Green Chemistry

PAPER

Cite this: *Green Chem.*, 2014, **16**, 2664

Aqueous-phase selective hydrogenation of phenol to cyclohexanone over soluble Pd nanoparticles

Jing-Fang Zhu,^{a,c} Guo-Hong Tao,^a Hang-Yu Liu,^a Ling He,*^a Qian-Hui Sun^b and Hai-Chao Liu*^b

The water-soluble metal nanoparticles (NPs) stabilized by poly(N-vinyl-2-pyrrolidone) (PVP) were prepared and examined as catalysts for the one-step selective hydrogenation of phenol to cyclohexanone in water. More than 99% conversion of phenol and selectivity to cyclohexanone was obtained at 90 °C and 1 atm H₂ for 16 h over "soluble" Pd NPs that were reduced by NaBH₄ and stabilized by PVP. These Pd NPs were stable, and no leaching or aggregation was detected after five successive runs, showing their advantage for catalyzing the efficient synthesis of cyclohexanone *via* the one-step selective hydrogenation of phenol under mild conditions.

Received 24th November 2013, Accepted 12th February 2014 DOI: 10.1039/c3gc42408a

5

www.rsc.org/greenchem

Introduction

Quasi-homogeneous or semi-heterogeneous catalysis based on metal nanoparticle (NP) catalysts combines the virtues of both homogeneous and heterogeneous catalysis in the efficiency and selectivity of reactions, and recovery and recyclability of catalysts, respectively.¹ These NPs are stabilized by polymeric molecules and are "soluble" in ionic liquids or other solvents.² They exhibit superior catalytic performances over conventional supported metal catalysts in a wide range of reactions and more intensively in hydrogenation reactions.³ Examples include ruthenium nanoclusters for hydrogenative cleavage of the C-O-C bonds in cellobiose,⁴ platinum nanoclusters for aerobic oxidation of alcohols,⁵ and copper nanoclusters for carbonylation of methanol,⁶ etc. Such superiority of the soluble metal NPs may have arisen from their unique properties such as rotational freedom, spherically symmetrical geometry, uniformly accessible sites, etc.^{2,3} Herein, we report a new application of the soluble metal NPs in selective hydrogenation of phenol to cyclohexanone in water, the most abundant, green solvent in nature.⁷

Cyclohexanone is an important chemical intermediate in the production of caprolactame and adipic acid, the key precursors for nylon 6 and nylon 66, respectively.⁸ Cyclohexanone is generally obtained from one-step or two-step phenol conversion.⁹ The two-step process involves hydrogenation of phenol to cyclohexanol and its subsequent dehydrogenation to cyclohexanone.¹⁰ But it requires high temperatures for the

E-mail: lhe@scu.edu.cn; Fax: (+86)-28-85470368; Tel: (+86)-28-85470368 ^bCollege of Chemistry and Molecular Engineering, Peking University, Beijing 100871,

China. E-mail: hcliu@pku.edu.cn; Tel: (+86)-10-62754031

endothermic dehydrogenation step of cyclohexanol to cyclohexanone. In contrast, the one-step selective hydrogenation of phenol to cyclohexanone is more advantageous in terms of energy efficiency and operation cost.

The cyclohexanone selectivity in the one-step hydrogenation of phenol is largely dependent on the catalyst properties.¹¹ Numerous studies have been devoted to the development of effective catalysts,¹² and currently supported Pd catalysts, due to their superior efficiency, are frequently used in phenol hydrogenation.^{9–16} One significant example is that Han and coworkers achieved nearly 100% phenol conversion and cyclohexanone selectivity within 7 h on Pd/C, Pd/Al₂O₃ or Pd/NaY assisted by the Lewis acid AlCl₃ in CH₂Cl₂ at 50 °C and 10 atm H₂.¹⁶ However, the current liquid-phase hydrogenation processes generally use environmentally unfriendly co-catalysts or organic solvents (*e.g.* AlCl₃ and CH₂Cl₂)^{16–18} or they are performed under high pressures.^{9,14}

In this work, we report that soluble Pd NPs are efficient for the one-step selective hydrogenation of phenol to cyclohexanone in benign water without the use of Lewis acids and other co-catalysts at atmospheric H₂ pressure (Scheme 1). The Pd NPs are stabilized by water-soluble poly(N-vinyl-2-pyrrolidone)(PVP),¹⁹ and the cyclohexanone product is slightly soluble in water, which facilitates the simple separation between the product and the catalyst.



Scheme 1 Catalytic selective hydrogenation of phenol to cyclohexanone.

View Article Online

^aCollege of Chemistry, Sichuan University, Chengdu 610064, China.

^cKunming Sino-Platinum Metals Catalyst Co., Ltd., Kunming 650101, China

Experimental

Synthesis of metal nanoparticles

For synthesis of Pd NPs, 10.0 mL of HCl (0.5 mol L⁻¹, 5 mmol) was mixed with a suspension of 443 mg PdCl₂ (2.5 mmol) to obtain an acidic H₂PdCl₄ solution (250 mL). The final concentration of H₂PdCl₄ was 1.0×10^{-2} mol L⁻¹. In a round bottle, H₂PdCl₄ (49.9 mg, 0.0963 mmol) and PVP (427 mg, 3.85 mmol) were added to 5 mL deionized water and stirred for 30 minutes in an ice-water bath. A fresh aqueous NaBH₄ solution (10.0 mL) was added into the mixture under vigorous stirring. The resulting solution immediately became black. After stirring for 2 h, a solution of Pd NPs was obtained. The molar ratio of Pd to PVP was varied in the range of 1/20 to 1/100. The Pd NP solution was simply diluted and directly used for the phenol conversion. In addition, other reduction reagents, including methanol, ethanol and glycol,^{15,20} were also used for the synthesis of Pd NPs.

In a similar way, other metal NPs of Ru, Pt and Au were synthesized with a molar ratio of metal to PVP of 1/20. The precursors of Ru, Pt and Au were RuCl₃·*x*H₂O, H₂PtCl₆·H₂O and AuCl₃·HCl·4H₂O, respectively.

The complete reduction of the metallic salts to metals was examined by UV-Vis spectroscopy before the dialysis procedure.

Characterization of metal NPs

The prepared metal NPs were characterized by Transmission Electron Microscopy (TEM). The TEM images were taken on a Hitachi 9000 NAR transmission electron microscope operating at 200 kV. Samples for TEM analyses were prepared by placing a droplet of the dispersed metal NP solution onto a carbon-coated copper grid. The size distributions of the NPs were determined by randomly measuring more than 300 particles on the images.

X-ray photoelectron spectra (XPS) were performed on a Kratos XASM800 X-ray photoelectron spectrometer with a mono Al K α source ($h\nu$ = 1486.7 eV) operated at 15 mA and 12 kV and a hemispherical electron analyzer connected to an eight-channel detector. The survey spectrum and the high resolution spectrum were scanned with pass energies of 20 eV. During the acquisition of a spectrum, charge neutralization was applied to compensate for the insulating problem of the sample. CASAXPS software was used for the data processing. Binding energies were referenced to C (1s) (at 284.7 eV).

X-ray diffraction (XRD) measurements for the fresh catalysts were recorded on a DX-1000 transmission X-ray powder diffraction system using Cu K α 1 radiation ($\lambda = 1.5406$ Å), operated at 30 kV and 100 mA. The 2 θ range angles were scanned from 15 to 80°, with a sweep speed of 3 °C per rain and 0.06 °C s⁻¹. The average crystallite sizes (*D*) were estimated by the Scherrer equation $D = k\lambda/\beta \cos \theta$, where θ is the diffraction angle, β is the full-width at half maximum of the peak at 2θ (fwhm), *k* is a constant (0.89), and λ is the wavelength of K α 1 radiation.

Hydrogenation of phenol

The hydrogenations of phenol were carried out in water. The 20 mL fresh metal NP solution (0.1 mmol) and the 0.5 mol L^{-1}

phenol solution (2.0 mmol) were placed in a 100 mL round bottle with a branch pipe and piston. The reactor was purged with 1 atm H₂ (99.999%) several times and then heated to the desired reaction temperatures with vigorous stirring. The final reaction mixtures were extracted by diethyl ether, and then the catalysts were collected for recycling. The products were analyzed by a Fuli 9790-II-GC equipped with a FID detector and an AT.SE-54 column (30 m \times 0.25 mm).

Results and discussion

Characterization of Pd NPs

The Pd NPs prepared at the mole ratio of $H_2PdCl_4:PVP:$ NaBH₄ of 1:20:7, as the representative sample, were characterized using UV-Vis, XRD, XPS, and TEM, as shown in Fig. 1–5.

The reduction of $Pd(\pi)$ ions by NaBH₄ was examined using UV-Vis spectroscopy. The spectra of the mixture of H_2PdCl_4 and PVP before and after reduction are shown in Fig. 1. Before reduction by NaBH₄, the absorption peaks of aqueous H_2PdCl_4 solution were observed at around 315 nm and 425 nm, which are characteristic of $Pd(\pi)$ ions. For the reduced sample, a line was recorded. The disappearance of the peaks at 315 nm and 425 nm indicated the complete reduction of $Pd(\pi)$ to Pd^0 NPs.

The formation of Pd NPs was also proven by powder XRD (Fig. 2). The diffraction peak at 20.1° in the XRD patterns shows the packing of PVP. The diffraction peaks at 40.1° , 46.7° , and 68.1° can be assigned to the (111), (200), (220) planes of the face centered cubic Pd particles, respectively. The diffraction peak at 40.1° was obviously found while other diffraction peaks were recorded to be very weak. The mathematical deconvolution of the intense peak by a Lorentz function permitted a better calculation of the peak parameters and then the Pd crystallite sizes. The average size of the Pd NPs was



Fig. 1 UV-Vis absorption spectra of H_2PdCl_4-PVP solution before (black) and after (red) reduction (room temperature, 2 h, Pd:PVP: NaBH₄ = 1:20:7).



Fig. 2 XRD pattern of the parent Pd NPs stabilized by PVP (Pd : PVP : NaBH_4 = 1 : 20 : 7).



Fig. 3 XPS spectra of Pd NPs reduced (a) by $NaBH_4$ at a ratio of Pd : $PVP : NaBH_4 = 1 : 20 : 7$, (b) by methanol, (c) by ethanol, and (d) by glycol.

calculated to be 3.0 nm from the diffraction peak (111) using the Scherrer formula, which is comparable to the value obtained from TEM results, as shown below.

The Pd NPs were characterized by XPS and the results are shown in Fig. 3. The spectrum of the Pd 3d of the Pd NPs reduced by NaBH₄ could be resolved into two peaks with $3d_{5/2}$ binding energies of 335.7 eV and $3d_{3/2}$ binding energies of 340.9 eV (Fig. 3, curve a) characteristic of fully reduced metallic Pd NPs (Pd⁰). The XPS result shows that nearly all of the Pd(II) ions were reduced, and Pd⁰ was the only form in the Pd NPs prepared by NaBH₄, which is consistent with the UV-Vis characterization. On the other hand, all the other Pd 3d spectra for the Pd NPs prepared under alcoholic conditions



Fig. 4 TEM images and size distributions of Pd NPs (a) freshly prepared, Pd: PVP: NaBH₄ = 1:20:7, (b) after five reaction cycles, Pd: PVP: NaBH₄ = 1:20:7 (90 °C, 1 atm H₂, 0.1 mmol Pd NPs, 2.0 mmol phenol in H₂O), (c) freshly prepared, Pd: PVP: NaBH₄ = 1:20:5, and (d) freshly prepared, Pd: PVP: NaBH₄ = 1:50:7.

could be resolved into two spin-orbit pairs with $3d_{5/2}$ binding energies of 335.7 eV and 337.4 eV, and with $3d_{3/2}$ binding energies of 340.9 eV and 342.1 eV, respectively (Fig. 3, curves b-d). The peaks at 337.4 eV (Pd $3d_{5/2}$) and 342.1 eV (Pd $3d_{3/2}$) are attributed to the oxidation state of Pd (Pd^{*n*+}).²¹ The estimated areas for the Pd⁰ peaks were clearly larger than those for the Pd^{*n*+} peaks. From the XPS data, it appears that most of the Pd(π) ions were reduced under alcoholic conditions and Pd⁰ was the major form in the Pd NPs.

Fig. 4 shows the TEM images of the Pd NPs prepared at three different mole ratios of $H_2PdCl_4:PVP:NaBH_4$, *i.e.* 1:20:7, 1:20:5, 1:50:7. These images reveal well-dispersed Pd particles with a mean size of 2.9 nm and a narrow size distribution, irrespective of the amounts of PVP stabilizer and NaBH₄ reductant. However, as shown in Fig. 4(d), the Pd NPs aggregated slightly in the presence of a larger amount of PVP,



Fig. 5 TEM images and size distributions of (a) Ru NPs, (b) Pt NPs, and (c) Au NPs (metal : PVP : $NaBH_4 = 1 : 20 : 7$).

most likely due to the role of the excess PVP in preventing the dispersion of the Pd NPs. The catalytic activity of these aggregated Pd NPs decreased rapidly in the selective hydrogenation

of phenol. For comparison, the Ru, Pt, and Au NPs (prepared at the mole ratio of metal: $PVP: NaBH_4$ of 1:20:7) were also characterized by TEM, which possessed similar mean diameters of 1.6, 2.0, and 2.3 nm, respectively, with narrow size distributions (Fig. 5).

Phenol hydrogenation activity and selectivity on soluble Pd NPs

Soluble metal NPs, Ru, Pt, Pd, and Au, with similar mean diameters (ca. 1.6-3.0 nm) were examined for the selective hydrogenation of phenol. As shown in Table 1, Pd NPs catalyzed the hydrogenation of phenol to exclusively form cyclohexanone. A conversion of phenol as high as >99% was achieved at 90 °C and 1 atm H₂ for 16 h with the cyclohexanone selectivity above 99% (Table 1, entry 1). The conversion of phenol exceeded 99% on Ru NPs, which however dominantly formed cyclohexanol, instead of cyclohexanone, with a selectivity of 99.8% (Table 1, entry 2). The phenol conversion decreased to 19.2% on Pt NPs and the cyclohexanone selectivity was as low as 77.2% (Table 1, entry 3). Under the identical conditions, Au NPs exhibited a negligible activity (Table 1, entry 4), similar to that in the absence of the metal NPs (Table 1, entry 5). For comparison with the Pd NPs, 5 wt% Pd/C was also examined in the hydrogenation of phenol, which showed a lower phenol conversion (80.2%) although this catalyst possessed a similar Pd mean diameter of ~3 nm. Addition of PVP with the 5 wt% Pd/C catalyst (Pd/PVP = 1:20) led to a sharp decrease in the phenol conversion from 80.2% to 20.6%, most likely due to the covering of the Pd sites with PVP and thus decrease of their accessibility to the reactants (Table 1, entry 12). These results reveal that the soluble Pd NPs are efficient and highly selective for catalyzing the selective hydrogenation of phenol to cyclohexanone, which provides a new semi-heterogeneous

Table 1 The results of hydrogenation of phenol by metal NPs under different conditions^a

Entry	Catalysts	Reductant	T (°C)	<i>t</i> (h)	Conversion (%)	Selectivity ^{b} (%)	
						C=0	C-OH
1	Pd-PVP	$NaBH_4$	90	16	99.7	99.5	0.5
2	Ru-PVP	NaBH ₄	90	16	99.8	0.2	99.8
3	Pt-PVP	NaBH ₄	90	16	19.2	77.2	22.8
4	Au-PVP	NaBH ₄	90	16	<1	_	_
5	PVP		90	16		_	_
6	Pd-PVP	CH ₃ OH	90	16	17.0	97.6	2.4
7	Pd-PVP	CH ₃ CH ₃ OH	90	16	12.6	99.1	0.9
8	Pd-PVP	HOCH ₂ CH ₂ OH	90	16	43.5	97.0	3.0
9	Pd-PVP ^c	NaBH ₄	90	16	79.4	98.0	2.0
10	$Pd-PVP^d$	$NaBH_4$	90	16	55.8	98.1	1.9
11	5 wt% Pd/C		90	16	80.2	98.7	1.3
12	5 wt% Pd/C, PVP		90	16	20.6	98.5	1.5
13	Pd-PVP	$NaBH_4$	25	16	4.1	95.4	4.6
14	Pd-PVP	$NaBH_4$	50	16	46.3	96.0	4.0
15	Pd-PVP	NaBH ₄	70	16	93.6	98.3	2.7
16	Pd-PVP	$NaBH_4$	80	16	96.5	98.5	1.5
17	Pd-PVP	$NaBH_4$	90	2	29.5	99.0	1.0
18	Pd-PVP	$NaBH_4$	90	8	87.6	99.2	0.8

^{*a*} Reaction conditions: 5 mol% Pd relative to phenol, 1 atm P_{H2} , Pd : PVP = 1:20 unless otherwise stated. ^{*b*} C=O indicates cyclohexanone and C-OH indicates cyclohexanol. ^{*c*} Pd : PVP = 1:50. ^{*d*} Pd : PVP = 1:100.

(or semi-homogeneous) route for the synthesis of cyclohexanone *via* selective hydrogenation of phenol.

Such superior properties of the Pd NPs relative to the other metal NPs in the formation of cyclohexanone may be ascribed to the favourable desorption of cyclohexanone on the Pd surfaces, inhibiting its further hydrogenation to cyclohexanol. Such a proposition, which needs to be further studied, is consistent with the effects of the reaction time and temperature. As shown in Table 1, with prolonging the reaction time from 2 h to 8 h and 16 h at 90 °C, the phenol conversion increased from 29.5% to 87.6% and >99%, respectively, while the cyclohexanone selectivity remained constant (i.e. >99%). This result indicates that cyclohexanone is stable on Pd under the conditions employed. However, when the reaction temperature decreased from 90 °C to 25 °C, both the phenol conversion (99.7% to 4.1%) and the cyclohexanone selectivity (99.5% to 95.4%) were decreased (Table 1, entries 1 and 13-16). Such a decrease in the selectivity may be due to the stronger adsorption of cyclohexanone at lower temperatures. Clearly, high temperature is in favour of the cyclohexanone synthesis. These preliminary results offer us directions to optimize the reaction conditions and catalytic activities.

The recycling ability of the Pd NPs was investigated in selective hydrogenation of phenol in water. This catalyst in aqueous solution can be recycled after a simple extraction by diethyl ether. As shown in Fig. 6, the phenol conversion and cyclohexanone selectivity remained essentially constant, being above 99.5%, after recycling Pd catalyst over five times, demonstrating the excellent stability of the Pd NPs. TEM characterization (Fig. 4b) results showed no obvious growth or aggregation for the used Pd NP catalyst. These results also indicated that PVP can efficiently stabilize the Pd NPs as catalysts in the selective hydrogenation of phenol.

The catalytic properties of the Pd NPs are affected by the amounts of PVP (*i.e.* PVP/Pd ratios) and reductants used. As mentioned before, >99% phenol conversion was obtained on the Pd NPs with the PVP/Pd ratio of 20:1. Increasing the ratio



Fig. 6 Recycling of the Pd NPs in the hydrogenation of phenol to cyclohexanone (0.1 mmol Pd NPs, 2.0 mmol phenol in H_2O , 90 °C, 1 atm H_2 , 16 h).

to 50:1 resulted in a decline in the conversion to 79.4% (Table 1, entry 9). However, no significant change in the cyclohexanone selectivity was observed at higher PVP concentrations. Notably, the presence of a 100:1 ratio of PVP/Pd NPs still led to a reasonable 55.8% phenol conversion with a 98.1% cyclohexanone selectivity (Table 1, entry 10). TEM characterization showed that the sizes of the Pd NPs were independent of the PVP/Pd ratios, being around 2.9-3.0 nm with narrow size dispersions (Fig. 4). Thus, the decrease in the phenol conversion with increasing the PVP concentration is not due to the growth in the size of the Pd NPs or the difference in their size dispersions, but may be due to the decrease in the number of the Pd sites accessible to the reactants, most likely as a result of the covering of the Pd sites with excess PVP molecules. Such a phenomenon was also found in other reactions catalyzed by PVP-stabilized metal NPs.² Compared with NaBH₄, the Pd NPs prepared by the other reductants, alcohols, methanol, ethanol and glycol yielded much lower phenol conversions (12.6%-43.5%) with the cyclohexanone selectivities in the range of 97%-99%. The lower conversions of phenol may be attributed to the incomplete reduction of the palladium precursor under the alcoholic conditions, as observed in the XPS spectra (Fig. 3).

Conclusions

The direct synthesis of cyclohexanone from the selective hydrogenation of phenol has been achieved on soluble Pd NPs with a good efficiency in water. These Pd NPs exhibit excellent stability, and can be readily recycled without noticeable deactivation. Such properties of the Pd NPs, together with the green nature of the reaction in water, show their promising potential for the practical production of cyclohexanone.

Acknowledgements

We gratefully acknowledge the support of NSFC (no. 21103116 and 21303108), SRFDP (no. 20100181120042), and SRF for ROCS, SEM (no. 2012170774).

Notes and references

- 1 D. Astruc, *Nanoparticles and Catalysis*, VCH, Weinheim, 2008.
- 2 (a) L. S. Ott and R. G. Finke, Coord. Chem. Rev., 2007, 251, 1075; (b) J. Dupont and J. D. Scholten, Chem. Soc. Rev., 2010, 39, 1780; (c) D. Astruc, F. Lu and J. R. Aranzaes, Angew. Chem., Int. Ed., 2005, 44, 7852; (d) N. Yan, C. Xiao and Y. Kou, Coord. Chem. Rev., 2010, 254, 1179; (e) V. I. Pârvulescu and C. Hardacre, Chem. Rev., 2007, 107, 2615; (f) N. Yan, Y. Yuan and P. J. Dyson, Dalton Trans., 2013, 42, 13294; (g) Y. Kou and L. He, Prog. Chem., 2008, 20, 6.

- 3 (a) A. Roucoux, J. Schulz and H. Patin, Chem. Rev., 2002, 102, 3757; (b) J. A. Widegren and R. G. Finke, J. Mol. Catal. A: Chem., 2003, 191, 187; (c) C. Xiao, Z. Cai, T. Wang, Y. Kou and N. Yan, Angew. Chem., Int. Ed., 2008, 47, 746; (d) A. Gual, C. Godard, S. Castillón and C. Claver, Dalton Trans., 2010, 39, 11499; (e) N. Mejías, R. Pleixats, A. Shafir, M. Medio-Simón and G. Asensio, Eur. J. Org. Chem., 2010, 5090; (f) R. Venkatesan, M. H. G. Prechtl, J. D. Scholten, R. P. Pezzi, G. Machado and J. Dupont, J. Mater. Chem., 2011, 21, 3030; (g) P. Debouttière, Y. Coppel, A. Denicourt-Nowicki, A. Roucoux, B. Chaudret and K. Philippot, Eur. J. Inorg. Chem., 2012, 1229; (h) K. L. Luska and A. Moores, ChemCatChem, 2012, 4, 1534; (i) M. Sankar, N. Dimitratos, P. J. Miedziak, P. P. Wells, C. J. Kiely and G. J. Hutchings, Chem. Soc. Rev., 2012, 41, 8099; (j) M. A. Mahmoud, R. Narayanan and M. A. El-Sayed, Acc. Chem. Res., 2013, 46, 1795.
- 4 N. Yan, C. Zhao, C. Luo, P. J. Dyson, H. C. Liu and Y. Kou, J. Am. Chem. Soc., 2006, **128**, 8714.
- 5 (a) T. Wang, H. Shou, Y. Kou and H. C. Liu, *Green Chem.*, 2009, **11**, 562; (b) H. Miyamura, R. Matsubara, Y. Miyazaki and S. Kobayashi, *Angew. Chem., Int. Ed.*, 2007, **46**, 4151.
- 6 L. He, H. C. Liu, C. X. Xiao and Y. Kou, *Green Chem.*, 2008, 10, 619.
- 7 (a) D. Dallinger and C. O. Kappe, *Chem. Rev.*, 2007, 107, 2563; (b) V. Polshettiwar and R. S. Varma, *Green Chem.*, 2010, 12, 743; (c) G. H. Tao, L. He, W. S. Liu and Y. Kou, *Green Chem.*, 2006, 8, 639; (d) J. L. Song, H. L. Fan, J. Ma and B. X. Han, *Green Chem.*, 2013, 15, 2619.
- 8 *Kirk-Othmer Encyclopedia of Chemical Technology*, ed. M. Howe-Grant, Wiley, New York, 1991.
- 9 M. Chatterjee, H. Kawanami, M. Sato, A. Chatterjee, T. Yokoyama and T. Suzuki, *Adv. Synth. Catal.*, 2009, **351**, 1912.
- 10 V. Z. Fridmanand and A. A. Davydov, *J. Catal.*, 2000, 195, 20.
- 11 S. G. Shore, E. Ding, C. Park and M. A. Keane, *Catal. Commun.*, 2002, 3, 77.
- 12 (a) S. Narayanan and K. Krishna, *Appl. Catal., A*, 1998, 174, 221; (b) P. Claus, H. Berndt, C. Mohr, J. Radnik, E. J. Shin

and M. A. Keane, *J. Catal.*, 2000, **192**, 88; (c) S. Scirè, S. Minicè and C. Crisafulli, *Appl. Catal.*, *A*, 2002, **235**, 21.

- 13 (a) G. Neri, A. M. Visco, A. Donate, C. Milone, M. Malentacchi and G. Gubitosa, Appl. Catal., A, 1994, 110, 49; (b) N. Mahata, K. V. Raghavan and V. Vishwanathan, Appl. Catal., A, 1999, 182, 183; (c) N. Mahata and V. Vishwanathan, J. Catal., 2000, 196, 262; (d) F. Lu, J. Liu and J. Xu, Mater. Chem. Phys., 2008, 108, 369; (e) Y. Wang, J. Yao, H. R. Li, D. S. Su and M. Antonietti, J. Am. Chem. Soc., 2011, 133, 2362; (f) Y. Pérez, M. Fajardo and A. Corma, Catal. Commun., 2011, 12, 1071; (g) L. M. Sikhwivhilu, N. J. Coville, D. Naresh, K. V. R. Chary and V. Vishwanathan, Appl. Catal., A, 2007, 324, 52.
- 14 (a) C. V. Rode, U. D. Joshi, O. Sato and M. Shirai, *Chem. Commun.*, 2003, 1960; (b) P. Makowski, R. D. Cakan, M. Antonietti, F. Goettmann and M. M. Titirici, *Chem. Commun.*, 2008, 999; (c) H. L. Liu, Y. W. Li, R. Luque and H. F. Jiang, *Adv. Synth. Catal.*, 2011, 353, 3107.
- 15 J. A. Baeza, L. Calvo, M. A. Gilarranz, A. F. Mohedano, J. A. Casas and J. J. Rodriguez, *J. Catal.*, 2012, 293, 85.
- 16 H. Z. Liu, T. Jiang, B. X. Han, S. G. Liang and Y. X. Zhou, *Science*, 2009, **326**, 1250.
- 17 H. Li, J. Liu, S. H. Xie, M. H. Qiao, W. L. Dai, Y. F. Lu and H. X. Li, *Adv. Funct. Mater.*, 2008, **18**, 3235.
- 18 Y. Motoyama, M. Takasaki, S. Yoon, I. Mochida and H. Nagashima, *Org. Lett.*, 2009, **11**, 5042.
- 19 N. Toshima, in *Fine Particles Sciences and Technology: From Micro to New Particles*, ed. E. Pellizzetti, Kluwer, Dordrecht, 1996.
- 20 F. A. Harraz, S. E. El-Hout, H. M. Killa and I. A. Ibrahim, *J. Catal.*, 2012, **286**, 184.
- 21 (a) S. M. Chergui, A. Ledebt, F. Mammeri, F. Herbst, B. Carbonnier, H. B. Romdhane, M. Delamar and M. M. Chehimi, *Langmuir*, 2010, 26, 16115; (b) M. Caporali, A. Guerriero, A. Ienco, S. Caporali, M. Peruzzini and L. Gonsalvi, *ChemCatChem*, 2013, 5, 2517; (c) Z. Cui, P. J. Kulesza, C. M. Li, W. Xing and S. P. Jiang, *Int. J. Hydrogen Energy*, 2011, 36, 8508; (d) D. Bera, S. C. Kuiry, M. McCutchen, S. Seal, H. Heinrich and G. C. Slane, *J. Appl. Phys.*, 2004, 96, 5152.