Catalysis Science & Technology

PAPER

View Article Online View Journal | View Issue

Cite this: *Catal. Sci. Technol.,* 2013, **3**, 1123

Received 9th October 2012, Accepted 18th December 2012

DOI: 10.1039/c2cy20692g

www.rsc.org/catalysis

One-pot synthesis of gold nanoparticles embedded in silica for cyclohexane oxidation

Cuihua Wang, Lifang Chen* and Zhiwen Qi*

Highly-dispersed gold nanoparticles embedded in amorphous silica (Au/M-SiO₂) were prepared by a facile one-pot process utilizing thioether functional groups to anchor $AuCl_4^-$. A surprisingly high TOF up to 21097 h⁻¹ was obtained over the 0.2% Au/M-SiO₂ catalyst, and the 1.5% Au/M-SiO₂ catalyst exhibited a high catalytic activity of 22.7% for cyclohexane conversion and 80.6% selectivity to cyclohexanol and cyclohexanone under dipolar non hydrogen bond donor (HBD) acetone solvent at 423 K and 1.5 MPa O₂ for 3 h.

Introduction

The selective oxidation of cyclohexane to cyclohexanone and cyclohexanol (also known as K/A oil) is significant, which attracts particular interest in the chemical industry because the two main products are important intermediates for the manufacture of nylon 6 and nylon 6,6 polymers.¹ In the present industrial processes, the aerobic cyclohexane oxidation is operated at 415–435 K and 1–2 MPa, in which the conversion is kept at about 4% to suppress the further formation of by-products, giving 70%–85% selectivity towards K/A oil.² The catalysts currently used, such as Mn and Co naphthenates, are homogeneous, undesirable to the environment and energy-saving, but they are still widespread. These disadvantages make it necessary and urgent to design and cultivate effective heterogeneous catalysts to active hydrocarbons using an environmentally benign oxidant.

Recently, gold-based catalysts have received increasing interest and demonstrated promising activity for different types of oxidative reactions³ since gold nanoparticles were discovered to display a surprisingly high catalytic activity in the oxidation of CO at low temperatures.⁴ Moreover, different kinds of goldbased homogeneous and heterogeneous catalysts in the form of metal complexes or nanoparticles have been developed.⁵ In general, the catalytic properties of the heterogeneous gold catalysts strongly depend on the size, stability, and amount of gold nanoparticles. However, Au nanoparticles supported on inert supports that were reported recently were mostly prepared directly during the synthesis process by an *in situ* addition.⁶ Thus, high calcination temperatures were needed to remove the templating agents, resulting in large Au particles.⁷ In order to obtain very small gold nanoparticle sizes and highly active gold catalysts, a chemical grafting and reduction process was reported. Grafting ligands, such as amine,⁸ thiol^{6a} and thioether^{6c} have been applied to anchor gold nanoparticles because of the weak interaction between AuCl₄⁻⁻ and unshared pair electrons of organic groups, followed by a reduction procedure to achieve gold nanoparticles supported on the surface of pure supports.⁷ However, gold nanoparticles are mobile on the surface of most supporting oxides. One of key problematic issues is the stability of Au nanoparticles against sintering under reaction conditions.

In this work, we present a novel and facile one-pot synthesis of highly dispersed gold nanoparticles embedded in amorphous silica in the absence of any template. A thioether organosilane [1,4-bis(triethoxysily)] propane tetrasulfide, TESPTS] was used to anchor AuCl₄⁻ and connect tetraethyl orthosilicate forming organic–inorganic hybrid linkers *via* co-condensation. Calcination of the catalyst precursors removed organic moieties and reduced the gold salt to gold nanoparticles. The reaction performance showed that the 1.5% Au/M-SiO₂ catalyst displayed high activity in the selective cyclohexane oxidation to K/A oil with molecular oxygen. The effects of traditional solvents on the catalytic performances of the Au catalysts were also investigated.

Experimental

The Au catalysts were prepared using a facile one-pot synthesis process. A mixture of 2 mL TEOS and 35 μ L TESPTS was dissolved in 30 mL isopropanol quickly added with vigorous magnetic stirring at room temperature, followed the pre-designated amounts of aqueous AuCl₄⁻ solution were added dropwise. After about 20 min, 2 mL deionized water was added dropwise

State Key Laboratory of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China. E-mail: lchen@ecust.edu.cn, zwqi@ecust.edu.cn; Fax: +86 21 64253528; Tel: +86 21 64250935

and kept at \sim pH 8 by adding a small amount of aqueous ammonia. The solution was stirred for 30 h at room temperature. The solid was filtered off, washed with water and ethanol three times, air-dried at 333 K overnight and calcined at 723 K for 5 h.

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2550 X-ray diffractometer with a Cu-K α radiation of wavelength λ = 1.5418 Å, in the 2 θ range of 10–90°. N₂ absorption-desorption isotherms were measured on a Micrometrics ASAP 2010 spectrometer at 77.35 K after being degassed in a vacuum at 473 K for more than 4 h prior to the measurement. Ultraviolet-visible (UV-vis) spectra were performed on a Shimadzu, UV-2450 spectrophotometer. Transmission electron microscopic (TEM) characterizations of the samples were carried out on a JEM-2010 operated at 200 kV. The samples were prepared by spreading an ultrasonicated suspension in ethanol onto a grid. The histogram of the Au particle sizes was established from the measurement of more than 300 particles. The size limit for the detection of Au particles on SiO₂ is about 1 nm.

The selective oxidation of cyclohexane was carried out in a 100 mL Parr batch autoclave with a polytetrafluoroethylene (PTFE) liner. Typically, 2 mL cyclohexane, 5 mg catalyst, 0.08 g tert-butyl hydroperoxide (TBHP) (as radical initiator) and 20 mL conventional solvent were added into the reactor. After purging with O_2 5 times to remove residual air in the reactor, the mixture was stirred at 600 rpm, 423 K and 1.5 MPa O₂ for the desired time. After cooling to room temperature, the products were analyzed using a gas chromatogram (Agilent 7890A) with a capillary column (PEG-20M) before and after adding an excessive amount of triphenylphosphine to completely reduce cyclohexyl hydroperoxide, which is an intermediate in reaction. The used catalyst was collected from the reaction system by centrifugation, washed with acetone, dried at 343 K for 6 h. The catalyst reusability was examined using the recovered solid catalyst under the optimized reaction conditions.

Results and discussion

The one-pot synthesis process of Au catalysts embedded in modified silica is illustrated in Scheme 1. TEOS as a starting silicon source and thioether organosilane as a $AuCl_4^-$ ion dispersing and attracting agents were added to an isopropanol solution (I). After stirring for 30 h, TEOS and TESPTS form a three-dimensional netting structure through hydrolysis and polycondensation (II). During calcination, the organic groups



Fig. 1 N_2 adsorption/desorption isotherms and BJH pore size distribution curve (inset) of 1.5% Au/M-SiO₂ catalyst.

were removed, and gold salts were reduced into metallic gold nanoparticles (III). In addition, the colors of the prepared samples change from pink to dark red with increased Au loading.

A number of analytical studies have been carried out to gain information about the Au nanoparticles confined in modified amorphous silica. Fig. 1 shows the N₂ adsorption/desorption isotherms and the BJH pore size distribution curve of the 1.5% Au/M-SiO₂ catalyst. The isotherm shows an irreversible type IV adsorption isotherm with an H-1 hysteresis loop as defined by IUPAC, suggesting that the sample is a mesoporous material. The pore size distribution curve obtained by the BJH method is relatively broad, implying unordered mesopores. A relatively high surface area of 230 m² g⁻¹, with a 129 m² g⁻¹ micropore area and 101 m² g⁻¹ external surface area, is obtained considering the removal of organic groups during the synthesis process. The average pore diameter is 15.9 nm, while the pore size distribution curve is at ~ 40 nm. It is due to the existence of large amounts of micropores which can be reached from large micropore area (129 $m^2 g^{-1}$) as well as the BJH pore size distribution curve being less than 4 nm. The existence of micropores may be due to the formation of void defects after removing the organic groups during the annealing process.^{6a,c}

Au nanoparticles have a characteristic absorption band in the visible light region of the electromagnetic spectra at \sim 520 nm, which is caused by the surface plasmon resonance (SPR) of colloidal gold.⁹ Fig. 2 displays the expected UV-vis



Scheme 1 Illustration of the one-pot synthesis process of Au/M-SiO₂



Fig. 2 UV-vis spectra of the catalysts (a) 0.2% Au/M-SiO₂, (b) 0.5% Au/M-SiO₂, (c) 1.0% Au/M-SiO₂, (d) 1.5% Au/M-SiO₂, (e) 2.0% Au/M-SiO₂, and (f) 2.5% Au/M-SiO₂.

spectra of supported Au/M-SiO₂ with different Au loadings. Fig. 2a and b exhibit very weak peaks due to the low Au loading. Samples with a 1.0–2.5% Au loading show evident absorption bands with UV-vis absorption peaks being slightly shifted to longer wavelength with increased Au loading, indicating bigger particle sizes.¹⁰

As shown in Fig. 3a, the TEM images of the 1.5% Au/M-SiO₂ catalyst clearly show that the Au particles are successfully embedded and well-dispersed in the amorphous silica. The diameters of more than 300 Au particles were measured and plotted as the histograms in Fig. 3b. It shows that a Au particle size distribution that mainly ranges from 4–7 nm was obtained with retained monodispersity when the calcination temperature was high to 723 K for 5 h. The particle size is relatively uniformed which may be attributed to the removal of dispersing and attracting organic groups from the three-dimensional netting structure. As a result, the uniformed particle size plays an important role in the catalytic performance.⁷ Besides, large amounts of unordered pores can be seen, owed to the decomposition of the organic moieties, which is consistent with the results of N₂ adsorption/desorption measurements.

Fig. 4 shows the XRD patterns of the catalysts with different Au loadings. The characteristic peaks at 38.2° , 44.4° , 64.7° , 77.7° and 81.8° are assigned to the (111), (200), (220), (311) and (222) reflections of cubic Au particles (JCPDS card no. 4-784). The catalysts with a Au loading less than 1.0% only display partial peaks due to the low Au concentration and small Au particles in the silica support. The peaks become narrower and sharper with increased Au loading, implying relatively larger Au particles.

The catalytic performances of the catalysts were investigated in the selective oxidation of cyclohexane with molecular oxygen. In the reaction system, the substrate cyclohexane is a non-polar organic compound, while products cyclohexanone and cyclohexanol are polar compounds. Certain solvents can change the polarity of the reaction system, providing the possibility of improving the conversion and inhibiting deep oxidation.



Fig. 3 (a) TEM images of the 1.5% Au/M-SiO $_2$ catalyst, (b) size histogram of the Au particles.



Fig. 4 XRD patterns of the catalysts (a) 0.2% Au/M-SiO₂, (b) 0.5% Au/M-SiO₂, (c) 1.0% Au/M-SiO₂, (d) 1.5% Au/M-SiO₂, (e) 2.0% Au/M-SiO₂, and (f) 2.5% Au/M-SiO₂.

So a series of traditional solvents were chosen to evaluate the solvent effects, as shown in Table 1. As is known, the polarity of solvents can play a very important role in some catalytic oxidation reactions during the stabilization of the reaction intermediate states due to solute–solvent interactions.¹¹ Therefore, ethylbenzene, as a non-polar solvent (entry 5, Table 1), clearly exhibits a lower conversion than that of conventional polar solvents. However, for most of the polar solvents, the catalytic reactions were faster in dipolar non-hydrogen bond

 Table 1
 Effects of solvent on cyclohexane oxidation^a

Entry	Solvent	Conversion (mol%) CyH	Selectivity (mol%)					
			СуО	СуОН	СуООН	Others ^b	Yield ^c (mol%)	$\operatorname{TOF}^{d}\left(\mathrm{h}^{-1} ight)$
1	Acetone	14.5	52.4	30.7	4.5	12.5	12.1	7079
2	Ethanol	0.5	0	75.7	0	24.3	0.4	234
3	Acetic acid	9.0	44.6	39.4	3.4	12.6	7.6	4392
4	Benzonitrile	8.9	32.9	63.7	2.9	0.4	8.6	4353
5	Ethylbenzene	8.3	40.2	19.4	2.0	38.5	5.0	4051
6	Acetonitrile	12.4	20.1	25.7	0.0	54.2	5.7	6018

^{*a*} Reaction conditions: cat. 0.5% Au/M-SiO₂ 5 mg, CyH 2 mL, solvent 20 mL, TBHP 0.08 g, 423 K, 1.5 MPa, 600 rpm, 3 h, 100 mL PTFE-lined autoclave. CyH, cyclohexane. CyO, cyclohexanone. CyOH, cyclohexanol. CyOOH, cyclohexyl hydroperoxide. ^{*b*} By-products are mainly adipic acid, δ -valerolactone, hexanoic acid, valeric acid, *etc.* ^{*c*} Yield is calculated by moles of generated CyO and CyOH per mole of CyH converted. ^{*d*} TOF is calculated by moles of cyclohexane converted per mole of Au per hour.

donor (HBD) solvents because the reaction intermediate is much more solvated by protic solvents than by dipolar non-HBD solvents, and this outweighs any effects due to the solvation of the transition state molecule.¹² Moreover, protic solvents have a higher internal pressure and exhibit a negligible solvent dependence of the reaction intermediate decomposition rate. Thus, the catalytic activity is extremely low for the HBD solvent ethanol. Besides, the functional groups and the steric hindrance of the dipolar non-HBD solvents may have a considerable influence on the oxidation reaction.¹³ Carbonylcontaining solvents and products can form $R-O-H\cdots O=C$ hydrogen bonds to some extent. All factors taken into account, in this work acetone becomes the most appropriate solvent for the oxidation of cyclohexane.

The effect of acetone was intensively investigated to optimize the selected solvents. Fig. 5 depicts the reaction time effect on the cyclohexane oxidation and CyO/CyOH selectivities. The cyclohexane oxidation reaction makes a lot of progress from 1 to 5 h, affording a conversion of 14.5% and a selectivity of 83.0% to the two desired oxygenates at 3 h. Different from results reported previously,¹⁴ the oxidation reaction does not appear to slow down with time, suggesting that there is no loss of catalytic activity. The conversion and the ratio of CyO/CyOH increase, while the values of CyOH and CyOOH decrease with increased reaction time. Fig. 6 displays the variation in the selectivity to the three products and the yield of CyO and CyOH versus CyH conversion from 1 to 5 h. In all cases, the selectivities to CyOOH and CyOH decrease with increased CyH conversion, while the selectivity to CvO increases firstly then decreases, exceeding the 15% CyH conversion. The selectivity of the individual product decreases with a high conversion of more than 15% due to the side products formed, such as adipic acid, δ-valerolactone, hexanoic acid, valeric acid, etc. In addition, cyclohexane oxidation is a complicated, multistage, free-radical chain reaction with degenerated chains, comprising of different chain initiation, propagation and termination steps.¹⁵ CyOOH is the first oxygenated product in the autocatalytic process^{15,16} and some catalytic processes.¹⁷ The selectivity of CyOOH decreases with increased conversion, as shown in Fig. 5 and 6, which indicates that CyOOH could also be the first oxygenated product in the oxidation process. Furthermore, CyOOH is decomposed into CyOH and CyO with a ratio CyO/CyOH < 1 at low CyH conversion. As time proceeds, CyOH is consecutively oxidized to CyO with a corresponding increase in CyO selectivity. However, both CyO and CyOH may be oxidized to deep oxides at high CyH conversion, and the selectivities of CyO and CyOH reduce after 3 h in Fig. 5, implying an increased rate of over oxidation.¹⁸



Fig. 5 Effects of reaction time on the cyclohexane oxidation. Reaction conditions: cat. 0.5% Au/M-SiO₂ 5 mg, CyH 2 mL, acetone 20 mL, TBHP 0.08 g, 423 K, 1.5 MPa, 600 rpm, 100 mL PTFE-lined autoclave.

We herein found that the 0.5% Au/M-SiO₂ catalyst was an exceptionally good catalyst for cyclohexane oxidation using



Fig. 6 Selectivities of products and yield of CyO and CyOH *versus* conversion based on the data of Fig. 5.

Table 2 Effects of Au loading on the cyclohexane oxidation reac	tion ^a
---	-------------------

Entry		Conversion (mol%) CyH	Selectivity (mol%)					
	Catalyst		СуО	СуОН	СуООН	Others	Yield (mol%)	TOF (h^{-1})
1	0.2% Au/M-SiO ₂	17.3	56.8	30.3	2.4	10.5	15.1	21 097
2	0.5% Au/M-SiO ₂	14.5	52.4	30.7	4.5	12.5	12.1	7079
3	1.0% Au/M-SiO ₂	15.3	57.4	25.1	4.3	13.2	12.7	3734
4	1.5% Au/M-SiO ₂ -1st ^b	22.7	45.9	34.7	2.5	16.9	18.3	3677
5	2.0% Au/M-SiO ₂	19.1	49.8	34.9	2.1	13.2	16.2	2326
6	2.5% Au/M-SiO ₂	18.7	54.2	29.8	2.3	13.8	15.7	1825
7	1.5% Au/M-SiO ₂ -2nd ^b	27.1	45.2	33.3	2.7	18.8	21.3	4402
8	1.5% Au/M-SiO ₂ -3rd ^b	29.5	44.2	33.6	2.1	20.0	22.9	4792
9	1.5% Au/M-SiO ₂ -4th ^b	31.0	43.3	32.8	1.9	22.0	23.6	5033
10	0.55 Au/ZSM5^{c}	7	36	55			6.4	3092
11	1.0 Au/Al ₂ O ₃ ^{d}	10.9	54	30.3	2.8		9.2	2592

^{*a*} Reaction conditions: cat. 5 mg, CyH 2 mL, TBHP 0.08 g, acetone 20 mL, 423 K, 1.5 MPa, 3 h, 600 rpm, 100 mL PTFE-lined autoclave. ^{*b*} The 1.5% Au/M-SiO₂ catalyst was reused. Designations 1st–4th indicates the cycle number of the same catalyst. ^{*c*} Reaction conditions of ref. 5: cat. 5 mg, CyH 2 mL, 423 K, 1.0 MPa, 3 h. ^{*d*} Reaction conditions of ref. 17: cat. 50 mg, CyH 20 mL, 423 K, 1.0 MPa, 3 h.

acetone as the solvent (Table 1). Moreover, the catalytic performance of Au based catalysts in cyclohexane oxidation reaction using molecular oxygen as an oxidant has been widely reported with high cyclohexane conversions (Table 2, entries 10-11).^{5,17} However, the amount and sizes of the gold nanoparticles play very important roles in the oxidation process. Table 2 displays the effects of gold loading on cyclohexane oxidation. Among the catalysts with different amounts of gold, the 1.5% Au/M-SiO₂ catalyst shows the best performance with respect to cyclohexane conversion and selectivity to CyO and CyOH. The overall tendency of the cyclohexane conversion first increases and then decreases with increased Au loading, reaching the maximum CyH conversion of 22.7% with the 1.5% Au/M-SiO₂ catalyst. However, the conversion of the oxidation reaction with the 0.2% Au/M-SiO₂ catalyst exceeds that of the 0.5% Au/M-SiO₂ and 1.0% Au/M-SiO₂ catalysts. A surprisingly high TOF of up to 21 097 h^{-1} was obtained over 0.2% Au/M-SiO₂ catalyst, which endows this system with the best activity ever reported for cyclohexane oxidation in terms of TOF value. The catalytic properties of the heterogeneous Au catalysts have been found to strongly depend on the particle sizes and number of Au nanoparticles. The gold nanoparticle sizes increase with increased Au loadings according to the XRD results in Fig. 4. For the 0.2% Au/M-SiO₂ catalyst, we could hardly observe any gold characteristic peaks, except weak the (111) reflection. This indicates that the catalyst exhibits super highly dispersed and small gold nanoparticles, and shows the highest TOF value owing to it having the largest number of active sites per mole of Au in the catalytic system.¹⁹ The lower Au loaded catalysts have smaller and more dispersed Au nanoparticles with relatively more active sites, while the higher Au loading catalysts may have less active sites due to the bigger Au nanoparticles. Thus, the best catalytic activity of 1.5% Au/M-SiO₂ is attributed to the best combination of Au loading and particle sizes. Moreover, the TOF value decreases with increased Au loading, which demonstrates that smaller Au particles have relatively more active sites per mole of gold. In addition, heterogeneous catalysts often suffer extensive leaching of the active metal species during the reaction, accompanied by loss of catalytic

activity. However, the recycling test shows that the catalytic activity of the 1.5% Au/M-SiO₂ catalyst keeps increasing even after four cycles of reuse, similar to the results of previous reports.^{6b,20} During our preparation process, gold nanoparticles were embedded in silica and hindered the aggregation of neighbouring Au nanoparticles under the reaction conditions. Moreover, the microscopic structure of the catalyst may change to a more favourable direction for mass and heat transfer, feasibly leading to an even higher catalytic activity after every oxidation process.

Conclusions

A novel one-pot synthesis method of Au nanoparticles embedded in amorphous silica was put forward and demonstrated to be a facile approach to prepare well distributed gold catalysts in silica. Results showed that the catalysts exhibited high catalytic activities in selective cyclohexane oxidation with molecular oxygen, using acetone as the solvent. The functional groups and dipolar non-HBD solvents played important roles in the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone. The catalytic activity of the Au catalysts strongly depends on the particle size and the amount of the Au loading.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21006029, 21076074), National High Technology Research and Development (863 Program 2012AA061601), Shanghai Natural Science Foundation (10ZR1407200), and the Fundamental Research Funds for the Central Universities of China. The financial support by the Max Planck Partner Group Funding from the Max Planck Society, Germany, is greatly acknowledged.

Notes and references

1 *Ullmanns Encyklopädie der Technischen Chemie*, ed. E. Bartholomé, Weinheim, vol. 4, 1972.

- 2 Metal-Catalyzed Oxidations of Organic Compounds, ed. R. A. Sheldon and J. K. Kochi, Academic press, New York, 1981.
- 3 (a) G. C. Bond and D. T. Thompson, *Catal. Rev. Sci. Eng.*, 1999, **41**, 319; (b) A. S. K. Hashmi and G. J. Hutchings, *Angew. Chem., Int. Ed.*, 2006, **45**, 7896.
- 4 (a) M. Haruta, T. Kobayashi, H. Sano and N. Yamada, *Chem. Lett.*, 1987, 405; (b) M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet and B. Delmon, *J. Catal.*, 1993, 144, 175.
- 5 R. Zhao, D. Ji, G. M. Lv, L. Yan, X. L. Wang and J. S. Suo, *Chem. Commun.*, 2004, 904.
- 6 (a) P. P. Wu, P. Bai, Z. B. Lei, K. P. Loh and X. S. Zhao, Microporous Mesoporous Mater., 2011, 141, 222; (b) P. P. Wu,
 Z. G. Xiong, K. P. Loh and X. S. Zhao, Catal. Sci. Technol., 2011, 1, 285; (c) L. F. Chen, J. C. Hu and R. Richards, J. Am. Chem. Soc., 2009, 131, 914; (d) L. F. Chen, J. C. Hu, Z. W. Qi,
 Y. J. Fang and R. Richards, Ind. Eng. Chem. Res., 2011, 50, 13642.
- 7 M. P. Mokhonoana, N. J. Coville and A. Datye, *Stud. Surf. Sci. Catal.*, 2004, **154**, 827.
- 8 (a) K. K. Zhu, J. C. Hu and R. Richards, *Catal. Lett.*, 2005, 100, 195; (b) H. Zhu, B. Lee, S. Dai and S. H. Overbury, *Langmuir*, 2003, 19, 3974.
- 9 S. Link, M. Mohamed and M. El-Sayed, J. Phys. Chem. B, 1999, 103, 3073.

- 10 K. H. Su, Q. H. Wei, X. Zhang, J. J. Mock, D. R. Smith and S. Schultz, *Nano Lett.*, 2003, 3, 1087.
- 11 Solvents and Solvent Effects in Organic Chemistry, ed. C. Reichardt, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003.
- 12 (a) A. J. Parker, Q. Rev. Chem. Soc., 1962, 16, 163;
 (b) M. J. Kamlet and R. W. Taft, J. Am. Chem. Soc., 1976, 98, 377;
 (c) R. W. Taft and M. J. Kamlet, J. Am. Chem. Soc., 1976, 98, 2886.
- 13 L. Chen, T. Zhou, L. F. Chen, Y. M. Ye, Z. W. Qi, H. Freund and K. Sundmacher, *Chem. Commun.*, 2011, 47, 9354.
- 14 Z. Y. Cai, M. Q. Zhu, H. Dai, Y. Liu, J. X. Mao, X. Z. Chen and C. H. He, *Adv. Chem. Eng. Sci.*, 2011, 1, 15.
- 15 B. P. C. Hereijgers and B. M. Weckhuysen, *J. Catal.*, 2010, **16**, 270.
- 16 A. Ramanathan, M. S. Hamdy, R. Parton, T. Maschmeyer, J. C. Jansen and U. Hanefeld, *Appl. Catal.*, A, 2009, 355, 78.
- 17 L. X. Xu, C. H. He, M. Q. Zhu and S. Fang, *Catal. Lett.*, 2007, **114**, 202.
- 18 L. F. Chen, J. C. Hu, S. S. Mal, U. Kortz, H. Jaensch, G. Mathys and R. M. Richards, *Chem.-Eur. J.*, 2009, **15**, 7490.
- 19 G. M. Lv, D. Ji, G. Qian, Y. X. Qi, X. L. Wang and J. S. Suo, *Appl. Catal.*, A, 2005, 280, 175.
- 20 S. Talwalkar, P. Kumbhar and S. Mahajani, *Catal. Commun.*, 2006, 7, 717.