the BET (Brunauer-Emmett-Teller) surface area of  $Fe_3O_4@SiO_2-NH_2-RhNPs@mSiO_2$  is calculated to be 302.992 m<sup>2</sup>/g.

The elemental status and electronic properties of catalysts were investigated by X-ray photoelectron spectroscopy (XPS). The survey XPS result of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs presented in Figure 3a verifies the existence of O, Rh, Si and C. The peaks of N and Fe were difficult to be detected because of the small amount for N and compact silica shell for Fe. Moreover, to understand the relationship between the electronic properties of Rh NPs and functional groups, we synthesized a series of diverse functionalized catalyst with different silica coupling reagent. Besides --NH<sub>2</sub>, we investigated the functionalities including –SH, –SO<sub>3</sub>H, –N=CH<sub>2</sub>, –Cl, –NHCOCH<sub>3</sub> and –NHCH<sub>2</sub>Ph. The Rh 3d regions of catalysts varied with different functional groups are also presented in Figure 3b-3 h. The peaks at 307.2 and 308.7 eV in Figure 3b can be ascribed to Rh<sup>0</sup> and Rh<sup>3+</sup>, respectively, and the Rh<sup>0</sup>/Rh<sup>3+</sup> ratio of each catalyst is listed in Table 1. Higher Rh<sup>0</sup>/Rh<sup>3+</sup> ratio could be observed for the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs with electron rich amino groups in Rh<sup>0</sup>/Rh<sup>3+</sup> Table 1, entry 1. Obviously, the ratio of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NHPh-RhNPs are apparently lower than other catalysts owing to the majority of oxidation state rhodium, as showed in Table 1, entry 5. However. neither





Figure 3. XPS spectra: (a) survey result of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs; (b-h) Rh 3d regions of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--SH--RhNPs, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs

 $Fe_3O_4@SiO_2--NHCOCH_3--RhNPs$  nor  $Fe_3O_4@SiO_2--CI--RhNPs$  shows obvious peaks that could be detected in Rh 3d regions, this may be due to their poor coordination ability, which makes it difficult to load Rh NPs.<sup>[31]</sup> The above results suggest that Rh NPs on the catalysts with electron-donating groups have a higher Rh<sup>0</sup>/Rh<sup>3+</sup> ratio because of its electron rich properties, which have a positive effect on loading metal NPs on the catalysts.

#### **Catalytic Activity Tests**

We examined the catalytic hydrogenation of nitro compounds using *p*-nitrophenol as the model substrate under ambient conditions in water and isopropanol, which are commonly used in this reaction. As shown in Table 2 entries 1–4, compared with isopropanol, the conversion is higher in water system using  $Fe_3O_4$ -Rh NPs and  $Fe_3O_4@SiO_2$ -Rh NPs as catalyst. Once the silica



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Table 2. Catalytic hydrogenation of p-nitrophenol with diverse catalysts under mild conditions. <sup>[a]</sup>							
			HO NH <sub>2</sub>				
	Entry	Catalyst	Solvent	Conversion/%			
	1	Fe <sub>3</sub> O <sub>4</sub> -Rh NPs	Isopropanol	11.8			
	2	Fe <sub>3</sub> O <sub>4</sub> -Rh NPs	H <sub>2</sub> O	28.2			
	3	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Rh NPs	Isopropanol	49.8			
	4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Rh NPs	H <sub>2</sub> O	53.1			
	5 <sup>b</sup>	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub> -Rh NPs	Isopropanol	>99			
	6	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub> -Rh NPs	H <sub>2</sub> O	>99			
	7 <sup>c</sup>	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub> -Rh NPs@mSiO <sub>2</sub>	Isopropanol	>99			
	8	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub> -Rh NPs@mSiO <sub>2</sub>	H <sub>2</sub> O	67.1			

[a] Reaction conditions: 1 mmol *p*-nitrophenol, 3 mL solvent, 1 bar H<sub>2</sub>, 40 mg catalyst (29 wt%), the reaction was carried out at room temperature for 16.5 h and conversion was detected by HPLC and GC-MS. [b] The metal/substrate molar ratio is 0.47 mmol%. [c] The metal/substrate molar ratio is 0.23 mmol%.



**Figure 4.** (a) The conversion of *p*-nitrophenol as a function of time catalyzed by  $Fe_3O_4@SiO_2-NH_2-RhNPs$  and  $Fe_3O_4@SiO_2-NH_2-RhNPs@mSiO_2$ . (b) The yield of 2-chloro-3-aminopyridine as a function of time in the presence of catalysts with different functional groups. (The yield = conversion × selectivity) (c) Selectivity as a function of  $Rh^0/Rh^{3+}$  ratio and (d)  $Rh^0/Rh^{3+}$  ratio as a function of F value over catalysts functionalized with different groups.

shell is covered with a layer of amino groups, the reaction in isopropanol is better. We attribute this to the hydrophobicity of amino propyl in consideration of the hydroxyl groups on the Fe<sub>3</sub>O<sub>4</sub> or silica surface. Herein, isopropanol is selected as the solvent of the catalytic hydrogenation. To estimate the influence of the mesoporous silica shell on the activity of the

catalyst, the hydrogenation of *p*-nitrophenol catalyzed by  $Fe_3O_4@SiO_2-NH_2-RhNPs$  and  $Fe_3O_4@SiO_2-NH_2-RhNPs@mSiO_2$  was examined and the results are shown in Figure 4a. The reaction could be completed within 6 h when  $Fe_3O_4@SiO_2-NH_2-RhNPs$  was applied. After covered with an outer mesoporous shell, the activity gently decreased due to the lower metal/



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Table 3. The effect of surface groups over Rh NPs on catalytic hydrogenation of 2-chloro-3-nitropyridine. <sup>[a]</sup>								
	$ \begin{array}{c} (\mathbf{N}, \mathbf{C}) \\ (\mathbf{N}, \mathbf{O}_2) \end{array} + \mathbf{H}_2 \xrightarrow{\text{Catalyst}} \begin{array}{c} (\mathbf{N}, \mathbf{C}) \\ (\mathbf{N}, \mathbf{H}_2) \end{array} $							
-						Rh 3d	<sub>5/2</sub> (eV)	
_	Entry	Catalyst	Con.(%) <sup>b</sup>	Sel.(%) <sup>b</sup>	Rh <sup>0</sup> /Rh <sup>3+</sup>	$Rh^0$	Rh <sup>3+</sup>	F
	1	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub> -RhNPs	>99	>98	3.458	307.24	308.70	0.08
	2	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -N=CH <sub>2</sub> -RhNPs	>99	95.4	3.037	307.06	308.37	0.10
	3	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SH-RhNPs	>99	86.6	2.002	307.12	308.36	0.30
	4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SO <sub>3</sub> H-RhNPs	>99	93.6	2.077	306.96	308.69	0.29
	5	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NHCH <sub>2</sub> Ph-RhNPs	>99	78.6	0.371	307.98	309.28	0.18
	6	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Cl-RhNPs	57.9	95.3	-	-	-	0.42
	7	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NHCOCH <sub>3</sub> -RhNPs	3.1	-	-	-	-	0.31

[a] Reaction conditions: 1 mmol 2-chloro-3-nitropyridine, 3 mL solvent, 1 bar  $H_{2^{\prime}}$  40 mg catalyst (25 wt%), the reaction was carried out at room temperature for 22 hours. [b] Conversion and selectivity were detected by HPLC and GC-MS, respectively.

substrate ratio (0.23 mmol% vs. 0.47 mmol%). However, the outer silica shell can effectively elevate the stability of the catalyst.

The catalysts with different functional groups are evaluated with the hydrogenation of 2-chloro-3-nitropyridine, as its dechlorination usually occurs severely in this reaction.<sup>[32]</sup> The reaction time was fixed to 22 hours, and most of the catalysts achieved full conversion (Table 3 entries 1-5) except the CI- and -NHCOCH<sub>3</sub> decorated ones, whose poor performance can be ascribed to the fact that Rh atoms have not been successfully coordinated with the electron withdrawing groups from entries 6-7, which has been verified by XPS. However, there are apparent disparities in the selectivity for the catalysts with different functional groups. Then we monitored the reactions of various catalysts, and the results are shown in Figure 4b and Figure S5-S6. It is clear that Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N=CH<sub>2</sub>-RhNPs exhibit excellent selectivity. Thus, we can conclude that the catalysts with higher Rh<sup>0</sup>/Rh<sup>3+</sup> ratios have better selectivity for reduction of nitro-groups.<sup>[21,33]</sup> To understand the effect of different functional groups on catalysts, field inductive parameter (F), which is used to describe the electronic inductive effect, [34] was introduced and presented in Table 3. With the enhancement of F, the group's electron cloud density decreases then results the lower Rh<sup>0</sup>/Rh<sup>3+</sup> ratios, which lead to the lower selectivity. Low F value of 0.08 and 0.10 can be observed in entries 1-2, and corresponding high selectivity can be obtained. With the increase of F value, the selectivity decreases in entries 3–7. The -SH and  $-SO_3H$ contained catalysts give acceptable selectivity (entries 3 and 4). It is perhaps due to the dissociation properties of -SH and -SO<sub>3</sub>H. The low selectivity of catalysts containing -NHCH<sub>2</sub>Ph could be the result of a poor Rh<sup>0</sup>/Rh<sup>3+</sup> ratio, as the coordination as well as steric hindrance effect of benzylamine group impedes the reduction of Rh<sup>3+</sup>. The poor performance of catalysts in Table 3, entries 6–7 can be explained as low loading of Rh, which the XPS results has shown.

The general applicability of the catalysts was investigated by introducing a variety of nitro-compounds in our reaction systems (Table 4). There is no doubt that those substrates with a simple functional group could be converted to their corresponding amino compounds completely (Table 4, entries 1-4). 2-chloro-3-nitropyridine could be reduced to 2-chloro-3aminopyridine smoothly, and our catalytic protocol exhibits perfect tolerance toward chlorine as shown in Table 4, entry 7. When other substrates with halogen at different position were reduced to their corresponding amines, our catalytic system exhibits outstanding conversion and selectivity. Besides chlorine, other reducible groups such as acid and amino on nitroarenes showed excellent tolerant properties in our catalytic reactions, and all of these functionalized nitrobenzenes were converted into aniline without any by-products. The fabulous performance of our catalyst can be attributed to the following reason: the electron rich amino groups can serve as an electron donor to enrich the electron of the Rh NPs, and the nitro group, rather than chlorine or other reducible groups, is prone to be adsorbed on Rh NPs with high electron density due to its strong electron-withdrawing properties.<sup>[35]</sup> Consequently, excellent selectivity could be obtained.

#### The reusability of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>-RhNPs@mSiO<sub>2</sub>

The magnetic properties of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs@mSiO<sub>2</sub> at an applied field of 10000 Oe are shown in Figure 5a. There is no obvious hysteresis phenomenon can be observed, which clearly demonstrates that all of those materials are superparamagnetic. Thus, the catalysts can be separated easily by an external magnet from a solution.



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ble 4. The hy	Ie 4. The hydrogenation of nitroarenes catalyzed by $Fe_3O_4@SiO_2-NH_2-RhNPs@mSiO_2$ . <sup>[a]</sup>						
		R <sup>II</sup> +	H <sub>2</sub>	Catalyst	R II NH2		
	Entry	Substrate	Time/h	Product	Conv.(%) <sup>b</sup>	Sel.(%) <sup>b</sup>	
	1	NO <sub>2</sub>	16	NH <sub>2</sub>	>99	100	
	2	H <sub>3</sub> C NO <sub>2</sub>	16	H <sub>3</sub> C NH <sub>2</sub>	>99	100	
	3	HO NO2	16	HO NH <sub>2</sub>	>99	100	
	4	NO <sub>2</sub>	16	NH <sub>2</sub>	>99	100	
	5	CI NO2	24	CI NH2	>99	100	
	6	CI NO2	24	NH <sub>2</sub>	>99	100	
	7		22	NH <sub>2</sub> NCI	>99	100	
	8	O <sub>2</sub> N N CI	24	H <sub>2</sub> N N CI	>99	>98	
	9	HOOC NO2	24	HOOC NH2	>99	100	
	10	H <sub>2</sub> N NO <sub>2</sub>	16	H <sub>2</sub> N NH <sub>2</sub>	>99	100	

[a] Reaction conditions: nitroarenes (1 mmol), hydrogen (1 atm), catalyst (40 mg, 0.23 mmol% Rh), isopropanol (3 mL), room temperature. [b] Conversion and selectivity were determined by HPLC and GC-MS using trimethylbenzene as external standard.



 $\label{eq:Figure 5. (a) Room temperature hysteres is loops of Fe_3O, Fe_3O_4@SiO_2-NH_2-RhNPs and Fe_3O_4@SiO_2-NH_2-RhNPs@mSiO_2. (b) The reusability of Fe_3O_4@SiO_2-NH_2-RhNPs@mSiO_2. (b) The reusability of Fe_3O_4@SiO_2-NH_2-RhNPs@mSiO_2. (c) The reusability of Fe_3O_4. ($ 



To investigate the stability and reusability of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs@mSiO<sub>2</sub>, the catalyst was employed in hydrogenation of 2-chloro-3-nitropyridine at the optimized reaction conditions. After each cycle test, the catalyst can be separated by an external magnet instead of centrifugation or filtration because of its excellent paramagnetic properties. As shown in Figure 5b, with the increasing number of cycles, there is no loss of catalytic performance that can be observed. The catalyst can still maintain its inherent activity and selectivity even after being reused up to 10 times. The outstanding stability of the catalyst could be attributed to the following two points: (1) the active centers of the catalyst in hydrogenation reaction are Rh nanoparticles, which are linked and fixed by the amino functional groups on the surface of the inner silica shell. In addition to the physical fixation effect of the amino group, electrons migration plays an important role in protecting the Rh nanoparticles from oxidation. (2) The catalyst is encapsulated by a layer mesoporous silica shell, which can effectively prevent the losing of Rh NPs. Besides, the sandwich structure consisting of two silicon shells retard agglomerating of Rh NPs, which usually lead to the deterioration of catalytic performance.

#### Mechanism

Based on those experimental data presented above and previous literatures,<sup>[36]</sup> a plausible reaction mechanism is proposed in Figure 6. Initially, molecular  $H_2$  diffuse through the mesoporous silica, then it is absorbed and activated followed by producing of active H species on Rh NPs. Meanwhile, the nitroarenes are adsorbed on Rh NPs as well. In virtue of the electron rich properties of Rh NPs, the electrophilic nitro-groups are prone to be adsorbed on Rh NPs and come into contact with those active H species to produce the intermediates of nitrosobenzenes and hydroxylamines. Finally, those intermediates are reduced to corresponding amines and desorbed from Rh NPs due to the reduced electrophilicity, which effectively



Figure 6. Possible mechanism for the reduction of nitroarenes with atmospheric  $\mathrm{H}_{\! 2}$ 

ChemCatChem 2019, 11, 1–11 www.chemcatchem.org 8 These are not the final page numbers!

avoid dehalogenation or hydrogenation of other reducible groups.

### Conclusions

In summary, the rhodium NPs based core-shell structured catalyst were investigated in the application of nitro compounds hydrogenation. By tuning the kind of supporting groups, the active sites' properties have been verified, and the SAR between catalytic site and supported surface groups has been systematically investigated with XPS. The electron-donating groups with a lower F value, especially for -NH<sub>2</sub>, can effectively increase the electron density of catalytic sites and the ratio of Rh<sup>0</sup>/Rh<sup>3+</sup>, which results in the promotion of activity and selectivity. The explanation is that the electrophilic nitro groups, instead of chlorine or other reducible groups on nitroarenes, are inclined to be adsorbed on the surface of electron rich Rh NPs. Owing to high catalytic performance of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>--NH<sub>2</sub>--RhNPs@mSiO<sub>2</sub>, the reaction can go smoothly with high yield and selectivity under mild reaction conditions. The catalyst exhibited excellent stability even after 10 cycles due to the protection of mesoporous silica shell. The significance of electron-donating support groups can provide a promising methodology for enhancing catalytic performance in other reactions.

## **Experimental Section**

#### Materials

 $\rm Fe_3O_4$  nano-sphericals with diameter of 100–300 nm are provided by Aladdin Reagent Co., Ltd, China. Hydrochloric acid, NaBH\_4, RhCl\_3·3H\_2O, cetyltrimethyl ammonium bromide (CTAB) and all of the nitro compounds are purchased from Sinopharm Chemical Reagent Co., Ltd, China. Tetraethyl orthosilicate (TEOS), ammonia, 3-aminopropyl-triethoxysilane (APTES), 3-mercaptopropyltrimethoxysilane, 3-chloropropyltrimethoxysilane, glacial acid and carbon tetrachloride are purchased from the Tianjin Yongda Chemical Reagent Co., Ltd, China. All chemical reagents are analytic grade and used without any further purification.

#### Instrumentation

The materials morphology was observed by JEM-2100F high resolution transmission electron microscopy (HR-TEM). The scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) are accessories of the HR-TEM apparatus. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo ESCALAB 250, and the binding energy determination was based on the carbon contamination C 1s at 284.6 eV. A VSM (cryogenic Mini-CFM measurement system) was used to measure the magnetic property of the sample. The samples X-ray diffraction (XRD) experiments were recorded on a PANalytical Empyrean, diffractometer using Cu K $\alpha$  radiation. Room-temperature Fourier-transform infrared (FT-IR) spectra was obtained by using a Bruker Vertex spectrometer in the region of 30000–10 cm<sup>-1</sup> with a spectral resolution of 16 cm<sup>-1</sup> using a KBr pellet. Nitrogen adsorption-desorption isotherms (American Micromeritics ASAP 2020 sorptometer) were measured at 77 K to determine the specific



surface area of the samples using the Brunauer-Emmett-Teller (BET) analysis method.

#### **General Fabrication Procedure of Rh-based Catalysts:**

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>-RhNPs: the preparation method of silica coated  $Fe_3O_4$  can be found elsewhere.<sup>[24]</sup> In brief, 50 mL diluted HCI solution are added into  $0.2 \text{ g Fe}_3O_4$  powders, following by ultrasonic treatment to disperse agglomerated particles. After washing with deionized water to remove residual acid, those magnetic spheres are redistributed in a mixed solution of 40 mL water and 160 mL ethanol, and 4 mL ammonia water is used to adjust pH value. Secondly, 0.5 mL tetraethyl orthosilicate (TEOS) is added into above mixture under stirring and kept for 6 h. The prepared Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> is collected using an external magnet. For aminofunctionalization, 0.5 mL 3-aminopropyl-triethoxysilane is added dropwise into 200 mL isopropanol with Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> inclusion under 80°C for 3 h. After magnetic separation from the suspension, the solid are redispersed in 80 mL ethanol. 5 mg RhCl<sub>3</sub>·3H<sub>2</sub>O are dissolved in 20 mL ethanol and added dropwise into the suspension and keep on stirring overnight. To reduce the  $Rh^{3+},\ 0.1\,g$ sodium borohydride is dissolved in 20 mL methanol and added into the mixture. After stirring for 30 min, the product is separated and washed with ethanol for several times.

 $Fe_3O_4@SiO_2-NH_2-RhNPs@mSiO_2$ : The mesoporous layer of silica is manufactured according to the literature.<sup>[37]</sup> Typically, 0.3 g Cetyltrimethyl Ammonium Bromide (CTAB) is dissolved in the mixed solution of 60 mL ethanol and 2.5 mL ammonia water. At the same time, the as-prepared  $Fe_3O_4@SiO_2-NH_2-RhNPs$  are redispersed in 80 mL H<sub>2</sub>O. Then the above-mentioned mixed solution is added into the suspension. After keep on stirring for 30 min, 1 mL TEOS is added dropwise and keep on vigorously stirring for another 6 h. Then the solid are separated and stir vigorously in 150 mL boiling ethanol for 3 h and three times to remove the CTAB embedded in the silica shell. Finally, the obtained material is washed with ethanol and dried under 60 °C.

 $Fe_3O_4@SiO_2-SH$ : the procedure is much the same as  $Fe_3O_4@SiO_2-NH_2$  except that the APTES is replaced by 0.5 mL 3-mercaptopropyltrimethoxysilane.

 $Fe_3O_4@SiO_2-SO_3H$ : the obtained  $Fe_3O_4@SiO_2-SH$  is redispersed into 80 mL hydrogen peroxide (30 wt%), and stirs for 12 h under room temperature to get  $Fe_3O_4@SiO_2-SO_3H$ .

 $Fe_3O_4@SiO_2-CI:$  in this case, 0.5 mL 3-chloropropyltrimethoxysilane acts as the corresponding silane coupling reagent instead of APTES.

**General catalytic hydrogenation of nitro compounds**: 1 mmol nitro compound, 40 mg catalyst and 3 mL isopropanol are added in a 50 mL round bottomed flask with a magnetic stir bar inside. Before reaction starting, air in the flask is replaced with hydrogen for three times in a balloon. Then the reaction is conducted at room temperature. The conversion and selectivity are detected by GC-MS and HPLC.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Nos. 21872020, 81872835 and 21621003), the Ministry of Science and Technology (Nos. 2017YFC0906902 and 2017ZX09301032). The China Scholarship Council (No. 201806085012) is also acknowledged.

## **Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** Electron density · Functional groups · Rh nanoparticles · Atmospheric hydrogen · Catalytic hydrogenation

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Manuscript received: August 15, 2019 Accepted manuscript online: August 31, 2019 Version of record online:



# **FULL PAPERS**

Functionalized surfaces: Rh nanoparticles supported on magnetic silica spheres with various functional groups were tested in the catalytic hydrogenation of nitroarenes under mild conditions. Electron-donating groups can effectively increase the electron density of catalytic sites and the ratio of  $Rh^0/Rh^{3+}$ , which results in the promotion of the selectivity of the catalyst for hydrogenation at room temperature under atmospheric conditions.



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1 – 11

Rh Catalyzed Selective Hydrogenation of Nitroarenes under Mild Conditions: Understanding the Functional Groups Attached to the Nanoparticles