DOI: 10.1002/cjoc.201300310

Selective Reduction of Nitroarenes with Molybdenum Disulfide

Lei Huang, Pingfei Luo, Man Xiong, Rizhi Chen, Yong Wang, Weihong Xing, and Jun Huang*

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing, Jiangsu 210009, China

Commercial MoS_2 was found to be a highly selective catalyst for the reduction of nitrobenzenes to the corresponding anilines with hydrazine under mild conditions. MoS_2 is not only much cheaper, but also more selective than noble metal catalysts for the reduction of functional nitrobenzenes to the corresponding anilines. Nitrobenzenes with halides (F, Cl, Br and I) were reduced selectively, and the corresponding anilines were obtained in excellent yields, and no dehalogenation was detected. Functional groups such as NH_2, OH, alkene groups were tolerated during the reduction of the nitro compounds. The reduction of *p*-chloronitrobenzene was studied over MoS_2 and Pd/C respectively with hydrazine. The yield of *p*-chloroaniline was much higher with MoS_2 than that with Pd/C at full conversion.

Keywords anilines, reduction, molybdenum disulfide, nitrobenzenes

Introduction

Aromatic amines are important intermediates for the production of fine chemicals, pharmaceutical and agricultural products.[1] The traditional synthesis routes based on iron and hydrogen chloride (Bechamp reaction) are not environmental benign because of the low selectivity of the target amine and the emission of large amount of toxic waste.[2] The alternative approach was the catalytic hydrogenation by transition metal (Pt,[3] Pd,[4] Ru,[5] Au,[6] Ni[7]) catalysts with H_2, which shows high activity and good selectivity for the reduction of the nitrobenzene. However, the selectivity of the corresponding amine was not high enough, especially when other reducible groups are present in the same molecules. For example, when halides such as F, Cl, Br and I were in the nitroarenes, dehalogenation was always the side-reaction for the reduction of nitroarenes with transition metal catalysts. Moreover, the selective reduction of a nitro group is also a challenge when alkene groups are present in the same molecules. Cardenas-Lizana *et al*. reported the hydrogenation of functional nitrobenzenes over supported Au and Ag, and excellent selectivity was achieved at a continuous gas phase reactor.[8] In addition, other hydrogen sources (such as HCOOH, $HCOONH_4$, $PhSiH_3$, H_2NNH_2, H_2O) were applied for the catalytic hydrogenation of nitro compounds, and high selectivity was obtained.[9] Recently, we have reported Pt and Rh nanocatalysts for the selective reduction of nitrobenzenes with H_2 and hydrazine respectively.[10]

Molybdenum disulfide was used widely as hydrotreating catalyst in the early twentieth century, as it was much cheaper than noble metal catalysts.[11] Afterwards, it was studied extensively in CO reduction[12] and the hydrodesulfurization[13] processes for the production of clean fuels. Molybdenum disulfide used as catalyst for the reduction nitrobenzenes is rare. Sun *et al*. reported Zr-intercalated MoS_2 for the reduction of nitrobenzene, but the activity was not high enough.[14] Recently, Ruiz reported the reduction of 2-methoxyphenol based on MoS_2.[15] Moreover, Beller group reported a homogeneous catalyst based on Mo_3S_4 cluster, which was highly selective for the reduction of nitrobenzenes.[16]

Herein, we reported that MoS_2 was used as a highly selective catalyst for the reduction of nitrobenzenes with hydrazine under mild conditions. When halides such as F, Cl, Br and I were present in the nitrobenzenes, the corresponding anilines were obtained in quantitative yield and no dehalogenation happened. Functional groups such as NH_2, OH and alkene groups were tolerated during the reduction of the nitrobenzenes. It is highly favourable to use MoS_2 instead of the noble metal catalysts, as MoS_2 is much cheaper than noble metal catalysts. Furthermore the selectivity was much higher than noble metal catalysts for the reduction of NO_2 group to NH_2 group, especially for the reduction of nitrobenzenes with halides, since the dehalogenation side-reaction was hard to avoid with noble metal catalysts.

---

* E-mail: junhuang@njut.edu.cn; Tel.: 0086-025-83172276; Fax: 0086-025-83172261
Received April 14, 2013; accepted June 5, 2013; published online XXXX, 2013.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201300310 or from the author.

Experimental

Reagents and analytical methods

All reagents were purchased from Aladdin Reagent Company, Sigma-Aldrich Company and Alfa-Aesar Company without further purification.

Gas chromatography analyses were performed on a Hewlett Packard 5890 instrument with a FID detector and Hewlett Packard 24 m×0.2 mm i.d. HP-5 capillary column. The specific surface areas and the average pore sizes of the materials were measured on a Belsorp II physical adsorption apparatus by BET and BJH methods.

Reduction of nitrobenzenes

Typical procedure for the reduction of nitrobenzenes with hydrazine: The schlenk tube with a stir bar was flushed with Ar more than three times to remove the air, and filled with Ar. Then, nitrobenzene (1.0 mmol), hydrazine monohydrate (3.0 mmol), MoS_2 (0.1 mmol, 16 mg) and toluene (2.0 mL) were added into the tube. After the tube was closed, the reaction was kept at 25—80 ℃ for a desired time with continuously stirring. After the reaction was completed, 100 μL of $C_{16}H_{34}$ was added to the reaction mixture. The MoS_2 catalyst was filtrated off and washed with ethanol (2.0 mL×3). The products (in the filtrate mixture) were analyzed by GC. All prepared anilines are commercially available and identified by comparison (GC/MS) with authentic samples (purchased from Aladdin Reagent, Alfa-Aesar and Sigma-Aldrich Company). The Pd/C (16 mg, Pd: 5 wt%)catalysed hydrogenation of nitrochlorobenzene with hydrazine was performed in a similar way.

Reusability of the MoS_2

When the reaction was completed and the reaction mixture was cooled, the catalyst was collected by filtration. The catalyst was washed by ethanol (2.0 mL×3) and dried under vacuum at 25 ℃ for 12 h, and then used again for the next reaction cycle.

Results and Discussion

On the basis of the nitrogen adsorption-desorption analysis, the BET surface areas of MoS_2 was 4 m^2/g (Figure 1).

The reduction of nitrobenzene with hydrazine was performed as a model reaction, and the results are listed in Table 1. Toluene, THF, H_2O, cyclohexane (Table 1, Entry 1—4) were good solvents, and aniline could be obtained in good yield. But, ethanol and 1,4-dioxane (Table 1, Entry 5—6) were less effective solvents for the transformation. The reduction of nitrobenzene afforded aniline in good yield also without solvent (Table 1, Entry 7). No aniline was obtained when H_2 was used as reducer or without MoS_2 catalyst (Table 1, Entry 8, 9). When the reaction was scaled up to 10 times (10 mmol nitrobenzene) with low catalyst loading (1 mol% MoS_2), aniline was obtained quantitatively also, but the reaction required longer time (Table 1, Entry 10).

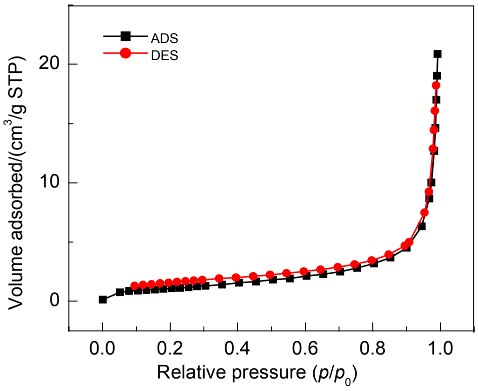
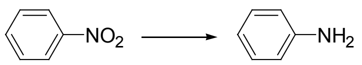


Figure 1 Nitrogen adsorption-desorption isotherms of MoS_2.

Table 1 MoS_2 catalyzed reduction of nitrobenzene to aniline with hydrazine[a]



Entry	Solvent	(Conv./Yield)/%
1	Toluene	100/>99
2	THF	100/95
3	H_2O	97/88
4	Cyclohexane	100/>99
5	Ethanol	100/75
6	1,4-Dioxane	100/42
7	Solvent free	100/96
8[b]	Toluene	0/0
9[c]	Toluene	0/0
10[d]	Toluene	100/>99

[a] Reaction conditions: nitrobenzene, 1.0 mmol; MoS_2, 0.1 mmol, 16 mg; $N_2H_4{\bullet}H_2O$, 3.0 mmol; 60 ℃; in 3 h; 2.0 mL solvent. The conversions and yields were determined by GC ($C_{16}H_{34}$ used as internal standard). [b] 1.0 atm H_2 was used as reducer. [c] Without catalyst. [d] Nitrobenzene, 10 mmol; MoS_2, 0.1 mmol, 16 mg; $N_2H_4{\bullet}H_2O$, 30 mmol; 60 ℃; 12 h.

The reusability of the MoS_2 catalyst was tested and the results are shown in Table 2. The MoS_2 catalyst was easily recycled by filtration and reused for the next reaction cycle. The MoS_2 can be reused at least 8 times without loss of activity (Table 2).

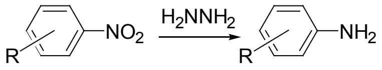
Table 2 The reusability of the MoS_2 for the reduction of nitrobenzene[a]

Recycled	1	2	3	4	5	6	7	8
Conv./%	100	100	100	100	100	100	100	100
Yield/%	>99	>99	>99	>99	>99	>99	>99	>99

[a] Reaction conditions: nitrobenzene, 1.0 mmol; MoS_2, 0.1 mmol, 16 mg; $N_2H_4{\bullet}H_2O$, 3.0 mmol; 60 ℃; in 3 h; 2.0 mL toluene as solvent. The conversions and yields were determined by GC ($C_{16}H_{34}$ used as internal standard).

The reduction of various functional nitroarenes was studied with hydrazine, and the results are summarized in Table 3. For the hydrogenation of nitro aromatics with halides (F, Cl, Br and I), the MoS_2 catalyst showed excellent activity and selectivity. The corresponding anilines were obtained in excellent yield, and no aniline was observed, which indicated no dehalogenation occurred (Table 3, Entries 1—7). OH and NH_2 groups were also tolerated during the hydrogenation of NO_2, and the corresponding anilines were obtained in good yields (Table 3, Entries 8—11). The 2,6-dimethylnitrobenzene was hydrogenated to 2,6-dimethylaniline in good yield also (Table 3, Entry 12). Moreover, the hydrogenation of 3-nitrostyrene gave 3-aminestyrene quantitatively (Table 3, Entry 13).

Table 3 MoS_2 catalyzed reduction of substituted nitroarenes with hydrazine[a]



Entry	R	Time/h	(Conv./Yield)/%
1	2-F	3	100/>99
2	4-F	3	100/>99
3	2-Cl	3	100/>99
4	3-Cl	3	100/>99
5	4-Cl	3	100/>99 (98[f])
6	2-Br	3	100/>99
7[b]	3-I	24	100/>99
8	2-NH_2	10	100/>99
9	4-NH_2	10	100/>99
10	3-OH	6	100/>99
11	4-OH	6	100/>99 (>99[f])
12[b]	2,6-CH_3	24	100/>99
13[c]	3-C=C	6	100/>99
14[d]	4-Cl	10	100/>99

[a] Reaction conditions: nitrobenzene, 1.0 mmol; MoS_2, 0.1 mmol, 16 mg; 60 ℃; $N_2H_4•H_2O$, 3.0 mmol. The conversions and yields were determined by GC ($C_{16}H_{34}$ used as internal standard). [b] 80 ℃, $N_2H_4•H_2O$, 5.0 mmol used. [c] 3-Vinylaniline yield. [d] At 25 ℃. [f] Isolated yield.

In addition, the MoS_2 catalysed hydrogenation process of *p*-chloronitrobenzene with hydrazine monohydrate was investigated, and the results are shown in Figure 2. The NO_2 was reduced smoothly to NH_2 with MoS_2 catalyst, and no side-reaction (dechlorination) was found. All the *p*-chloronitrobenzene was converted to *p*-chloroaniline in 100% yield in 3 h, and no aniline was observed. It is important to test the selectivity of catalysts under harsher conditions (longer reaction time and higher reaction temperature), as it is not easy to control the reaction conditions in large scale processes. It is found that the dechlorination will not occur with MoS_2 catalyst even in longer reaction time (10 h) or at higher reaction temperature (60 ℃) (Table 3, Entries 5, 14), which facilitated the industrial design of the selective hydrogenation processes.

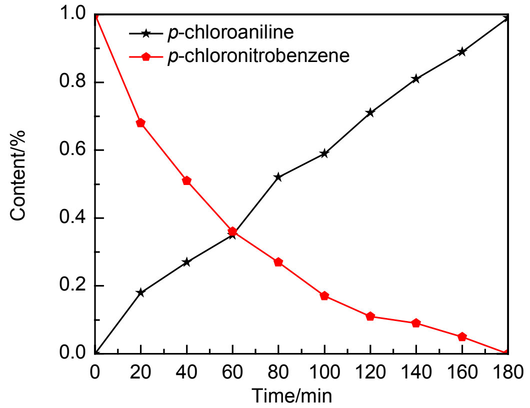


Figure 2 MoS_2 catalyzed hydrogenation of *p*-chloronitrobenzene with $N_2H_4•H_2O$. Reaction conditions: *p*-chloronitrobenzene, 1.0 mmol; MoS_2 catalyst, 16 mg; $N_2H_4•H_2O$, 3.0 mmol; at 25 ℃; 2.0 mL toluene as solvent.

To compare MoS_2 catalyst with the commercial catalyst (Pd/C Pd: 5.0 wt%), we performed the Pd/C catalyzed hydrogenation of *p*-chloronitrobenzene with hydrazine monohydrate under similar reaction conditions, and the results are shown in Figure 3. From Figure 3, we can see that the consumption of *p*-chloronitrobenzene was faster with Pd/C than that with MoS_2, but the selectivity of *p*-chloroaniline was low, and the hydrogenation of the NO_2 was always accompanied with the dechlorination during the reaction process. In the end, *p*-chloroaniline and aniline were obtained in 75% yield and 25% yield respectively at full conversion of *p*-chloronitrobenzene with Pd/C catalyst. The selectivity with MoS_2 was much better than that with Pd/C catalyst. High selectivity was highly desirable for modern chemical industry, which may simplify the product separation, avoid waste disposal and develop greener processes.

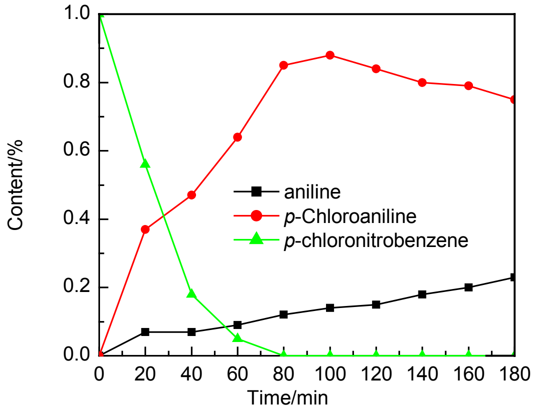
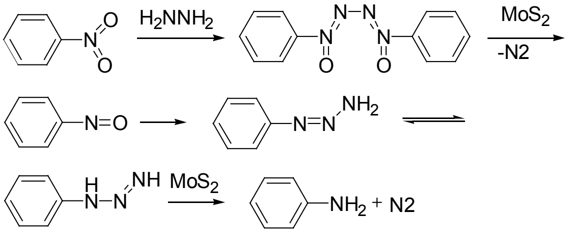


Figure 3 Pd/C catalyzed hydrogenation of *p*-chloronitrobenzene with $N_2H_4•H_2O$. Reaction conditions: *p*-chloronitrobenzene, 1.0 mmol; Pd/C catalyst (Pd: 5.0 wt%), 16 mg; $N_2H_4•H_2O$, 3.0 mmol; at 25 ℃; 2.0 mL toluene as solvent.

Hydrazine is a good reducer, but H_2 gas is nearly not an effective reducer for the reduction of nitrobenzene to aniline (Table 1, Entry 8), which indicated that the condensation of nitro group with hydrazine is preferentially happened. Mo is the key element of nitrogenase in plants for the fixation of N_2[17] and the important catalytic center for the synthesis of NH_3 from N_2 and H_2.[18] Therefore, MoS_2 may be favorable for the H-transformation and the emission of N_2 to form the corresponding aniline. We have proposed the pathway of the reduction of nitrobenzene with hydrazine over Rh/HAP catalyst,[10c] and similar pathway was suggested over MoS_2. An intermediate is formed firstly through the condensation of the nitro group with N_2H_4, and then the decomposition of the intermediate by MoS_2 gives nitrosobenzene and N_2. The condensation of nitrosobenzene with N_2H_4 is followed by H-transformation, and then the decomposition leads to aniline with N_2 gas (Scheme 1).

Scheme 1 A possible pathway for the reduction of nitrobenzene with H_2NNH_2



Conclusions

In summary, we demonstrated MoS_2 catalyst reduced nitroarenes efficiently and selectively into corresponding anilines with hydrazine monohydrate under mild conditions. To the hydrogenation of substituted nitrobenzenes, nitroarenes with halides (F, Cl, Br and I) were reduced selectively, and the corresponding anilines were obtained in excellent yields, none of aniline was observed. Functional groups such as NH_2, OH, alkene groups were tolerated during the hydrogenation of the nitro compounds, and the corresponding anilines were obtained in good yields. The MoS_2 was used as a catalyst in the hydrogenation of *p*-chloronitrobenzene, and 100% selective reduction of NO_2 group was achieved at complete conversion of the nitroarene. In contrast, Pd/C (5 wt%), used as a benchmark catalyst, was nonselective and generated aniline from a combined hydrodechlorination/hydrogenation. Our results demonstrate the potential of MoS_2 to promote the clean production of amino-compounds with multiple industrial applications.

Acknowledgement

This work was supported by the National Natural Science of Foundation of China (Nos. 21136005, 21125629), the National High Technology Research and Development Program of China (No. 2012AA03A606), Foundation from State Key Laboratory of Materials-Oriented Chemical Engineering (Nos. ZK201003, ZK201011), and Graduate Education Innovation Project in Jiangsu Province (No. CXZZ12_0447).

References

[1] Booth, G. *Ullmanns Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag, Weinheim, Germany, **2002**.

[2] Sheldon, R. A.; van Bekkum, H. *Fine Chemicals through Heterogeneous Catalysis*, Wiley-VCH, Weinheim, **2001**.

[3] (a) Wang, F.; Liu, J.; Xu, X. *Chem. Commun.* **2008**, *17*, 2040; (b) Li, M.; Hu, L.; Cao, X.; Hong, H.; Lu, J.; Gu, H. *Chem. Eur. J.* **2011**, *17*, 2763; (c) Pandarus, V.; Ciriminna, R.; Beland, F.; Pagliaro, M. *Adv. Synth. Catal.* **2011**, *353*, 1306; (d) Nie, R.; Wang, J.; Wang, L.; Qin, Y.; Chen, P.; Hou, Z. *Carbon* **2012**, *50*, 586; (e) Motoyama, Y.; Kamo, K.; Nagashima, H. *Org. Lett.* **2009**, *11*, 1345; (f) Lian, C.; Liu, H.; Xiao, C.; Yang, W.; Zhang, K.; Liu, Y.; Wang, Y. *Chem. Commun.* **2012**, *48*, 3124; (g) Liu, H.; Lu, G. *Chinese. J. Inorg. Chem.* **2011**, *27*, 2045; (h) Han, X.; Li, J.; Zhou, R. *Chin. Chem. Lett.* **2009**, *20*, 96.

[4] (a) Pandarus, V.; Ciriminna, R.; Beland, F.; Pagliaro, M. *Catal. Sci. Technol.* **2011**, *1*, 1616; (b) Li, J.; Shi, X.; Bi, Y.; Wei, J.; Chen, Z. *ACS Catal.* **2011**, *1*, 657; (c) Zhang, R.; Liu, J.; Li, F.; Wang, S.; Xia, C.; Sun, W. *Chin. J. Chem.* **2011**, *29*, 525; (d) Yan, R.; Xu, J.; Zhang, Y.; Wang, D.; Zhang, M.; Zhan, W. *Chem. Eng. J.* **2012**, *200—202*, 559; (e) Chatterjee, M.; Ishizaka, T.; Suzuki, T.; Suzuki, A.; Kawanami, H. *Green Chem.* **2012**, *14*, 3415; (f) Harraza, F. A.; El-Houta, S. E.; Killab, H. M.; Ibrahima, I. A. *J. Catal.* **2012**, *286*, 184.

[5] (a) Zhao, S.; Liang, H.; Zhou, Y. *Catal. Commun.* **2007**, *8*, 1305; (b) Chary, K. V. R.; Srikanth, C. S. *Catal. Lett.* **2009**, *128*, 164; (c) Cui, X.; Shi, F.; Deng, Y. *ChemCatChem* **2012**, *4*, 333; (d) Antonetti, C.; Oubenali, M.; Galletti, A. M. R.; Serpb, P.; Vannucci, G. *Appl. Catal. A*: *Gen.* **2012**, *421—422*, 99.

[6] (a) Corma, A.; Serna, P. *Science* **2006**, *313*, 332; (b) Corma, A.; Concepcion, P.; Serna, P. *Angew. Chem.*, *Int. Ed.* **2007**, *46*, 7266; (c) Makosch, M.; Sa, J.; Kartusch, C.; Richner, G.; van Bokhoven, J. A.; Hungerbuhler, K. *ChemCatChem* **2012**, *4*, 59; (d) Boronat, M.; Concepcion, P.; Corma, A.; Gonzalez, S.; Illas, F.; Serna, P. *J. Am. Chem. Soc.*, **2007**, *129*, 16230.

[7] (a) Li, H.; Xu, Y.; Yang, H.; Zhang, F.; Li, H. *J. Mol. Catal. A*: *Chem.* **2009**, *307*, 105; (b) Lin, M.; Zhao, B.; Chen, Y. *Ind. Eng. Chem. Res.* **2009**, *48*, 7037; (c) Li, H.; Zhao, Q.; Li, H. *J. Mol. Catal. A*: *Chem.* **2008**, *285*, 29; (d) Mohan, V.; Pramod, C. V.; Suresh, M.; Hari Prasad Reddy, K.; David Raju, B.; Rama Rao, K. S. *Catal. Commun.* **2012**, *18*, 89; (e) Lin, W.; Cheng, H.; Ming, J.; Yu, Y.; Zhao, F. *J. Catal.* **2012**, *291*, 149; (f) Raj, K. J. A.; Prakash, M. G.; Mahalakshmy, R.; Elangovan, T.; Viswanathan, B. *Chin. J. Catal.* **2012**, *33*, 1299; (g) Bai, Y.; Zhu, X.; Zhang, L.; Xu, N. *Chin. J. Catal.* **2013**, *34*, 263.

[8] (a) Cardenas-Lizana, F.; Gomez-Quero, S.; Perret, N.; Keane, M. A. *Catal. Sci. Technol.* **2011**, *1*, 652; (b) Cardenas-Lizana, F.; de Pedro, Z. M.; Gomez-Quero, S.; Keane, M. A. *J. Mol. Catal. A* **2010**, *326*, 48.

[9] (a) Wienhofer, G.; Sorribes, I.; Boddien, A.; Westerhaus, F.; Junge, K.; Junge, H.; Llusar, R.; Beller, M. *J. Am. Chem. Soc.* **2011**, *133*, 12875; (b) Lou, X.; He, L.; Qian, Y.; Liu, Y.; Cao, Y.; Fan, K. *Adv. Synth. Catal.* **2011**, *353*, 281; (c) Junge, K.; Wendt, B.; Shaikh, N.; Beller, M. *Chem. Commun.* **2010**, *46*, 1769; (d) Jagadeesh, R. V.; Wienhofer, G.; Westerhaus, F. A.; Surkus, A.; Pohl, M.; Junge, H.; Junge, K.; Beller, M. *Chem. Commun.* **2011**, *47*, 10972; (e) Gowda, S.; Gowda, D. C. *Indian J. Chem.* **2003**, *42B*, 180; (f) Hirashima, T.; Manabe, O. *Chem. Lett.* **1975**, 259; (g) Zhou, H.; Shi, L.; Sun, Q. *Chin. J. Catal.* **2012**, *33*, 1463; (h) Jiang, H.; Dong, Y. *Chin. J.*

Chem. **2008**, *26*, 1407.

[10] (a) Xu, K.; Zhang, Y.; Chen, X.; Huang, L.; Zhang, R.; Huang, J. *Adv*. *Synth*. *Catal*. **2011**, *353*, 1260; (b) Luo, P.; Xu, K.; Zhang, R.; Huang, L.; Wang, J.; Xing, W.; Huang, J. *Catal*. *Sci*. *Technol*. **2012**, *2*, 301; (c) Huang, L.; Luo, P.; Pei, W.; Liu, X.; Wang, Y.; Wang, J.; Xing, W.; Huang, J. *Adv*. *Synth*. *Catal*. **2012**, *354*, 2689.

[11] (a) Okuhara, T.; Tanaka, K. *J*. *Chem*. *Soc*., *Faraday Trans*. *1* **1979**, *75*, 1403; (b) Wambeke, A.; Jalowiecki, L.; Kasztelan, S.; Grimblot, J.; Bonnelle, J. P. *J*. *Catal*. **1988**, *109*, 320.

[12] (a) Huang, M.; Cho, K. *J*. *Phys*. *Chem*. *C* **2009**, *113*, 5238; (b) Surisetty, V. R.; Tavasoli, A.; Dalai, A. K. *Appl*. *Catal*. *A*: *Gen*. **2009**, *365*, 243.

[13] (a) Sampieri, A.; Pronier, S.; Blanchard, J.; Breysse, M.; Brunet, S.; Fajerweg, K.; Louis, C.; Perot, G. *Catal*. *Today* **2005**, *107*－*108*, 537; (b) Tye, C. T.; Smith, K. J. *Catal*. *Today* **2006**, *116*, 461; (c) Yoosuk, B.; Kim, J. H.; Song, C.; Ngamcharussrivichai, C.; Prasassarakich, P. *Catal*. *Today* **2008**, *130*, 14; (d) Ho, T. C.; McConnachie, J. M. *J*. *Catal*. **2011**, *277*, 117.

[14] Sun, D.; Lin, B.; Xu, B.; He, L.; Ding, C.; Chen, Y. *J*. *Porous Mater*. **2008**, *15*, 245.

[15] Ruiz, P. E.; Frederick, B. G.; De Sisto, W. J.; Austin, R. N.; Radovic, L. R.; Leiva, K.; Garcia, R.; Escalona, N.; Wheeler, M. C. *Catal*. *Commun*. **2012**, *27*, 44.

[16] Sorribes, I.; Wienhofer, G.; Vicent, C.; Junge, K.; Llusar, R.; Beller, M. *Angew*. *Chem*., *Int*. *Ed*. **2012**, *51*, 7794.

[17] Schwarz, G.; Mendel, R. R.; Ribbe, M. W. *Nature* **2009**, *460*, 839.

[18] Bullock, R. M. *Catalysis without Precious Metals*, Wiley-VCH, Weinheim, **2010**.

(Pan, B.; Lu, Z.)