Article

Journal of
Nanoscience and Nanotechnology
Vol. 18, 8201–8206, 2018
www.aspbs.com/jnn

Selective Reduction of Nitro Group in Aryl Halides Catalyzed by Silver Nanoparticles Modified with β-CD

Xu Ding, Geng Zhu, Jian-Ning Guan, and Guo-Zhi Han*

School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 210009, China

In this paper, we first report the selective reduction of nitro group in aryl halides catalyzed by silver nanoparticles modified with β-CD. Taking advantage of hydrophobic lumen and donor–acceptor behavior of β-CD, the halogenated alkyl groups on the aromatic ring can be enveloped in the inner cavity that thereby inhibits the reduction of the halogen. For validating the mechanism proposed by us, different silver nanoparticles were applied in parallel experiments. In our experiments, UV-vis spectra and NMR spectra were used to characterize the selectivity. This strategy represents an outstanding improvement on the synthesis of halogenated aromatic amines in comparison with the traditional route, and greatly expands the application of silver nanoparticles in catalytic field.

Keywords: Selective Reduction, Nitro Group, Catalysis, Silver Nanoparticles, β-CD, Aryl Halides.

1. INTRODUCTION

Halogenated aromatic amines are an important class of organic synthesis intermediates, which were widely applied in many aspects such as pharmaceutical intermediates, dyes and pesticides, etc.[1–2] Due to their great value in industry of fine chemicals, the synthesis of halogenated aromatic amines has attracted intensive interests in the broad chemistry community for many years, and dozens of synthetic methods for halogenated aromatic amines have been reported.[3–6] Generally, halogenated aromatic amines are mainly prepared by the reduction of halogenated aromatic nitro compounds, and the routes usually include chemical reduction, electrochemical reduction and catalytic hydrogenation. However, there is an unavoidable matter of dehalogenation in the synthesis processes, especially when the halogens are in the side chain of aromatic ring.[7–9] To date, although there are many reported routes, the synthesis of halogenated aromatic amines still faces enormous challenges for high cost, tedious steps as well as heavy pollution.

In past decade, rapid progress in the nanosciences including preparation, characterization and synthetic applications of metal nanoparticles was observed.[10] Particularly, noble metal nanoparticles are currently being employed as catalysts for a number of chemical transformations.[11–16] For example, gold nanoparticles can act as biological enzymes to catalyze the reduction of nitro group.[17–18] Although the noble nanoparticles are promising heterogeneous catalysts due to their unique physicochemical properties,[19] most examples are thus far limited to single functional group transformations.[20] In contrast, identification of multifunctional group reaction of noble nanoparticles, especially toward the selective reduction, is highly underdeveloped and represents a bourgeoning area in organic synthesis. At present, a few reports about selective catalysis of noble nanoparticles are only focused on different stages of single functional group in transformation.[21–24] Simultaneously, reduction of nitro group to amino group often acts as a classical model to evaluate the catalytic activity of noble nanoparticles.[25–27] Since the nitro group is a reactive and strong electron-accepting group, selective reduction of nitro group in multifunctional compounds based on noble metal nanoparticles is predictable.[28] On the other hand, researches of catalytic ability of noble metal nanoparticles in selective reduction should offer opportunities for simplifying some complex organic synthesis processes. Herein, inspired by above idea and our previous researches,[29–30] we present our findings on the selective reduction of nitro group in aryl halides catalyzed by silver nanoparticles (AgNPs) modified with β-CD.

*Author to whom correspondence should be addressed.

Taking the advantage of hydrophobic lumen and donor–acceptor behavior of β-CD on the surface of AgNPs, the halogenated alkyl groups on the aromatic ring can be enveloped in the inner cavity that thereby inhibits the reduction of the halogen. To our best knowledge, there has been no report about the aspect.

2. EXPERIMENTAL DETAILS

2.1. Materials

β-Cyclodextrin (β-CD), silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$) and other chemical reagents were purchased from Aladdin reagent Co. Ltd. All reagents were of analytical grade and used with no purification. 4-bromomethyl nitrobenzene was synthesized according to literature.[31]

^{1}H NMR spectra were recorded on a JMN-LA 500 spectrometers (JEOL, Japan) operated at 400 MHz. Transmission electron microscopy (TEM) images were investigated by a JEM-2100 microscope (JEOL, Japan) operated at 200 kV. The UV-vis spectra were recorded on a UV-3600 spectrophotometer (Shimadzu, Japan). The FT-IR spectra of the AgNPs were examined by a Nicolet, AVATAR360 Fourier infrared spectroscopy (Nicolet, USA).

2.2. Preparation of AgNPs Modified with β-CD

Silver nanoparticles (AgNPs) modified with β-CD were prepared according to our previous report.[29] The details were described as follows. Typically, 20 mL of 0.05 M NaOH solution containing 0.33 g β-CD and 20 mL 0.05 M $AgNO_3$ solution were gradually added to 60 mL β-CD (0.80 g) aqueous solution respectively. The solution was stirred at speed of 500 rpm. Soon the reaction solution changed quickly from colorless to light brown and become turbid. After standing overnight, the solution becomes dark brown and transparent. The resulting silver particles were collected by centrifugation and washed at least three cycles using deionized water. Figure 1 shows the FTIR spectra of the as-prepared AgNPs modified with β-CD, in which the broad peaks at 3419 cm^{-1} and 1647 cm^{-1} are assigned to the vibration of the β-CD-OH. Asymmetric C–O–C stretching vibration in β-CD and AgNPs modified with β-CD can be seen at 1151 cm^{-1} and 1159 cm^{-1}, respectively. The infrared spectrum of AgNPs modified with β-CD has a strong characteristic peak at 1647 cm^{-1}, which is attributed to the oxidation of hydroxyl groups in the reduction process.

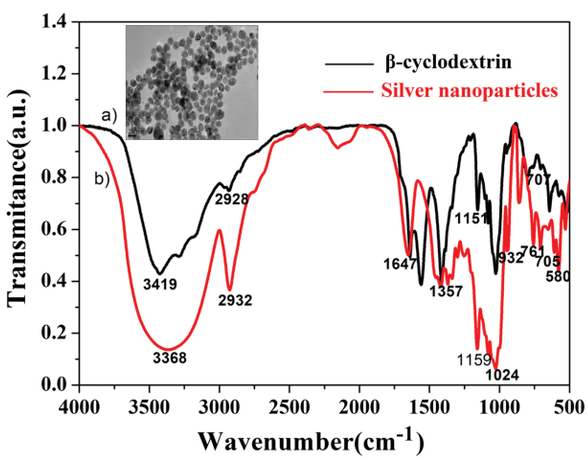


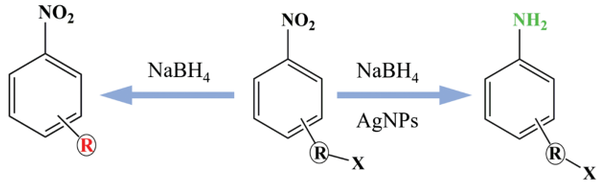
Figure 1. The FT-IR spectra of the AgNPs modified with β-CD.

2.3. Catalytic Reduction of Nitro Group in Aryl Halides

Firstly, 20 mL of 2.36 M freshly prepared $NaBH_4$ aqueous solution was added to 10 mL of 0.218 M 4-bromomethyl nitrobenzene ethanol solution. Then a small amount of AgNPs modified with β-CD was added to the above mixed solution at once. The solution was stirred for 12 h at room temperature. After filtering off the precipitate, the filtrate was extracted with dichloromethane twice. The organic phase was combined and the solvent was removed under vacuum to afford a yellow solid product. Furthermore, two other halogenated aromatic nitro compounds were used to conduct parallel test.

3. RESULTS AND DISCUSSION

An important potential application of silver particles is the catalysis of certain reduction reactions which would otherwise not happen. Usually, the classical reduction of nitro group to amino group by sodium borohydride ($NaBH_4$) is chosen to evaluate the catalytic activity of AgNPs and 4-nitrophenol is selected as a model molecule,[32–33] and the catalytic process is often monitored by UV-vis spectra. However, whether this catalytic reduction route is suitable for aromatic nitro compounds with other reactive functional groups is currently not reported. Namely, selective reduction of nitro group based on silver nanoparticles is a huge challenge and seems incredible. The research on this aspect would greatly expand the synthesis of polyfunctional aromatic amines along with application of noble nanoparticles in catalysis field. In this paper, due to its great application value, halogenated aromatic amines entered our field of vision. Our strategy is to obtain halogenated aromatic amines by selective reduction of halogenated aromatic nitro compounds. Firstly, 4-bromomethyl nitrobenzene was selected to study the selective catalytic ability of silver nanoparticles, and the corresponding target product is 4-bromomethylaniline which is an important halogenated aromatic amine intermediate. However, it is no doubt that the bromine atom in bromomethyl group is very active and easy to be reduced to methyl group by $NaBH_4$. On the other hand, another possible route to obtain 4-bromomethyl aniline is the bromination of 4-methyl aniline. Unfortunately, the presence of amino groups would greatly disturb the bromination process. Therefore, it is not a feasible way for the synthesis of 4-bromomethyl aniline.



Scheme 1. The plausible reduction reaction of halogenated aromatic nitro compounds by $NaBH_4$.

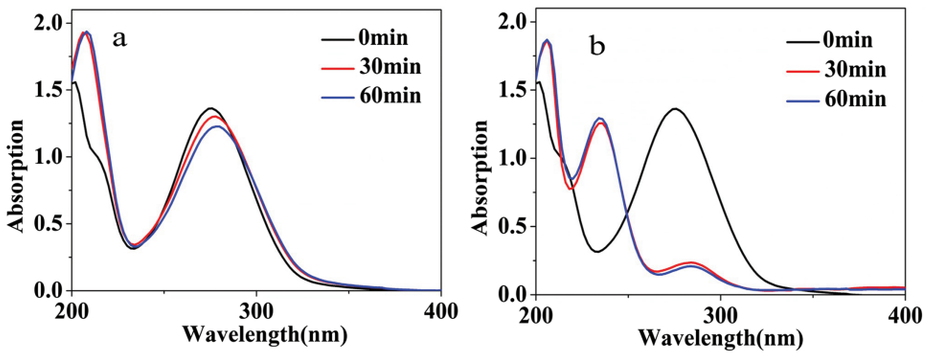


Figure 2. UV-vis spectra of reduction process of 4-bromomethyl nitrobenzene with and without AgNPs (a: Without AgNPs; b: With AgNPs).

Inspired by our previous researches and donor–acceptor behavior of β-CD, we propose a novel selective reduction of nitro group based on AgNPs modified with β-CD. The corresponding reaction equation in our strategy is shown in Scheme 1.

In this study, UV-vis spectra were similarly applied to monitor the reduction process. Figure 2 illustrates the reduction process of 4-bromomethyl nitrobenzene by $NaBH_4$ with and without AgNPs modified with β-CD as catalyst. Experimental results indicated that UV-vis spectra of the two reactions showed distinct characteristics. As for UV-vis spectra of 4-bromomethyl nitrobenzene, the peak at 276 nm is assigned to the B-band absorption of benzene ring, whereas peaks around 204 nm can be attributed to the E-band absorption of benzene ring. Without the AgNPs, the UV-vis spectra of the reduction process changed little, and the characteristic peak at 270 nm underwent a very weak red shift. In addition, the peaks around 204 nm degenerated to form a single peak. It can be concluded that only bromomethyl group was reduced by $NaBH_4$ in the absence of the AgNPs. Then the weak electron-withdrawing group of bromomethyl converted into a weak electron-donating group of methyl which resulted in the weak red shift. However, in the presence of AgNPs modified with β-CD, obvious red shift was observed in the UV-vis spectra of reduction process. The maximum absorption wavelength shifted from 276 nm to 286 nm, forming the characteristic B-band absorption of aromatic amines. The phenomenon may infer structural change of nitro group which acts as the strong chromophore. On the other hand, red shift of E-band from 204 nm to 233 nm is consistent with the transition of the nitro group to amino group. It is credible that bromomethyl group can be protected in the presence of AgNPs modified with β-CD. Next, these inferences were confirmed by ^{1}H NMR spectra as shown in Figure 3.

Combining the above experimental results, we proposed a possible reaction mechanism as shown in Figure 4. In a typical mechanism of reduction of nitro group catalyzed by AgNPs, the first step of electron transfer is determined

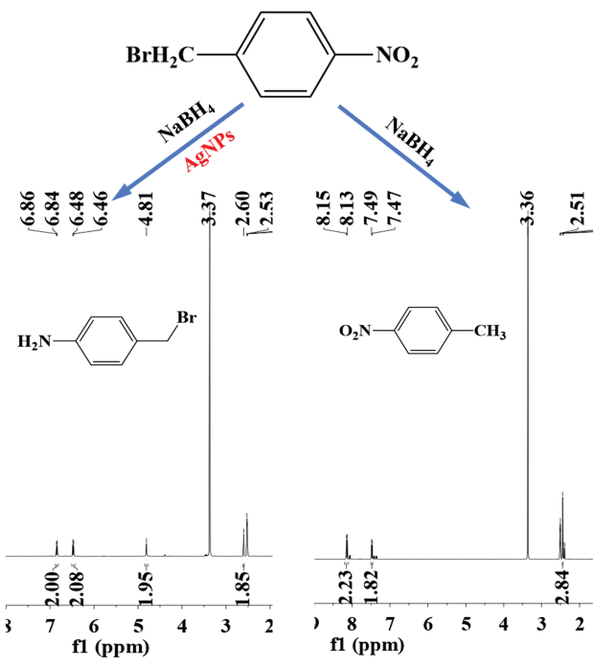


Figure 3. ^{1}H NMR spectra of the product of 4-bromomethyl nitrobenzene reduced by $NaBH_4$ with and without AgNPs modified with β-CD.

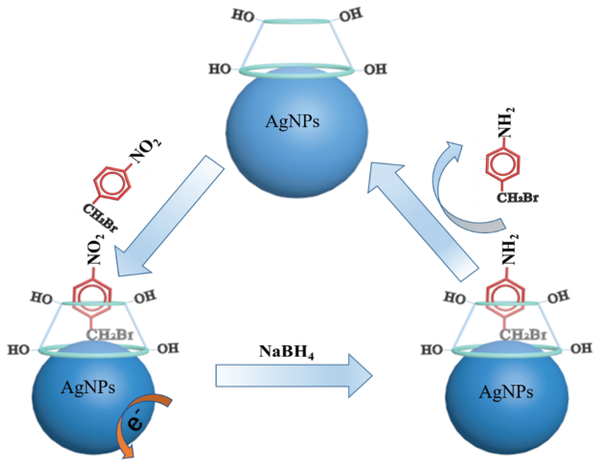


Figure 4. The plausible reduction mechanism of 4-bromomethyl nitrobenzene catalyzed by AgNPs modified with β-CD.

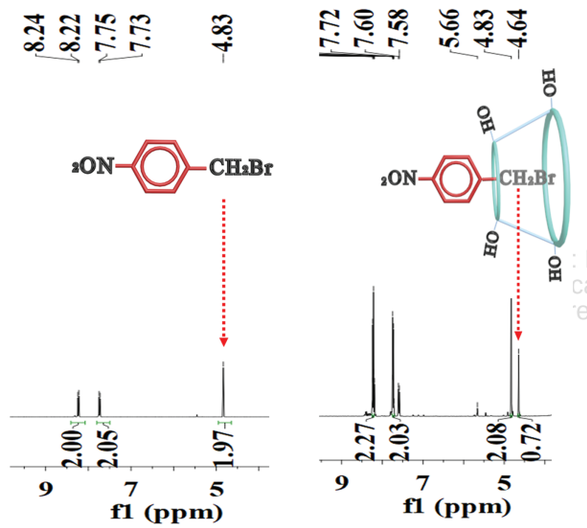


Figure 5. ^{1}H NMR spectra of pure 4-bromomethyl nitrobenzene and the mixture of 4-bromomethyl nitrobenzene with AgNPs modified with β-CD.

by the diffusion of molecule to the surface of metal nanoparticles.[34–35] In this mechanism, due to the hydrophobic lumen and donor–acceptor behavior of β-CD, the bromomethyl group can be enveloped in the inner cavity of β-CD that thereby inhibits the reduction of the halogen. The reason is on account of that the nature of the reduction by $NaBH_4$ is a substitution reaction by the hydrogen anion whereas the hydrogen anion is a hydrophilic group.

Although the mechanism proposed by us is credible, we further conducted a series of ^{1}H NMR tests to validate the claim. Figure 5 shows the ^{1}H NMR spectra of pure 4-bromomethyl nitrobenzene and the mixture of 4-bromomethyl nitrobenzene with AgNPs modified with β-CD. The experimental results indicated that the chemical shift of hydrogen on the methylene of 4-bromomethyl nitrobenzene was located at 4.83, whereas moved to 4.64 with the presence of the AgNPs. It should be attributed to the shielding effect of the cavity of β-CD on methylene. Interestingly, an unexpected coincidence was found that the chemical shift of hydrogen on the methylene of β-CD was also located at 4.83, but no peak was found at 4.64. The phenomenon can explain that why a strong peak at 4.83 in ^{1}H NMR spectra of 4-bromomethyl nitrobenzene in the presence of the AgNPs was still observed. Furthermore, compared with the pure 4-bromomethyl nitrobenzene, the chemical shift of hydrogen on the aromatic ring became complex in the presence of the AgNPs. It may be attributable to the coupling splitting between 4-bromomethyl nitrobenzene and β-CD.

To further demonstrate the selective catalytic ability of AgNPs modified with β-CD, we conducted the same reaction catalyzed by different AgNPs. Figure 6 shows the UV-vis spectra of the reduction process catalyzed by AgNPs prepared by β-CD and conventional sodium citrate, respectively. Experimental results indicated that, when the catalyst was replaced by AgNPs prepared by sodium citrate, red shift of the B-band absorption was observed. When the reaction was over, B-band absorption

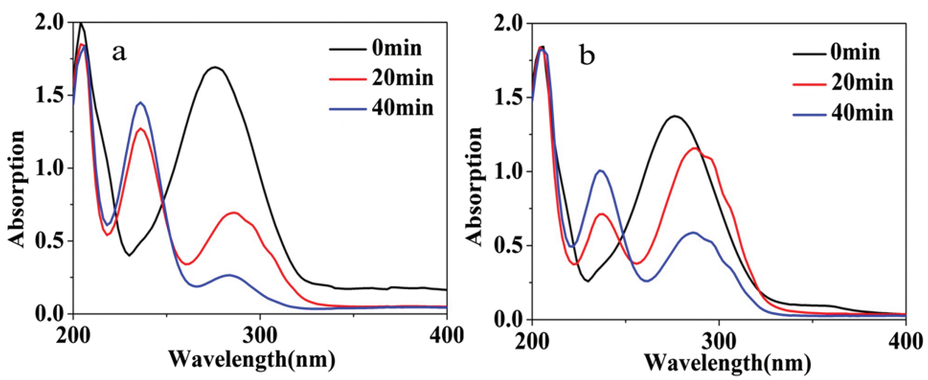


Figure 6. UV-vis spectra of the reduction reaction catalyzed by different AgNPs (295 K, a: AgNPs capped by β-CD, b: AgNPs capped by sodium citrate).

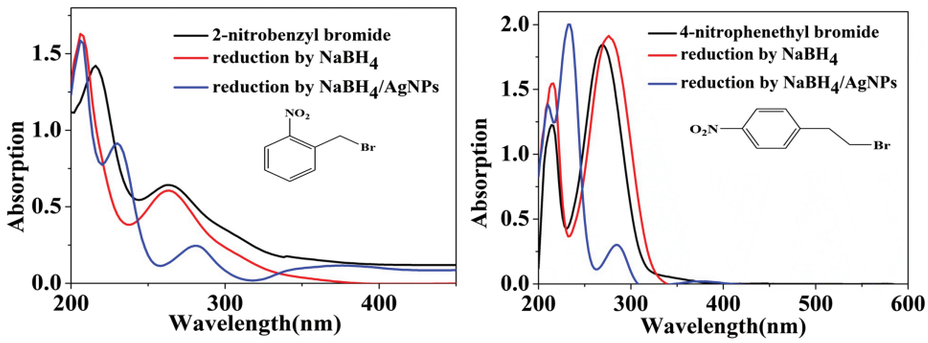


Figure 7. UV-vis spectra of reduction process of 2-nitrobenzyl bromide and 4-nitrophenylethyl bromide catalyzed by AgNPs modified with β-CD.

of the system catalyzed by AgNPs modified with β-CD was located at 283 nm, whereas that catalyzed by AgNPs prepared by sodium citrate shifted to 288 nm accompanied with the increase in absorption intensity. The phenomenon may be due to the simultaneous reduction of methyl bromide to methyl and then the push electron effect of methyl promotes the red shift of B band. This claim proposed by us was further confirmed by ^{1}H NMR spectra.

Finally, in order to investigate the suitable range of selective catalysis of the AgNPs modified with β-CD, 4-nitrophenylethyl bromide and 2-nitrobenzyl bromide were chose to conduct the same reaction. The UV-vis spectra of reduction process of the two compounds reflected the same selective catalytic features as shown in Figure 7. Similarly, ^{1}H NMR spectra were used to verify that the halogenated alkyl group was protected by β-CD in the reduction process. Therefore, we can conclude that the position of halogenated alkyl group on the aromatic ring and the length of the halogenated alkyl group have little effect on the selective catalysis of AgNPs modified with β-CD. Without doubt, the results of this study can greatly enhance the application value of AgNPs modified with β-CD in the synthesis of halogenated aromatic amines.

4. CONCLUSION

In summary, we first report a selective reduction of nitro group in aryl halides catalyzed by silver nanoparticles modified with β-CD. Taking the advantage of hydrophobic lumen and donor–acceptor behavior of β-CD, the halogenated alkyl groups on the aromatic ring can be enveloped in the inner cavity that thereby inhibits the reduction of the halogen. UV-vis spectra and ^{1}H NMR spectra were applied to verify the mechanism proposed by us. This study will open a new strategy for the synthesis of halogenated aromatic amines, and provides an idea for fabrication of novel selective catalyst.

Acknowledgments: This work was supported by the open project of the state key laboratory of bioelectronics of southeast university (Grant No. 20170118).

References and Notes

1. V. V. Annenkov, O. N. Verkhozina, T. A. Shishlyannikova, and E. N. Danilovtseva, *Anal. Biochem.* 486, 5 (**2015**).
2. M. S. Khan, A. Hanan, and A. Majeed, *J. Chem. Soc.* 10, 393 (**1988**).
3. R. S. Downing, P. J. Kunkeler, and H. Vanbekkum, *Catal. Today* 37, 121 (**1997**).
4. P. Ji, J. H. Atherton, and M. I. Page, *J. Org. Chem.* 77, 7471 (**2012**).
5. C. E. Hendrick and Q. Wang, *J. Org. Chem.* 80, 1059 (**2015**).
6. D. Herrmannsdörfer, M. Kaaz, O. Puntigam, J. Bender, M. Nieger, and D. Gudat, *Eur. J. Inorg. Chem.* 2015, 4819 (**2015**).
7. M. R. Naffziger, B. O. Ashburn, J. R. Perkins, and R. G. Carter, *J. Org. Chem.* 72, 9857 (**2007**).
8. W. Xu, J. J. Pignatello, and W. A. Mitch, *Sci. Technol.* 49, 3419 (**2015**).
9. F. Li, B. Frett, and H. Li, *Synlett* 25, 1403 (**2014**).
10. T. T. Li, J. J. Yang, Z. Ali, Z. L. Wang, X. B. Mou, N. Y. He, and Z. F. Wang, *Sci. China Chem.* 60, 370 (**2017**).
11. N. Kristian, Y. Yan, and X. Wang, *Chem. Commun.* 3, 353 (**2008**).
12. A. Aijaz, A. Karkamkar, Y. J. Choi, N. Tsumori, E. Rönnebro, T. Autrey, H. Shioyama, and Q. Xu, *J. Am. Chem. Soc.* 134, 13926 (**2012**).
13. S. K. Hanson and R. T. Baker, *Acc. Chem. Res.* 48, 2037 (**2015**).
14. X. Hong, D. Wang, S. Cai, H. Rong, and Y. Li, *J. Am. Chem. Soc.* 134, 18165 (**2012**).
15. S. N. Mohammad, *J. Mater. Chem.* 22, 21560 (**2012**).
16. R. W. J. Scott, O. M. Wilson, and R. M. Crooks, *Chem. Mater.* 16, 5682 (**2004**).
17. Q. Xiao, Z. Liu, F. Wang, S. Sarina, and H. Y. Zhu, *Appl. Catal. B* 209, 69 (**2017**).
18. M. J. Climent, A. Corma, J. C. Hernández, A. B. Hungría, S. Iborra, and S. Martínez-Silvestre, *J. Catal.* 292, 118 (**2012**).
19. J. Macanás, L. Ouyang, M. L. Bruening, M. Muñoz, J. C. Remigy, and J. F. Lahitte, *Catal. Today* 156, 181 (**2010**).
20. G. Budroni and A. Corma, *J. Catal.* 257, 403 (**2008**).
21. S. Gladiali and E. Alberico, *Chem. Soc. Rev.* 35, 226 (**2006**).
22. W. Cui, Q. Xiao, S. Sarina, W. Ao, M. Xie, H. Zhu, and Z. Bao, *Catal. Today* 235, 152 (**2014**).
23. J. S. M. Samec, J. Bäckvall, P. G. Andersson, and P. Brandt, *Chem. Soc. Rev.* 35, 237 (**2006**).
24. W. Zhang, G. Lu, C. Cui, Y. Liu, S. Li, W. Yan, C. Xing, Y. Chi, Y. Yang, and F. Huo, *Adv. Mater.* 26, 4056 (**2014**).
25. Y. Chen, J. Qiu, X. Wang, and J. Xiu, *J. Catal.* 242, 227 (**2006**).
26. A. Noschese, A. Buonerba, P. Canton, S. Milione, C. Capacchione, and A. Grassi, *J. Catal.* 340, 30 (**2016**).
27. H. Fu, L. Zhang, Y. Wang, S. Chen, and Y. Wan, *J. Catal.* 344, 313 (**2016**).
28. R. K. Rai, A. Mahata, S. Mukhopadhyay, S. Gupta, P. Li, K. T. Nguyen, Y. Zhao, B. Pathak, and S. K. Singh, *Inorg. Chem.* 53, 2904 (**2014**).

29. P. Li, S. Li, Y. Wang, Y. Zhang, and G. Han, *Colloids Surf. A* 520, 26 (**2017**).
30. Y. Cai, K. Gao, G. Li, Z. Deng, and G. Han, *Colloids Surf. A* 481, 407 (**2015**).
31. A. S. Achalkumar, B. N. Veerabhadraswamy, U. S. Hiremath, D. S. S. Rao, S. K. Prasad, and C. V. Yelamaggad, *Dyes and Pigments* 132, 291 (**2016**).
32. Z. Dong, X. Le, X. Li, W. Zhang, C. Dong, and J. Ma, *Appl. Catal. B* 158–159, 129 (**2014**).
33. J. R. Chiou, B. H. Lai, K. C. Hsu, and D. H. Chen, *J. Hazard. Mater.* 248–249, 394 (**2013**).
34. N. Chouhan, R. Ameta, and R. K. Meena, *J. Mol. Liq.* 230, 74 (**2017**).
35. A. Hernández-Gordillo, M. Arroyo, R. Zanella, and V. Rodríguez-González, *J. Hazard. Mater.* 268, 84 (**2014**).

Received: 17 April 2018. Accepted: 16 June 2018.