# **RSC Advances**



View Article Online

View Journal | View Issue

# PAPER



Cite this: RSC Adv., 2015, 5, 22863

Received 22nd January 2015 Accepted 18th February 2015

DOI: 10.1039/c5ra01318f

www.rsc.org/advances

## 1 Introduction

The precursor of Nylon-6 is  $\varepsilon$ -caprolactam and it is primarily manufactured by a cyclohexanone hydroxylamine route.<sup>1,2</sup> However, cyclohexanone is obtained from a very low efficiency cyclohexane oxidation process. Moreover, the cyclohexanone hydroxylamine route results in the formation of a large amount of ammonium sulfate and wastes.<sup>3,4</sup> Researchers have been trying to find novel and environmental friendly methods for producing cyclohexane oxime and  $\varepsilon$ -caprolactam.<sup>5</sup> The route of cyclohexane nitration and reduction to cyclohexanone oxime and caprolactam might be a good choice. The reduction process of nitrocyclohexane (NC) is shown in Fig. 1.

The earliest research on nitrocyclohexane (NC) hydrogenation was reported by DuPont<sup>6,7</sup> in liquid phase by using a Pd catalyst to give a 70% yield of cyclohexanone oxime at 413 K and 35 bar. Knifton<sup>8,9</sup> used homogenous Cu (I, II) and Ag (I) catalysts to reduce nitrocyclohexane with CO to give an 89% oxime yield; however, the catalyst was difficult to recover and the reaction was carried out under high pressure. Serna *et al.*<sup>10</sup> reported a Pt/ TiOx catalyst doped with sodium cation which provided 84.5% selectivity to make cyclohexanone oxime with 95% nitrocyclohexane conversion under 4.0 MPa and 383 K. Shimizu *et al.*<sup>11</sup> compared an Au/Al<sub>2</sub>O<sub>3</sub> catalyst and the catalyst with smaller particle sized gold showed better catalytic performance

# The influences of preparation methods on the structure and catalytic performance of single-wall carbon nanotubes supported palladium catalysts in nitrocyclohexane hydrogenation

Sihua Liu, Fang Hao, Pingle Liu\* and He'an Luo

Single-wall carbon nanotubes (CNTs) supported palladium catalysts were prepared by different methods. The influences of different preparation methods on the structure and catalytic performance in nitrocyclohexane hydrogenation were investigated. The catalysts were characterized by nitrogen adsorption-desorption, XRD, TEM, hydrogen chemisorption and X-ray photoelectron spectroscopy. The results show that Pd/SWCNTs prepared by a water impregnation method provide a smaller particle size of palladium. The reduction conditions have great influence on the valence state of palladium on the support. A catalyst with smaller particle size, better dispersion and higher content of monovalent palladium exhibits better catalytic performance in nitrocyclohexane hydrogenation to cyclohexanone oxime. Pd/SWCNTs-2 prepared by a water impregnation method and reduced at 723 K has 96.4% selectivity when synthesizing cyclohexanone oxime with a 96.0% conversion from nitrocyclohexane under mild conditions of 0.3 MPa and 323 K.

under 0.6 MPa and 373 K. Wang *et al.*<sup>12</sup> reported gas phase hydrogenation of nitrocyclohexane over oxide supported gold catalysts. Activated carbon and carbon nanotubes supported palladium catalysts were used in liquid phase hydrogenation of nitrocyclohexane to cyclohexanone oxime, and the single-wall carbon nanotubes supported palladium catalyst prepared by impregnation method and reduced under 523 K showed a catalytic performance of 98.9% conversion and 89.5% selectivity to cyclohexanone oxime.<sup>13-15</sup> Preparation methods can significantly influence the physical structure and chemical property of heterogeneous supported catalysts.<sup>16-19</sup> In this paper, singlewall carbon nanotubes supported palladium catalysts were



Fig. 1 Nitrocyclohexane hydrogenation process.

College of Chemical Engineering, Xiangtan University, Xiangtan, 411105, China. E-mail: liupingle@xtu.edu.cn; Fax: +86 73158298172; Tel: +86 73158298005

prepared by different methods, and the influences of different preparation methods on the structure and catalytic performance in nitrocyclohexane hydrogenation were investigated.

### 2 Experimental procedures

#### 2.1 Reagents

Nitrocyclohexane (95 wt%) was purchased from Tokyo Chemical Industry Corporation Limited. Carbon nanotubes were purchased from Shenzhen Nanotech Port Corporation Limited. PdCl<sub>2</sub>, KBH<sub>4</sub>, formaldehyde and ethylenediamine were analytical grade and purchased from Sinopharm Chemical Reagent Corporation Limited. H<sub>2</sub> (99.99%) was provided by Zhuzhou Diamond Gas Company.

#### 2.2 Catalyst preparation

Single-wall carbon nanotubes were pretreated in concentrated nitric acid (68 wt%) at 303 K overnight, then filtered and washed with distilled water until the pH = 7; finally, the carbon nanotubes were dried in vacuum at 383 K for 10 h.

**2.2.1 Methanol pregnation method.** The catalyst was prepared by referring to the following procedures.<sup>20</sup> PdCl<sub>2</sub> was dissolved into a solution of concentrated hydrochloric acid (38 wt%) and distilled water to prepare a  $H_2PdCl_4$  solution. Then, a sodium hydroxide solution (10 wt%) was dropped into the above solution to regulate it to pH = 5. Afterwards, the pretreated carbon nanotubes and methanol were added and stirred for 10 h. Finally, the mixture was dried at 383 K for 12 h under vacuum, calcinated at 473 K for 4 h under nitrogen, and reduced at 523 K for 3 h under hydrogen; the prepared catalyst was labeled as Pd/SWCNTs-1.

**2.2.2 Water pregnation method.** The preparation process was similar to the methanol pregnation method; however, distilled water instead of methanol was added to the carbon nanotubes mixture and stirred for 10 h. The prepared catalyst was labeled as Pd/SWCNTs-2.

**2.2.3 Two-step water pregnation method.** The preparation process was similar to the water pregnation method; however, PdCl<sub>2</sub> was added into the mixture two times. The prepared catalyst was labeled as Pd/SWCNTs-3.

**2.2.4 Ion exchange method.** An ammonia solution (38 wt%) was dropped into a solution of  $H_2PdCl_4$  to form the complex. Then, pretreated carbon nanotubes and water were added to undergo ion exchange in the above solution. Finally, the mixture was calcinated at 473 K for 4 h under nitrogen, and reduced at 523 K for 3 h under hydrogen; the prepared catalyst was labeled as Pd/SWCNTs-4.<sup>21</sup>

**2.2.5 Methanol reduction method.** The preparation process was similar to the water pregnation method; however, the catalyst was reduced in 37 wt% methanol solution at 333 K for 4 h, and then dried at 383 K for 12 h under vacuum. The prepared catalyst was labeled as Pd/SWCNTs-5.

**2.2.6 KBH<sub>4</sub> reduction method.** The preparation process was similar to the water pregnation method; however, the catalyst was reduced in 10 wt% KBH<sub>4</sub> solution in an ice-bath,

and then dried at 383 K for 12 h under vacuum. The prepared catalyst was labeled as Pd/SWCNTs-6.<sup>22</sup>

#### 2.3 Catalyst characterization

2.3.1 N<sub>2</sub> adsorption-desorption. Specific surface area, pore volume and pore size distribution of the samples were obtained by nitrogen adsorption-desorption on a Quantachrome NOVA-2200e automated gas sorption system. Specific surface areas and pore size distributions were calculated by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods.

**2.3.2 X-ray diffraction.** Powder X-ray diffraction (XRD) patterns were determined on a D/max2500 TC diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.542$  Å). The tube voltage was 40 kV, the current was 30 mA, and the scan range was  $2\theta = 5-90^{\circ}$  with a scanning rate of  $1^{\circ}$  min<sup>-1</sup>.

**2.3.3 Transmission electron microscopy.** The microstructure of the catalysts was observed by transmission electron microscopy (TEM) on a TecnaiG2 20 STwin electron microscope working at less than 200 kV. The instrumental magnification ranged from  $2 \times 10^4$  to  $10 \times 10^6$ . The samples were deposited on holey carbon coated Cu grids.

**2.3.4 Hydrogen chemisorption.** Hydrogen chemisorption was measured by using Quantachrome's ChemBET 3000 instrument. The samples had been previously reduced in a hydrogen stream and cooled to ambient temperature under a nitrogen stream. The hydrogen chemisorption was performed at 323 K, and the hydrogen pulses (0.02 mL) were injected until the eluted areas of consecutive pulses became constant.

2.3.5 X-ray photoelectron spectroscopy. X-ray photoelectron spectroscopy (XPS) was obtained on a K-Alpha 1063 from Thermo Fisher Scientific using Al K $\alpha$  X-rays and a micro gathered monochromator. The tube voltage was 12 kV, the current was 6 mA, and the analyzer was a 180° double gathered hemisphere (energy resolution = 0.5 eV, vacuum degree = 10–9 mBar, spot diameter = 400  $\mu$ m).

#### 2.4 Procedure for the catalyst test

Liquid phase hydrogenation of nitrocyclohexane was conducted as follows: ethylenediamine (4.8 g), nitrocyclohexane (0.6 g), and catalyst (0.1 g) were mixed in a 50 mL Teflon-lined stainlesssteel autoclave equipped with a magnetic stirrer. The reactor was filled with nitrogen and then evacuated to exclude air. It was then pressurized to 0.3 MPa with hydrogen, and heated to the setting reaction temperature. After the reaction, the reactor was cooled to ambient temperature and the catalysts were removed by filtration. The contents of the products were determined by GC (GC-14C, SHIMADZU) with a flame ionization detector (FID) and a 30 m DB-1701 capillary column using dimethyl phthalate (DMP) as an internal standard.

### 3 Results and discussions

#### 3.1 Characterization of the catalysts

**3.1.1** The effects of preparation methods. Fig. 2 shows the XRD patterns of the prepared catalysts. All of these catalysts



Fig. 2 XRD patterns of different catalysts.

present a diffraction peak of carbon around  $2\theta = 26^{\circ}$ , the peaks at  $2\theta = 32^{\circ}$ ,  $45^{\circ}$ , and  $57^{\circ}$  are ascribed to sodium chloride; and the peaks at  $2\theta = 40^{\circ}$  and  $47^{\circ}$  are ascribed to the face centered cubic structure of palladium.<sup>22</sup> It can be seen from Fig. 2 that the catalysts prepared by water impregnation exhibit significant characteristic diffraction peaks at  $2\theta = 40^{\circ}$  and  $47^{\circ}$  corresponding to palladium. However, there is a very weak diffraction peak around  $40^{\circ}$  and  $47^{\circ}$  in the XRD pattern of Pd/SWCNTs-1 and, as well, there is no obvious characteristic diffraction peak around  $40^{\circ}$  and  $47^{\circ}$  in the XRD pattern of Pd/SWCNTs-4.

Fig. 3 shows the nitrogen adsorption-desorption curves of Pd/SWCNTs. The isotherm of these catalysts shows an adsorption isotherm of type III according to the IUPAC classification, representing a weak interaction between Pd/SWCNTs and nitrogen. The hysteresis loops of these catalysts are of type H1, which is attributed to cylindrical pores with both sides open, and indicates a narrow pore size distribution of mesoporous



Fig. 3 N<sub>2</sub> adsorption–desorption isotherm and BJH pore size distributions of different catalysts.

materials. All of the catalysts have a mesoporous structure which means that the preparation methods have no obvious influence on the pore structure of the catalysts. It is well-known that a larger area of the hysteresis loop indicates more pores on the basis of the geometrical effect and Kelvin equation, which is in good agreement with the pore volumes listed in Table 1.

The hydrogen chemisorption data of different catalysts are summarized in Table 2. It can be seen from Table 2 that Pd/SWCNTs-2 demonstrates better dispersion, larger hydrogen uptake quantity, and larger metal surface area than other catalysts. This indicates that catalysts made by the water impregnation method and hydrogen reduction are more favorable for the dispersion of palladium; perhaps this is because diffusion of the precursor inside the pores during ion exchange is faster than during impregnation, which may cause a non-uniform distribution of the precursor inside the particle.<sup>16</sup>

The TEM images of catalysts prepared by different methods are shown in Fig. 4. The dark dots represent palladium particles on the surface of carbon nanotubes. The parallel graphite layer can be seen from the TEM images and the images show that palladium particles are well dispersed on the surface of the support. As shown in Fig. 3, the particle size of palladium is about 4.0 to 9.0 nm in Pd/SWCNTs-1, 3.5 to 6.0 nm in Pd/ SWCNTs-2, and 4.0 to 6.0 nm in Pd/SWCNTs-3. However, the particle size of palladium in Pd/SWCNTs-4 ranges from 6.5 to 13.5 nm, Pd/SWCNTs-5 ranges from 5.0 to 10.0 nm, and Pd/ SWCNTs-6 ranges from 5.0 to 12.0 nm. The catalysts prepared by impregnation methods have smaller particle sizes of palladium than the catalysts prepared by the chemical reduction method and ion exchange method, which is in agreement with the literature.<sup>23-25</sup>

**3.1.2** The effects of preparation conditions. Fig. 5 shows the XRD patterns of Pd/SWCNTs-2 prepared at different reduction temperatures. All of the samples show the diffraction peak

Table 1 Textural properties of the catalysts prepared by different methods

Catalysts	Surface area $(m^2 g^{-1})$	Average pore size (nm)	Pore volume $(cm^3 g^{-1})$
Pd/SWCNTs-1	275.8	3.8	1.3
Pd/SWCNTs-2	220.6	3.8	1.0
Pd/SWCNTs-3	263.9	3.6	1.1
Pd/SWCNTs-4	362.2	3.8	1.5
Pd/SWCNTs-5	319.3	3.8	1.5
Pd/SWCNTs-6	296.7	3.8	1.4

 Table 2
 Hydrogen chemisorption data of different catalysts

Catalysts	$H_2$ uptake (µmol g <sup>-1</sup> )	Metal surface area $(m^2 g^{-1})$	Dispersion (%)
Pd/SWCNTs-1	32.6	61.9	13.9
Pd/SWCNTs-2	77.7	147.4	33.0
Pd/SWCNTs-3	39.4	74.8	16.8
Pd/SWCNTs-4	19.7	37.5	8.4
Pd/SWCNTs-5	12.5	23.7	5.3
Pd/SWCNTs-6	19.6	37.7	15.3



**Fig. 4** TEM images of different preparation methods: (a) Pd/SWCNTs-1, (b) Pd/SWCNTs-2, (c) Pd/SWCNTs-3, (d) Pd/SWCNTs-4, (e) Pd/SWCNTs-5, and (f) Pd/SWCNTs-6.



Fig. 5 XRD patterns of Pd/SWCNTs-2 prepared at different reduction temperatures: (a) 523 K, (b) 623 K, and (c) 723 K.

of carbon around  $2\theta = 26^{\circ}$ ; the peaks at  $2\theta = 32^{\circ}$ ,  $45^{\circ}$ , and  $57^{\circ}$  are ascribed to sodium chloride, and the peaks at  $2\theta = 40^{\circ}$  and  $47^{\circ}$  are ascribed to the face centered cubic structure of palladium. It can be seen from Fig. 5 that the diffraction peaks at  $2\theta = 40^{\circ}$  and  $47^{\circ}$  corresponding to palladium get stronger along with the increase of the reduction temperature, which means that the higher reduction temperature causes larger particle sizes of palladium. This is consistent with the results of TEM.



Fig. 6 TEM images of Pd/SWCNTs-2 prepared at different reduction temperatures: (a) 623 K, and (b) 723 K.

The reason may be that a high reduction temperature makes the palladium particle more prone to sinter.

The TEM images of Pd/SWCNTs-2 prepared at different reduction temperatures are shown in Fig. 6. And Pd/SWCNTs-2 reduced at 523 K is shown in Fig. 4(b). The dark dots represent palladium particles on the surfaces of carbon nanotubes. The parallel graphite layer can be seen from the TEM images and they show that palladium particles are well dispersed on the surfaces of the support. The TEM micrographs show that palladium particles of the catalyst reduced at 523 K range from 3.5–6.0 nm while palladium particles of the catalyst reduced at 623 K and 723 K range from 4.0–6.5 nm and 4.0–7.0 nm respectively. These results show that the particle size of palladium increases slightly with a reduction in temperature.

The effects of reduced temperature on the valence state of palladium on the support are tested by X-ray photoelectron spectroscopy and the results are shown in Fig. 7. There are two peaks of Pd3d spectra; the right peak around 335 eV is attributed to the  $Pd3d_{5/2}$  spectral peak and the left peak around 341 eV is ascribed to the  $Pd3d_{3/2}$  spectral peak. The binding energy peaks and the valence peak could be shifted; the shift in the core level binding energies can be 1.0-1.3 eV in the highly dispersed samples.<sup>26,27</sup> The peaks around 335.5 eV, 336.1 eV and 337.6 eV are assigned to  $Pd^0$ ,  $Pd^+$  and  $Pd^{2+}$ . The surface compositions of different valence states of palladium are shown in Table 3. It can be observed that the  $Pd^{2+}$  turns into  $Pd^+$  when the reduction temperature increases, and this means that a



Fig. 7 XPS Pd 3d spectra of Pd/SWCNTs-2 prepared at different reduction temperatures: (a) 523 K, (b) 623 K, and (c) 723 K.

Table 3Surface compositions of the valence states of palladium withdifferent reduction temperatures

Reduction temperature (K)	Pd <sup>0</sup> (%)	$\mathrm{Pd}^{+}(\%)$	Pd <sup>2+</sup> (%)
523	30.1	33.0	37.7
623	30.4	33.8	35.8
723	29.5	38.7	31.9

reasonable reduction temperature is favorable for the formation of monovalent palladium.

#### 3.2 Catalytic performance

The results of liquid phase hydrogenation of nitrocyclohexane over Pd/SWCNTs catalysts prepared by different methods are shown in Table 4. The products include cyclohexanone oxime, cyclohexylamine, and a small amount of cyclohexanone and byproducts. It can be seen from Table 4 that Pd/SWCNTs-4 gives the lowest selectivity to cyclohexanone oxime at almost the same nitrocyclohexane conversion catalyzed by Pd/SWCNTs-1, Pd/SWCNTs-2, Pd/SWCNTs-3 and Pd/SWCNTs-6. Pd/SWCNTs-5 has the lowest conversion of nitrocyclohexane under the same reaction conditions. It can be seen from the hydrogen chemisorption data in Table 2 that Pd/SWCNTs-5 has the lowest hydrogen uptake quantity, metal surface area, and dispersion of palladium. Pd/SWCNTs-2 gives the best result of 85.9% selectivity to cyclohexanone oxime at a nitrocyclohexane conversion of 98.9%. Pd/SWCNTs-2 prepared by the water impregnation method and reduced by hydrogen produces the smallest particle size of palladium, the largest hydrogen uptake quantity, metal surface area, and highest dispersion of palladium, which favor the formation of cyclohexanone oxime.

Table 5 shows the results of the catalysts prepared by different reduction temperatures in the hydrogenation of nitrocyclohexane to cyclohexanone oxime. The hydrogenation reaction over these catalysts was carried out at 323 K and 0.3 MPa. It can be seen from Table 5 that higher reduction temperatures can promote selectivity to cyclohexanone oxime. All the catalysts reduced at 723 K gave the highest selectivity to cyclohexanone

Table 4 Nitrocyclohexane hydrogenation catalyzed by different catalysts<sup> $\alpha$ </sup>

	Conversion of NCH (%)	Selectivity (%)	
Catalyst		СНО	CHA
Pd/SWCNTs-1	99.7	70.5	2.8
Pd/SWCNTs-2	98.9	85.9	6.3
Pd/SWCNTs-3	99.6	79.7	2.0
Pd/SWCNTs-4	99.4	65.5	5.0
Pd/SWCNTs-5	79.7	85.4	0.2
Pd/SWCNTs-6	99.8	76.9	3.6

<sup>a</sup> Reaction conditions: nitrocyclohexane 0.6 g; temperature 323 K; time 6
h; pressure 0.3 MPa; ethylenediamine 5 mL; NCH = nitrocyclohexane;
CHO = cyclohexanone oxime; CHA = cyclohexylamine.

Catalyst	Reduction temp. (K)	Conversion of NCH (%)	Selectivity (%)	
			СНО	CHA
Pd/SWCNTs-1	523	99.7	70.5	2.8
	623	99.7	69.1	5.0
	723	99.1	85.5	4.2
Pd/SWCNTs-2	523	98.9	85.9	6.3
	623	98.5	93.5	4.2
	723	96.0	96.4	3.2
Pd/SWCNTs-3	523	99.6	79.7	2.0
	623	99.5	86.2	1.9
	723	99.8	86.3	1.6
Pd/SWCNTs-4	523	99.4	65.5	5.0
	623	99.5	65.5	4.6
	723	99.8	67.7	4.7

Table 5 Effect of reduction temperatures with catalysts on nitro-

cyclohexane hydrogenation<sup>a</sup>

<sup>*a*</sup> Reaction conditions: nitrocyclohexane 0.6 g; temperature 323 K; time 6 h; pressure 0.3 MPa; ethylenediamine 5 mL; NCH = nitrocyclohexane; CHO = cyclohexanone oxime; CHA = cyclohexylamine.

oxime. Pd/SWCNTs-2 reduced at 723 K gave 96.4% selectivity to cyclohexanone oxime with nitrocyclohexane conversion at 96.0%; the selectivity to cyclohexanone oxime is more than 10% higher than that reduced at 523 K. The different preparation methods may have influences on the interaction between the palladium and the support, and the reduction conditions can affect the valence state of the palladium on the support.<sup>16–19</sup> It can be seen from the results of XPS that Pd/SWCNTs reduced at 723 K has the highest content of Pd<sup>+</sup>. This indicates that mono valent palladium favors the formation of cyclohexanone oxime and prevents complete hydrogenation to other byproducts.

### 4. Conclusion

Single-wall carbon nanotubes supported palladium catalysts were prepared by different methods. The catalysts were characterized by nitrogen adsorption-desorption, XRD, TEM, hydrogen chemisorption and X-ray photoelectron spectroscopy. The results show that Pd/SWCNTs-2 prepared by a water impregnation method and reduced by hydrogen, produces smaller particle sizes of palladium, larger quantities of hydrogen uptake, higher metal surface area, and greater dispersion of palladium. The reduction conditions have great influence on the valence state of palladium on the support. Results show that a catalyst with smaller particles, better dispersion and higher content of mono valent palladium favors the formation of cyclohexanone oxime. Pd/SWCNTs-2 prepared by water impregnation and reduced by hydrogen at 723 K gives 96.4% selectivity to cyclohexanone oxime formation with a nitrocyclohexane conversion of 96.0% under the mild conditions of 0.3 MPa and 323 K.

### Acknowledgements

This work was supported by the NFSC (21276218), SRFDP (20124301110007), Scientific Research Fund of Hunan Provincial

Paper

15 Y. Yan, S. Liu, F. Hao, P. Liu and H. a. Luo, Catal. Commun.,

Education Department (13K043, CX2013B272) and Project of Hunan Provincial Science & Technology Department (2012FJ1001).

# References

- 1 H. Ichihashi and H. Sato, Appl. Catal., A, 2001, 221, 359–366.
- 2 US Pat., 5304643, 1994.
- 3 US Pat., 3644526, 1972.
- 4 H. X. Yuan, Q. H. Xia, H. J. Zhan, X. H. Lu and K. X. Su, *Appl. Catal.*, *A*, 2006, **304**, 178–184.
- 5 R. Raja, G. Sankar and J. M. Thomas, *J. Am. Chem. Soc.*, 2001, **123**, 8153–8154.
- 6 GB Pat., 857902, 1961.
- 7 GB Pat., 860340, 1961.
- 8 J. F. Knifton, J. Org. Chem., 1973, 38, 3296-3301.
- 9 J. F. Knifton, J. Catal., 1974, 33, 289-298.
- 10 P. Serna, M. López-Haro, J. J. Calvino and A. Corma, *J. Catal.*, 2009, **263**, 328–334.
- 11 K.-i. Shimizu, T. Yamamoto, Y. Tai and A. Satsuma, J. Mol. Catal. A: Chem., 2011, 345, 54–59.
- 12 X. Wang, N. Perret and M. A. Keane, *Appl. Catal., A*, 2013, **467**, 575–584.
- 13 H. G. Liao, Y. J. Xiao, H. K. Zhang, P. L. Liu, K. Y. You, C. Wei and H. a. Luo, *Catal. Commun.*, 2012, **19**, 80–84.
- P. L. Liu, H. K. Zhang, S. H. Liu, Z. J. Yao, F. Hao, H. G. Liao,
  K. Y. You and H. a. Luo, *ChemCatChem*, 2013, 5, 2932–2938.

- 2014, **50**, 9–12. 16 C. Perego and P. Villa, *Catal. Today*, 1997, **34**, 281–305.
- 17 M. L. Toebes, J. A. van Dillen and K. P. de Jong, *J. Mol. Catal. A: Chem.*, 2001, **173**, 75–98.
- 18 M. Turáková, M. Králik, P. Lehocký, Ľ. Pikna, M. Smrčová, D. Remeteiová and A. Hudák, *Appl. Catal., A*, 2014, 476, 103–112.
- 19 P. Zou, C. Tu and S. Cheng, Acta Pet. Sin., 2012, 1, 133-136.
- 20 C. Xiang, Z. Li Jin, G. Pei Guo and Z. Chong Yu, *J. Nanjing Univ. Sci. Technol.*, 2005, 5, 93–96.
- 21 T. C. Chang, J. J. Chen and C. T. Yeh, *J. Catal.*, 1985, **96**, 51–57.
- 22 T. Harada, S. Ikeda, M. Miyazaki, T. Sakata, H. Mori and M. Matsumura, *J. Mol. Catal. A: Chem.*, 2007, **268**, 59–64.
- 23 D. Liang, J. Gao, H. Sun, P. Chen, Z. Hou and X. Zheng, *Appl. Catal.*, *B*, 2011, **106**, 423–432.
- 24 D. Liang, J. Gao, J. Wang, P. Chen, Z. Hou and X. Zheng, *Catal. Commun.*, 2009, **10**, 1586–1590.
- 25 D. Liang, J. Gao, J. Wang, P. Chen, Y. Wei and Z. Hou, *Catal. Commun.*, 2011, **12**, 1059–1062.
- 26 Z. Bastl, O. Přibyl and P. Mikušík, *Czech J. Phys.*, 1984, 34, 981–988.
- 27 A. Fritsch and P. Légaré, Surf. Sci., 1985, 162, 742-746.