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Insight into the Mechanism of Gold-Catalyzed Reduction of Nitroarenes Based on Substituent Effect and *in-situ* IR

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Abstract

A study is presented here on the mechanistic pathway of catalytic reduction of nitroarenes which have diverse substituent groups in the presence of ultra small gold nanoparticles and NaBH₄. The kinetic data based on substituent effect and Hammett plot, together with the analyses of intermediates, revealed that this reaction followed a direct route and all the reaction steps were rapid without accumulation of intermediates. Especially, *in-situ* IR was found to be an effective method for real-time monitoring this model reduction in our catalytic system and confirmed the presence of intermediate of hydroxylamine. These results will provide a new insight into the mechanism of gold-catalyzed reduction of nitroarenes and offer a reference for future mechanism test of heterogeneous nanocatalysis.

1 Introduction

The catalytic reduction of nitroarenes with sodium borohydride to the corresponding amino compounds has been considered as one of the most trustful model reactions to test the activity of a given nanocatalyst.¹⁻⁶ However, for respective catalyst, this reaction remains controversial to the mechanistic pathways of reduction process. One proposed route is that the nitro group in nitroarenes is firstly reduced into nitroso and then hydroxylamine, finally aniline compound.⁷ Another route is a condensation

process, azoxy compound is firstly generated from nitroso and hydroxylamine compounds then reduced into a series of consecutive products, like azo, hydrazo, and aniline compounds.^{8,9} Thus, the number of papers related to the mechanism study of the reduction of nitroarenes with a given nanocatalyst is steadily increased.¹⁰⁻¹³

A variety of methods have been applied to take insight into the mechanistic pathway due to the controversy of reaction process. A. Noschese and co-workers¹⁴ monitored the reaction profiles by GC-MS and proved the presence of azo compound. Likewise, S. Kundu¹⁵ and K. Layek¹⁶ directly used the possible intermediates (nitroso and azo compound) as reactants instead of the parent substrates and proved mechanistic information for the reduction. Besides, S. Wunder and co-workers^{17, 18} presented a systematic kinetic analysis to study the true kinetic constant of the reaction along with the thermodynamic adsorption constants for both *p*-nitrophenol (p-Nip) and BH₄ on gold nanoparticles. By using kinetic isotope effect, S. Fountoulaki¹⁹ suggested that an *in situ*-formed gold hydride ([Au]-H) is responsible for the reduction of nitroarenes. Moreover, density functional theory method was also extended to study the reaction mechanism.^{20, 21} However, beside all these detailed studies, very little attention had been paid on the substituent effect in this heterogeneous catalysis which was always used as a delicate probe into the electronic demand of the reaction in physical organic chemistry²². Therefore, the study of substituent effect to understand the correlation of molecule structure with reactivity of substrates and explore the catalytic mechanism on nanocatalyst is full of interest.

Herein, we reported a mechanism pathway for the reduction of nitroarenes by NaBH₄ based on the substituent effect. Ultra small gold nanoparticles supported on silica (Au-SiO₂) were synthesized and used as the heterogeneous catalyst. It was found that the substituent group in nitroarenes had a profound effect on the Au-SiO₂ catalyzed reduction reactivity. By combining the analysis of substituent effect and Hammett plot, this finding deepened our understanding of the gold-catalyzed reduction of nitroarenes by NaBH₄. Besides, *in-situ* IR is found to be a suitable and direct analysis method for real-time tracing this Au-SiO₂ catalyzed reduction process which is beneficial to verify the mechanism pathway.

2 Experimental Details

2.1 Materials

Polyoxyethylene (20) cetyl ether (Brij®58) was purchased from Acros Organics. Chloroauric acid, sodium borohydride (NaBH₄), tetraethyl orthosilicate (TEOS), ammonium hydroxide (NH₃·H₂O, 25%–28%), cyclohexane, methanol, ethanol, isopropanol (IPA), tetrahydrofuran (THF) and all of nitro compounds were purchased from Sinopharm Chemical Reagent Co., Ltd.. All chemicals were analytical grade.

2.2 Preparation of Au-SiO₂

The Au-SiO₂ was synthesized as described previously.²³ Typically, the synthesis was carried out in a reverse microemulsion system consisted of 3.37 g of Brij®58 and 15 mL of cyclohexane at 52 °C. Aqueous chloroauric acid (0.1 M, 0.2 mL) was added dropwise into the system under stirring. After 5 min, NaBH₄ aqueous solution (0.14M, 0.7mL) was added and then maintained for 30 min. Finally, 0.5 mL NH₃·H₂O and 1.0 mL TEOS were introduced to prepare the silica support. The Au-SiO₂ sample was collected by centrifugation/washing cycle for three times. The product was dried at 100 °C for 10 h and calcined at 500 °C for 2 h in an air flow of 80 mL/min.

2.3 Catalytic Reaction

As a typical reaction, aqueous solution of nitroarenes (4 mmol/L, 50 mL), NaBH₄ powder (75 mg, 10-fold for nitroarenes) and Au-SiO₂ catalyst (20 mg, 1mol% Au) were added in reactor at room temperature under air. After each run, the Au-SiO₂ was collected by centrifugation/washing cycle three times. The product was detected by an Agilent 1100 HPLC and 6130 MSD and a Bruker Avance III 500 ¹H NMR.

Kinetic experiments: all the reactions proceeded with 50 mL of the nitroarenes solution (4 mmol/L in water), 75 mg of NaBH₄ and 20 mg of Au-SiO₂. Then the reduction progress was monitored by Agilent 8453 UV-vis spectrometer for p-nitrophenol, p-nitrobenzenethiol, m- and p-phenylenediamine, and by Agilent 1100 HPLC for m-nitrophenol, m- and p-nitrobenzoic acid. A comparison of these two methods was done in supporting information. Each reaction was repeated at least three times. In the *in-situ* IR investigation, the concentration of *p*-Nip was increased to enhance the intensity of the absorption peak. Reaction conditions: 50 mL of the *p*-Nip solution (40 mmol/L in water), 750 mg of NaBH₄, and 100 mg of Au-SiO₂, at room temperature.

3 Results and Discussion

3.1 Evaluation of the Reduction

The ultra small gold nanoparticles supported on silica in this study was generated as described previously.²³ The silica support was monodispersed with an average size around 28 nm, and the dark points dispersed on the nanosphere are the gold particles with an ultra small size. The amount of gold was obtained to be 2.02 wt% by inductively coupled plasma-optical emission spectrometer, Perkin Elmer Optima 2000 (ICP).



Figure 1 TEM morphology of Au-SiO₂ (inset showed HRTEM of Au-SiO₂)

At the initial stage of catalytic studies, the reduction of p-Nip by NaBH₄ was selected to check the catalytic activity of ultra small gold nanoparticles as it had been a model reaction for metal nanoparticles. The reaction was carried out using Au-SiO₂ (1 mol% for p-Nip) in water at room temperature under air. As shown in Figure 2a, the progress can be easily monitored by UV-vis spectrometer. After the addition of

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catalyst, the absorption of *p*-Nip ions at 400 nm decreased with reaction time. Finally, the reactant *p*-Nip was smoothly converted to product after 25 min with over 99% conversion. The only product observed was *p*-aminophenol and no by-product was detected by HPLC-MS and ¹H NMR.



Figure 2 UV–Vis profiles of the reduction of p-Nip by NaBH₄ in water (a), methanol (b), ethanol (c), and THF (d). Reaction conditions: 50 mL of p-Nip solution (4 mmol/L), 1 mol% Au-SiO₂, and 10-fold NaBH₄, at room temperature.

For metal nanoparticles-catalyzed reduction of p-Nip by NaBH₄, most of the reporters chose water as the solvent without a clear reason, therefore solvent effect was taken into account in this reaction. As is conjectured that water provides protonation for the reduction, other solvents with different proton-donating ability (methanol, ethanol and THF) were investigated to compare with water and the results are shown in Figure 2. It was found that solvent had a significant effect on the performance of reaction rate in the same experimental condition. It took only 25 minutes to accomplish the conversion of p-Nip in water, while over 2 hours was

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required in methanol, ethanol and THF. Meanwhile the reactivity decreased in different solvents in the following order: water > methanol > ethanol > THF. This result is in accordance with the previous conjecture that the protonation of solvent plays an important role in the reaction. Another way to modulate the protonation of solvent is changing the pH of the solution²⁴. As shown in Table S1 and Figure S2 in supporting information, it was found that the catalytic reduction proceeded much slower at higher pH values throughout the pH range from 8.21 to 12.0 without kinetic changes. These results proved again the great impact of protonation of solvent on our reaction system. On the other hand, due to the formation of *p*-Nip ions with the addition of NaBH₄, polar solvent is favorable to dissolve and stabilizes the charged species. As the polarity of water is much higher than that of others (dielectric constant: water 78.4, methanol 32.7, ethanol 24.5, THF 7.6²⁵), the reduction of *p*-Nip in water is the fastest. Therefore, water is not only an environmental solvent, but also plays an important role in the reduction of *p*-Nip.

3.2 Substituent effect and kinetic analysis

Organic compounds have a unique capacity that structural variation permits a significant effect on electrophilic or nucleophilic character in the vicinity of reaction center. The correlation of structure with reactivity could be used as a delicate probe into the electronic demand of the reaction. The use of this information in deducing mechanism is a highly developed art.²²

Currently, for gold-catalyzed reduction of nitroarenes by NaBH₄, the most widely reported was the reduction of *p*-Nip. However, for other substituent aromatic nitro compounds, very little is considered whether the nitroarenes with electron-donating or electron-withdrawing group will react faster or slower in the reduction, and the effect of substituent group has yet to be determined. So that substituent effect was investigated here to understand the correlation of structure with reactivity and the reduction mechanism.

In view of the substituent effect on the activity of $Au-SiO_2$ as catalyst for the reduction of nitroarenes, various types of nitro compounds were investigated in the reactions. All the reactions were performed in aqueous solution at room temperature.

The results are listed in Table 1. Obviously, all the nitroarenes with diverse substituent groups could be reduced into corresponding amino compounds with excellent yields (most of the conversions were higher than 99%). However, there was considerable diversity in the reaction time. The reduction of p-nitrobenzoic acid was the fastest, which took only 5 minutes to reach quantitative conversion, while it needed 50 minutes for p-nitrobenzenethiol to finish the reaction. These results reflected that substituent group has a great effect on the reactivity of nitroarenes for the reduction catalyzed by Au-SiO₂.

Substrate	Product	Time (min)	Conversion (%)	Selectivity (%)
		24	99.7	>99
		12	99.0	>99
H ₂ NNO ₂	H ₂ N	29	99.9	>99
H ₂ N NO ₂	H ₂ N NH ₂	15	99.3	>99
		5	99.2	>99
HOOC	HOOC NH ₂	9	98.8	>99
HO ₃ S-	HO ₃ S-NH ₂	30	98.2	>99
HS	HS	50	98.9	>99

Table 1 Reduction of various nitroarenes over Au-SiO₂

To rationalize the reason for the effect of substituent group in the gold-catalyzed

Reaction conditions: nitroarenes aqueous solution (4 mmol/L, 50mL), Au-SiO₂ (20 mg, 1 mol% Au), NaBH₄ (75 mg, 10-fold for nitroarenes), at room temperature under air. The products were detected by HPLC-MS and ¹H NMR.

reduction, detailed kinetic analyses were conducted during the reduction using NaBH₄ as reducing agents. And a powerful tool for providing valuable information about the substituent effect, Hammett equation²², was used for the interpretation of mechanism.

The kinetic analyses were determined by monitoring the reduction process of the substituted nitroarenes (Table 1) using HPLC. For an accurate comparison, all the kinetic analysis began with 50 mL of 4 mmol/L nitroarenes aqueous solution, 1 mol% Au-SiO₂, and 10-fold NaBH₄. Then the reduction progress was monitored along with reaction time. Each detection was repeated for at least three times, and the average values are depicted in Figure 3. All the plots of $\ln C_t$ versus reaction time yield straight lines, which indicated that the reduction is a pseudo-first-order reaction for nitroarenes in the presence of Au-SiO₂ using NaBH₄ as reducing agent²⁶. Considering that the excess enough of hydride species and the pseudo-first-order reaction on the nitroarenes, eq 1 can be applied:

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$$\ln C_t = -k_x t + \ln C_0$$
 (1)

where k is the rate constant, x is the substituted nitroarenes, C_t and C_0 represent the concentration of nitroarenes at reaction time t and the beginning, respectively. Therefore, the slope of the plots in Figure 3 is the rate constant k_x according to eq 1. It is worth noting that the kinetic activity of nitroarenes is significantly affected by the substituent group.



Figure 3 Evolution of the concentration of the nitroarenes with diverse substituent groups. Reaction conditions: 50 mL of 4 mmol/L nitroarenes aqueous solution, 20 mg Au-SiO₂, and 75 mg

NaBH₄, at room temperature.

On the basis of this kinetic analysis, there is a Hammett-typed correlation between the reaction rate constant of nitroarenes and the electron-donating ability of the substituent group. The Hammett equation^{22, 27} is written as

$$lg (k_x/k_H) = \rho \sigma_x$$
 (2)

where k is the rate constant, σ is the substituent constant, and ρ is reaction constant.

As strong resonance interaction occurs between reaction center and some substituents, the revised substituent constants are widely used for such situations instead of original σ .^{27, 28} The Hammett plot here shows a good correlation between the revised σ values and the rate constant k_x (Figure 4). The correlation gives positive slopes: ρ =0.54. This result revealed that the electron-donating group is not conducive to form and stabilize the transition state^{19, 22}, so that the reduction rate was associated with the electron-donating capacity of substituent groups. The result also suggested that there was a development of negative charge in the transition state, or there was a hydride transfer occurs in the reaction process.^{19, 22}



Figure 4 Hammett plot of the rate against revised substituent constants.

3.3 Mechanism

To deep understand the mechanism of the nitroarenes reduction, it is desirable to confirm the reaction route involved in Au-SiO₂. In general, there are two different

routes proposed at the reduction step. In the direct route, the nitro compound was reduced into the corresponding nitroso, hydroxylamine, and aniline compound consecutively. The second route was a condensation route, the forming nitroso and hydroxylamine reacted to give an azoxy compound and continued to be reduced in a series of steps to the azo, hydrazo, and aniline compound.^{8, 9, 15}

Comparing to the direct route, there is an extra azoxy compound generated in condensation route. So, this extra intermediate was subjected to the reduction process to check the reaction followed. It was found that when 4,4'-dihydroxyazobenzene was subjected to the reaction system instead of *p*-Nip under the same conditions, the conversion was only 39.2% in 2 hours. This reduction rate is far slower than that of p-Nip. Hence, the reduction of 4,4'-dihydroxyazobenzene must be the rate-determining step in the whole reduction process if the reduction pathway go through the condensation route, and the condensation intermediates should be accumulated. To verify this observation, HPLC-MS was used to monitor the whole reduction of p-Nip to check the intermediates. However, no traces of the corresponding azoxy-, azo-, or hydrazo benzenes was found in the reaction mixture. In addition, p-nitrobenzenethiol was also used as the substrate to check the the presence of intermediates during the reaction by HPLC-MS, which had been discovered the azobenzene intermediate in reports^{29, 30}. However, it is failed to find the trace of azobenzene in our reaction system. These results suggested that the condensation route did not occur in the reduction of nitroarenes involved in Au-SiO₂, and confirmed that the reduction followed a direct route. As only parent reactant and final product were found when using HPLC-MS to monitor the whole reduction, the reduction must proceed rapidly without accumulative intermediate. The absence of nitroso and hydroxylamine can attribute to their strong adsorption on hydride-modified gold surface and a very fast reduction before desorption.¹⁶ This also explains the reason that no formation of corresponding azoxy benzenes which generated based on the accumulation of nitroso and hydroxylamine. Therefore, the reduction of nitroarenes catalyzed by Au-SiO₂ followed direct pathway, and there was

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no accumulation of intermediates due to the high catalytic activity of gold nanopaticles.



Scheme 1 Proposed mechanistic pathway of the gold-catalyzed reduction of nitroarenes by NaBH₄ in aqueous solution. The reaction proceeded very fast following direct route without intermediate accumulation.

According to the analyses above, a reasonable mechanistic pathway was proposed for this Au-SiO₂ catalyzed reduction of nitroarenes by NaBH₄ in aqueous solution, that is, a direct route as shown in Scheme 1. Based on the substituent effect and Hammett plot, it is reasonable to say that the hydride transfer occured in the transition state. The reduction process on the surface of gold nanoparticles was that the activated hydride attack the reaction center in nitro group consecutively, meanwhile the solvent water provided protonation for the reduction. Hence the nitro compound was reduced into the corresponding nitroso, hydroxylamine, and amino compound consecutively. Due to the high catalytic activity of ultra small gold nanoparticles synthesized, the reduction proceeded rapidly without intermediate accumulation. In the meantime, the substituent group exhibited the significant impact on the reactivity, which attributed to that the presence of electron-withdrawing group which is beneficial to the attack of hydride to reduce nitro group into amino group. These results deepen our understanding of the mechanism of Au-SiO₂ catalyzed reduction of nitroarenes by NaBH₄. Comparing with the early reports, the mechanism of this model reaction in our reaction system is similar with the catalyst that gold nanoparticles supported on other carriers^{16, 19, 31, 32}, although the interactions between gold and carriers are different^{33, 34}. This demonstrated that the catalytic mechanism depends on the gold nanoparticles for this model reaction^{15, 29, 30}. Furthermore, the effect of protonation of water is proved for the mechanism in our reaction system, and the catalytic activities can be greatly modulated by modifying the molecular structure of substituent group due to the substituent effect, which provides insight into the future design of reactants with substituent group to improve reaction efficiencies in other reactions.

3.4 Investigation by in-situ IR

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Comparing with the analytical techniques mentioned for this reaction mechanism which require a considerable period of time to provide analytical responses^{19-21, 35}, *in-situ* IR is an on-line analytical technique which provides immediate analytical result, however, requires strict conditions.^{36, 37} It demands the IR absorption peaks of each component in reaction mixture do not overlap with each other. For this Au-SiO₂ catalyzed reduction of nitroarenes, the catalyst Au-SiO₂ will not interfere with spectrum evolution of the single substrate due to the chemical inertness and clean IR spectrum of silica support. Therefore, it is a good opportunity to monitor this catalytic reaction by *in-situ* IR.

The *in-situ* IR spectrum of Au-SiO₂ catalyzed reduction of *p*-Nip is shown in Figure 5. It is clear to see the peak changes of each component in the reaction mixture. The intensity of the peak at 1520 cm⁻¹, which corresponds to C-H bending absorption of aromatic amine, increased with the reaction time. While the peak at 1500 cm⁻¹, corresponding to the C-H bending absorption of hydroxylamine compound, appeared at the very beginning of the reduction and its intensity kept the original form, reflecting the constant concentration of this intermediate at this test condition. As expected, intensity of the peak at 1290 cm⁻¹, which corresponds to the NO₂ symmetric stretch absorption, decreased in reduction process.³⁸ These results directly proved the

presence of nitro, amino, and hydroxylamine compounds during the reduction, and definitely confirmed the direct mechanistic pathway for the Au-SiO₂ catalyzed reduction of *p*-Nip. Comparing with the common analysis method, such as GC-MS of reaction profiles¹⁶, kinetic isotope effect¹⁹, and substituent effect aforementioned, the *in-situ* IR exhibits a real-time evolution of this Au-SiO₂ catalyzed reaction system, and obtained a direct information specifically related to substrate, product, and intermediate during the reduction. Thus, the *in-situ* IR is a suitable and direct method for on-line tracing the model reaction in our system, which offer a reference for future mechanism test of heterogeneous nanocatalysis.



Figure 5 In-situ IR spectrum recorded during the reduction progress.

Reaction conditions: 50 mL of the *p*-Nip aqueous solution (40 mmol/L), 50mg Au-SiO₂, and 750 mg NaBH₄, at room temperature.

Reusability of Au-SiO₂ was tested by performing a series of five consecutive runs of the reduction of *p*-Nip. The recycling experiments proceeded with the same samples recovered by filtration/washing cycle for three times. It was observed that all the runs could be finished in 25 minutes with almost 99% conversion and 99% selectivity (Table S 2). This indicated the cycles proceed with neither deactivation of catalyst nor selectivity. TEM images of the five times used Au-SiO₂ did not show alteration of the catalyst morphology and no aggregation of gold nanoparticles (Figure S 3). Moreover, the content of gold ion in the solution was only 0.031 mg/L after the reaction, which illustrated there was no outflow of gold (7.5 mg/L addition). Thus, at present, the Au-SiO₂ catalyst reflected a good reusability.

4 Conclusions

In conclusion, a kinetic analysis based on substituent effect and Hammett plot was present to confirm the mechanism of the reduction of nitroarenes. The reduction of nitroarenes by NaBH₄ was carried out using Au-SiO₂ as the catalyst in water medium. It is remarkable that the substituent group in nitroarenes has a significant effect on the reaction efficiency that the nitroarenes substituted with electron-withdrawing groups are reduced much faster than the corresponding nitroarenes with electron-donating groups. The kinetic analysis based on this finding, together with analyses of intermediates, brings a conclusion that the reduction of nitroarenes catalyzed by Au-SiO₂ follows a direct route. It is also proved that the protonation of water gives a suitable and direct method to real-time record the reaction evolution of this Au-SiO₂ catalyzed reduction of nitroarenes and confirms the presence of hydroxylamine, which is consistent with the direct route previously.

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References

- 1. S. Xiong, Y. Wang, J. Zhu, et al., *Langmuir*, 2015, **31**, 5504-5512.
- 2. A. Corma and P. Serna, *Science*, 2006, **313**, 332-334.
- 3. M. V. Parmekar and A. V. Salker, *RSC Adv.*, 2016, **6**, 108458-108467.
- 4. B. Paul, K. Chakrabarti, S. Shee, et al., *RSC Adv.*, 2016, 6, 100532-100545.
- 5. S. M. El-Sheikh, A. A. Ismail and J. F. Al-Sharab, New J. Chem., 2013, 37, 2399.
- 6. H. Göksu, New J. Chem., 2015, 39, 8498-8504.
- 7. O. Mazaheri and R. J. Kalbasi, *RSC Adv.*, 2015, **5**, 34398-34414.

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- 8. P. Veerakumar, M. Velayudham, K.-L. Lu, et al., *Appl. Catal.*, *A*, 2012, **439-440**, 197-205.
- 9. A. Corma, P. Concepcion and P. Serna, *Angew Chem Int Ed Engl*, 2007, 46, 7266-7269.
- 10. M. Bano, D. Ahirwar, M. Thomas, et al., New J. Chem., 2016, 40, 6787-6795.
- 11. P. Herves, M. Perez-Lorenzo, L. M. Liz-Marzan, et al., Chem. Soc. Rev., 2012, 41, 5577-5587.
- 12. F. Yang, S. Dong, C. Wang, et al., *RSC Adv.*, 2016, 6, 52620-52626.
- 13. E. Blanco, I. Esteve-Adell, P. Atienzar, et al., *RSC Adv.*, 2016, 6, 86309-86315.
- 14. A. Noschese, A. Buonerba, P. Canton, et al., J. Catal., 2016, 340, 30-40.
- 15. S. Kundu, S. Lau and H. Liang, J. Phys. Chem. C, 2009, **113**, 5150-5156.
- 16. K. Layek, M. L. Kantam, M. Shirai, et al., Green Chem., 2012, 14, 3164-3174.
- 17. S. Wunder, F. Polzer, Y. Lu, et al., J. Phys. Chem. C, 2010, 114, 8814-8820.
- 18. S. Wunder, Y. Lu, M. Albrecht, et al., ACS Catal., 2011, 1, 908-916.
- 19. S. Fountoulaki, V. Daikopoulou, P. L. Gkizis, et al., ACS Catal., 2014, 4, 3504-3511.
- 20. L. B. Zhao, Y. F. Huang, X. M. Liu, et al., *Phys. Chem. Chem. Phys.*, 2012, 14, 12919-12929.
- 21. A. Mahata, R. K. Rai, I. Choudhuri, et al., *Phys. Chem. Chem. Phys.*, 2014, 16, 26365-26374.
- 22. N. S. Isaacs, Physical Organic Chemistry 2th, *Addison Wesley Longman Limited, London*, 1995, 146-150.
- 23. C. Wang, X. Lin, Y. Ge, et al., *RSC Adv.*, 2016, 6, 102102-102108.
- 24. L. Sun, Q. Zhang, G. G. Li, et al., ACS nano, 2017, 11, 3213–3228.
- N. S. Isaacs, Physical Organic Chemistry 2th, Addison Wesley Longman Limited, London, 1995, 199-207.
- 26. Peter Atkins, Atkins' Physical Chemistry, Oxford University Press, Oxford, 2006, 797.
- 27. J. A. Dean, Lange's handbook of chemistry 15th, McGraw-Hill, New York, 1999, 934-940.
- 28. C. Hansch, A. Leo and R. W. Taft, Chem. Rev., 1991, 91, 165-195.
- 29. Q. Zhang, D. A. Blom and H. Wang, Chem. Mater., 2014, 26, 5131-5142.
- 30. Q. Zhang and H. Wang, ACS Catal., 2014, 4, 4027-4033.
- 31. Y. Que, C. Feng, S. Zhang, et al., J. Phys. Chem. C, 2015, 119, 1960-1970.
- 32. H. Liu, J. Wang, Z. Feng, et al., Small, 2015, 11, 5059-5064.
- 33. H. Tang, J. Wei, F. Liu, et al., J. Am. Chem. Soc., 2016, 138, 56-59.
- 34. M. Turner, V. B. Golovko, O. P. Vaughan, et al., *Nature*, 2008, **454**, 981-983.
- 35. S. Gu, Y. Lu, J. Kaiser, et al., *Phys. Chem. Chem. Phys.*, 2015, **17**, 28137-28143.
- 36. I. Marziano, D. C. A. Sharp, P. J. Dunn, et al., Org. Process Res. Dev., 2000, 4, 357-361.
- 37. C. Sun and D. Xue, CrystEngComm, 2015, 17, 2728-2736.
- 38. F. Visentin, G. Puxty, O. M. Kut, et al., Ind. Eng. Chem. Res., 2006, 45, 4544-4553.

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A new insight into the Au-SiO₂-catalyzed reduction of nitroarenes based on substituent effect and *in-situ* IR.