J. Chem. Sci. Vol. 126, No. 1, January 2014, pp. 141–145. © Indian Academy of Sciences.

Selective hydrogenation of maleic anhydride over Pd/Al_2O_3 catalysts prepared via colloid deposition

HONGJING YUAN[a], CHUNLEI ZHANG[b], WEITAO HUO[a], CHUNLI NING[b], YONG TANG[b], YI ZHANG[b], DEQUAN CONG[a], WENXIANG ZHANG[a], JIAHUAN LUO[c], SU LI[a] and ZHENLU WANG[a,*]

[a]Key Laboratory of Surface and Interface Chemistry of Jilin Province, College of Chemistry, Jilin University, Qianjin Road 2699, Changchun 130012, PR China
[b]Shanghai Huayi (Group) Company Technology Research Institute, Longwu Road 4600, Shanghai 200241, PR China
[c]State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Qianjin Road 2699, Changchun 130012, PR China
e-mail: wzl@jlu.edu.cn

MS received 21 September 2013; revised 23 October 2013; accepted 24 October 2013

Abstract. Pd/Al_2O_3 catalysts were prepared via colloid deposition and the performance of the catalysts was examined in the selective hydrogenation of maleic anhydride to succinic anhydride. When the reaction was carried on in a batch system with 1,4-dioxane as the solvent (353 K and 1.0 MPa), high conversion of maleic anhydride (>98%) and high selectivity (>99%) for succinic anhydride were observed after 5 h. The as-prepared Pd/Al_2O_3 catalyst also showed excellent performance in solvent-free system and fixed-bed systems. The maleic anhydride (MA) conversion was greater than 98%, and high selectivity (>99%) for succinic anhydride was obtained after 1600 h in a fixed bed reacter. The results showed that the activity of the Pd/Al_2O_3 catalysts was excellent due to its high active surface area.

Keywords. Pd/Al_2O_3 catalyst; maleic anhydride; selective hydrogenation; succinic anhydride.

1. Introduction

The hydrogenation of maleic anhydride (MA) has attracted a significant amount of attention because the majority of its reaction products, including succinic anhydride (SA), γ-butyrolactone (GBL), tetrahydrofuran (THF) and 1,4-butanediol (BDO), are widely used in industrial applications.[1,2] In particular, SA is widely used in the manufacturing of polymeric materials, pharmaceuticals, agrochemicals, dyes, surface-active agents, organic flame retardant materials and fragrances.[3]

In the literature, different types of catalysts, including noble and non-noble metals, have been used for the hydrogenation of MA with different solvents in the liquid and gas phases.[4–6] Various products, including GBL, THF, BDO and butyric acid were obtained, depending on the catalysts and reaction conditions.[6–9] For example, when Pd/C was used as a catalyst in the hydrogenation of MA in supercritical carbon dioxide, 97.3% selectivity for GBL and 100% conversion of MA were achieved at an H_2 pressure of 4 MPa and reaction temperature of 473 K.[10]

Several catalysts have been investigated in the hydrogenation of MA to SA. For example, when $RhCl(PPh_3)_3$ was used as a catalyst in the liquid phase hydrogenation of MA in ethylene glycol dimethylether, 99% conversion of MA and 100% SA selectivity to SA were achieved under the optimal reaction conditions.[11] To avoid the high cost of separating the solvent from the reaction mixture, solvent-free hydrogenation of MA has been carried out using metallic nickel catalyst.[12] Several catalysts have been investigated in fixed bed reactors, which are suitable for sequential production processes used in commercial procedures. For example, Ni/SiO_2, Co/SiO_2 and Cu/SiO_2[1,13] have been used as catalysts in the hydrogenation of MA in a fixed bed reactor. However, partial deactivation occurred due to the deposition of carbonaceous species on the metallic phase. Although nickel–platinum catalysts are often used in the hydrogenation of MA, the addition of Pt increases the stability of the catalyst. Moreover, only a 4% loss of reaction activity was observed after 120 h.[3]

Noble catalysts, especially Pd-based catalysts, have shown excellent catalytic performance in hydrogenation

*For correspondence

reactions.[14–16] Several groups, including ours, have demonstrated that colloid-deposition methods are efficient procedures for the preparation of highly dispersed, supported noble metal catalysts.[17–22] In the present study, Pd/Al_2O_3 was prepared by the colloid-deposition method, and the catalytic performance of the resulting materials was investigated in the selective hydrogenation of MA to SA in both a batch and fixed bed system. The physical–chemical properties of the Pd/Al_2O_3 catalysts were determined to correlate the catalytic performance and characteristics of the catalysts.

2. Experimental

2.1 *Catalyst preparation*

Supported Pd/Al_2O_3 catalysts were prepared using the colloid-deposition method, according to the previously described procedure.[23,24]

Typically, poly(N-vinyl-2-pyrrolidone)-protected (PVP) and Na_2PdCl_4 (100 mL, 1.6 mM) were generated from of PVP, $PdCl_2$, NaCl and ethylene glycol. Subsequently, an ethylene glycol solution of NaOH was added, and the colour of the resulting mixture turned brown. After stirring for 2 h, Al_2O_3 and distilled water were added, and the mixture was heated to 353 K until the total deposition of Pd colloids occurred. After the deposition process, the material was washed with distilled water to obtain the separated solid. The product was dried at 373 K for 6 h and was reduced with H_2/Ar at 573 K for 2 h prior to use. The obtained catalyst was labelled as CD-Pd/Al_2O_3.[21,22]

To compare, 1 wt% Pd/Al_2O_3 catalyst was prepared by impregnation method.[25] After the impregnation step, the catalyst was dried at 373 K for 6 h, and then reduced with H_2/Ar at 573 K for 2 h before used, the obtained catalyst was recorded as IM-Pd/Al_2O_3.

2.2 *Catalyst characterization*

The X-ray diffraction (XRD) analysis of the catalysts were carried out using a D/Max-rA X-ray diffractometer operated at 30 kV and 40 mA employing nickel-filtered Cu K_α radiation. Transmission electron microscopic (TEM) images were obtained using H8100-IV electron microscopic operated at 200 kV. BET surface areas of catalysts were calculated according to the nitrogen adsorption isotherm at 77 K measured in a micromeritics ASAP2010 apparatus. The X-ray photoelectron spectra (XPS) measurements were carried out on an ESCALAB250 X-ray photoelectron spectrometer, using Al K_α radiation as the excitation source. The XPS spectra were corrected by adjusting the C 1speak to a position of 284.6 eV. The palladium content in the prepared catalysts were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES), in a Perkin-Elmer Optima 3300DV ICP-OES spectrometry.

The surface area of Pd[26] was calculated basing on the surface concentration of Pd determined by XPS and the BET surface area, assuming that the atomic cross sections are 0.059 nm^2 for Pd, 0.054 nm^2 for O^{2-} and 0.01 nm^2 for Al^{3+}, which were calculated from the atomic and ionic radii; the surface of Pd (S_{Pd}) is calculated by the equation: $S_{Pd} = S_{BET} \times \alpha_{Pd} \times c_{Pd} / (\alpha_{Pd} \times c_{Pd} + \alpha_{Al} \times c_{Al} + c_O)$, where S_{BET} is BET surface area, α_{Pd} and α_M are the atomic ratios of Pd/O and Al/O, c_{Pd}, c_{Al}, and c_O are the cross sections.

2.3 *Catalytic evaluation*

Selective hydrogenation of MA to SA was carried on both in batch system and fixed bed system.

In batch system, the reaction was performed in a 100 mL stainless steel autoclave. For the solvent system, the vessel was charged with MA (75 mmol), 1, 4-dioxane (50 ml) and catalyst (0.1 g, containing $8.5*10^{-3}$ mmol Pd), while for the solvent-free system, the vessel was charged with MA (75 mmol) and catalyst (0.1 g, containing $8.5*10^{-3}$ mmol Pd). After purged with hydrogen three times to remove the air, the reactor was pressured up to certain pressure. Under string at 800 rpm, the reaction was heated to certain temperature and carried out for certain time.

Fixed bed system was conducted in a stainless fixed tube at 0.2 MPa H_2 pressure. About 1.0 g catalyst (containing $8.5*10^{-2}$ mmol Pd) was packed into the centre of the tubular reactor. After the reactor was heated to 373 K at the flow of H_2, the reactant which consisted of a solution of MA in GBL (22 wt%) was injected simultaneity. The H_2 flow was controlled with H_2/MA = 21.4 (molar ratio). The weight hourly space velocity (WHSV) has been maintained at 0.61 h^{-1}.

All the collected products were analysed in a gas chromatograph (BEIFEN GC model 3420A) equipped with a flame ionization detector (FID) and a capillary Carbowax20000 column. The calculated method of MA conversion and selectivity to the products in fixed bed system was according to the literature.[9,27]

3. Results and discussion

3.1 *Characterization of Pd/Al_2O_3 catalysts*

The XRD patterns of Al_2O_3 and Pd/Al_2O_3 catalysts prepared according to different methods are presented

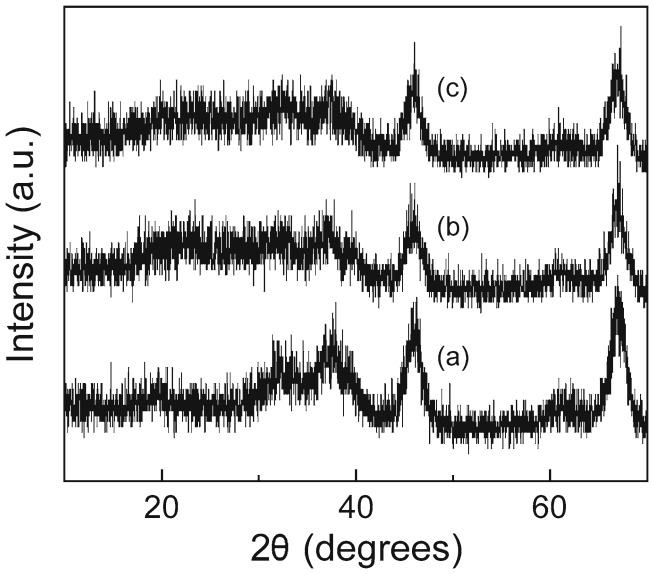

Figure 1. XRD patterns of (a) Al_2O_3 support; (b) IM-Pd/Al_2O_3; (c) CD-Pd/Al_2O_3 catalyst.

in figure 1. The Pd diffraction peak appeared at approximately $2\theta = 40.1°$, 46.8° and 68.2°.[28,29] As shown in the figure, for the CD-Pd/Al_2O_3 catalyst, only the characteristic peaks of the Al_2O_3 support were observed, indicating that Pd was highly dispersed on the catalyst. Compared to the CD-Pd/Al_2O_3 catalyst, a weak diffraction peak at $2\theta = 40.1°$ was observed on the IM-Pd/Al_2O_3 catalyst, suggesting that Pd dispersion was relatively poor.

Figure 2 shows the TEM images of Pd colloids (figure 2A) and CD-Pd/Al_2O_3 (figure 2B) and IM-Pd/Al_2O_3 catalysts (figure 2 C). The Pd clusters in the native solution were uniform spheres with particle sizes ranging from 1.5 to 3 nm (figure 2A). Compared to colloidal Pd particles, significant differences in the particle sizes of the CD-Pd/Al_2O_3 catalyst were not observed, and the average size was approximately 1.5–3 nm (figure 2B). For the IM-Pd/Al_2O_3 catalyst, the particle size of the Pd cluster was 6–10 nm (figure 2C), which indicated that the Pd particles in the IM Pd/Al_2O_3 catalyst were highly aggregated. Many studies have reported the aggregation of pure palladium catalysts prepared by the impregnation method.[2,30–32] The results of the current study showed that the CD-Pd/Al_2O_3 catalyst presented better Pd dispersion than the IM-Pd/Al_2O_3 catalyst, which was consistent with the XRD results.

The textural properties of the Pd/Al_2O_3 catalysts are presented in table 1. N_2 adsorption was used to investigate the specific surface area of the Al_2O_3 support, IM-Pd/Al_2O_3 catalyst and CD-Pd/Al_2O_3 catalyst. The Al_2O_3 support did not show significant changes after the addition of Pd. Furthermore, the ICP results revealed that the Pd content of the IM-Pd/Al_2O_3 catalyst and CD-Pd/Al_2O_3 catalyst was similar. The Pd surface area was calculated as demonstrated previously, and the results are also shown in table 1. The Pd surface area on the CD-Pd/Al_2O_3 catalyst was 3.7 times greater than that of the IM-Pd/Al_2O_3 catalyst, likely due to the formation of small Pd particles.[2,33]

3.2 *Catalytic performance*

Figure 3 presents the catalytic performance of the CD-Pd/Al_2O_3 catalyst and the IM-Pd/Al_2O_3 catalyst in the liquid phase hydrogenation of maleic anhydride. As shown in the figure, when the reaction was carried out at 353 K and 1.0 MPa of H_2 pressure in 1,4-dioxane, both catalysts showed high selectivity (>99%) for SA (results not shown). The activity over CD-Pd/Al_2O_3 was significantly higher than that over IM-Pd/Al_2O_3. After 2 h, 56% MA conversion was obtained over the CD-Pd/Al_2O_3 catalyst, while only 15% MA conversion was attained over the IM-Pd/Al_2O_3 catalyst.

These results indicated that Pd/Al_2O_3 catalysts prepared by the colloid deposition method were more

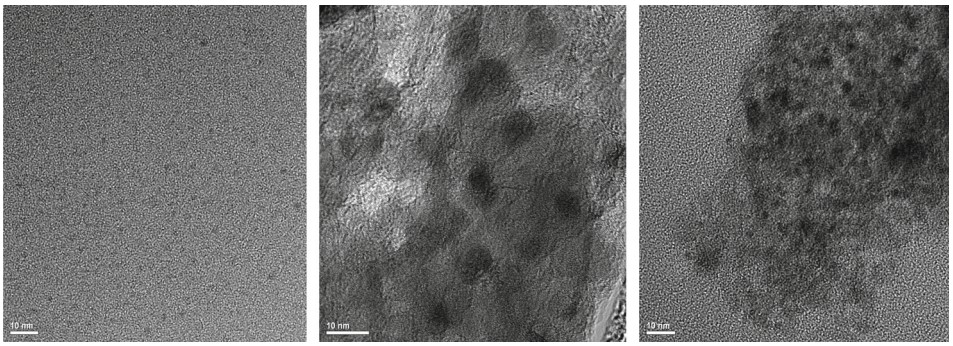

Figure 2. TEM images of (**A**): Pd colloid; (**B**): IM-Pd/Al_2O_3; (**C**) CD-Pd/Al_2O_3 catalyst.

Table 1. Some textural properties of Pd/Al_2O_3 catalysts.

Catalysts	Pd content (wt.%)	S_{BET} m^2/g	Pd surface area m^2/g	Pd dispersity on surface (%)[a]	Pd particle size (nm)[b]	TOF (mmol/hm^2·Pd)
Al_2O_3	–	115	–	–	–	–
IM-Pd/Al_2O_3	0.91	109	0.6	0.47	6–10	94
CD-Pd/Al_2O_3	0.89[c]	126	2.2	1.09	1.5–3	95
	0.87[d]					

[a]Defined by S_{Pd}/S_{BET}
[b]From TEM
[c]Before reaction
[d]After reaction for 1600 h

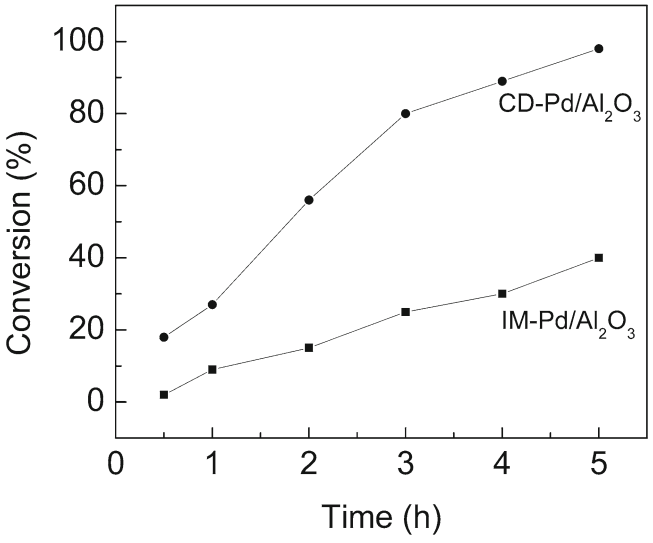

Figure 3. Liquid–phase selective hydrogenation of MA used catalysts prepared via different methods. Reaction condition: T = 353 K, P = 1.0 MPa, catalyst: 0.1 g, MA = 7.35 g, 1, 4-dioxane = 50 mL.

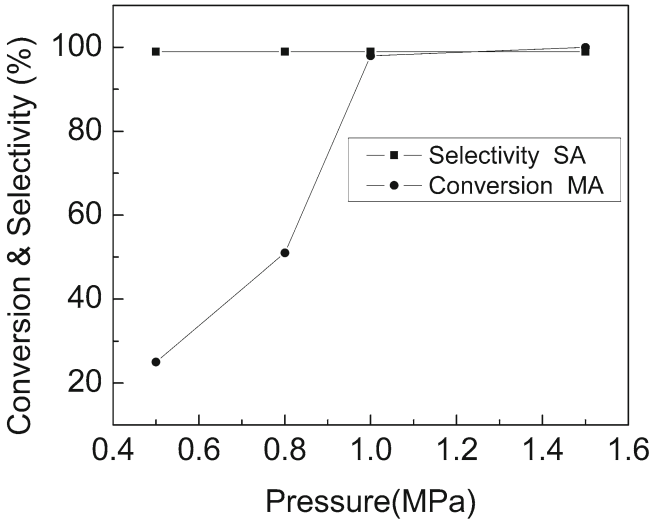

Figure 4. Effect of pressure on hydrogenation of MA over CD-Pd/Al_2O_3 catalyst. Reaction conditions: T = 353 K, P = 1.0 MPa, catalyst: 0.1 g, MA = 7.35 g.

active than catalysts prepared by the impregnation method, whereas the similar TOF results implied that both catalysts exhibited similar intrinsic activities (table 1). Thus, the higher activity of Pd/Al_2O_3 catalysts prepared by the colloid deposition method was attributed to its higher active surface area.

In order to avoid the cost of separating the solvent from the reaction mixture, the reaction was carried out without a solvent. The effect of the pressure on the catalytic performance of the CD-Pd/Al_2O_3 catalyst was also investigated (figure 4). When the reaction was carried out at 403 K for 4.5 h at 0.5, 0.8, 1.0 and 1.5 MPa, the conversion of MA was 25%, 51%, 99.8% and 99.9%, respectively. In the studied pressure range, the activity increased with an increase in pressure; however, differences in the selectivity for SA were not observed.

Compared to batch systems, fixed bed systems are more convenient for commercialization because they

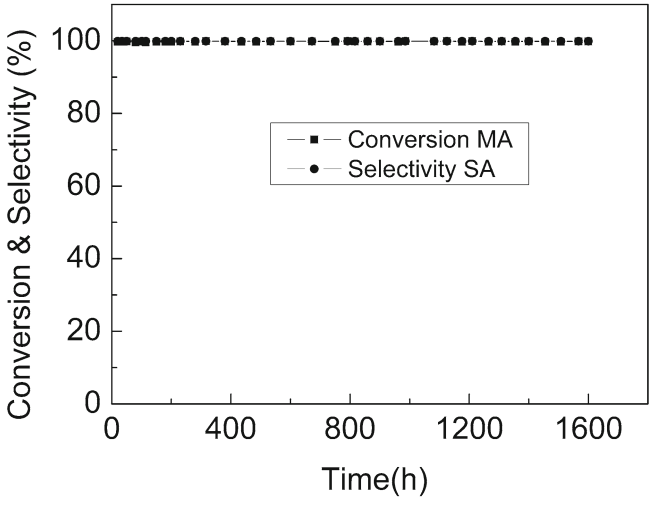

Figure 5. Time on steam of MA hydrogenation over CD-Pd/Al_2O_3 catalyst in fixed bed.

are suitable for sequential production, and the distribution of products is stable. To examine the stability of the catalyst in fixed bed systems, the catalytic performance of CD-Pd/Al_2O_3 in a fixed bed was investigated at 373 K and 0.2 MPa (figure 5). The CD-Pd/Al_2O_3 catalyst showed excellent catalytic performance in the hydrogenation of MA in a fixed bed system, and both the MA conversion and SA selectivity were greater than 98%. What need to notice was that deactivation was not observed when the reaction was carried out for 1600 h, The ICP results revealed that the Pd loading did not have obviously change after reaction for 1600 h, indicating that the Pd species were not leaching the support. So, it can be stated that CD-Pd/Al_2O_3 catalyst was a highly stable catalyst for this reaction at this condition.

4. Conclusions

Pd/Al_2O_3 catalysts prepared by the colloid deposition method showed remarkable catalytic performance in the selective hydrogenation of MA to SA in batch and fixed bed systems and showed significantly higher activity than Pd/Al_2O_3 catalysts prepared by the impregnation method. When the reaction was carried out on Pd/Al_2O_3 catalysts prepared by the colloid deposition method in 1,4-dioxane at 353 K and 1.0 MPa of H_2 pressure, the conversion and SA selectivity were greater than 99% after 5 h. The catalyst also showed excellent performance in solvent-free batch systems and fixed bed systems. Moreover, the MA conversion did not decrease significantly after 1600 h in a fixed bed system. These results demonstrated that CD-Pd/Al_2O_3 catalysts prepared by the colloid deposition method are high-performance catalysts for the selective hydrogenation of MA to SA.

Acknowledgements

This work was supported by the Technology Institute of Shanghai Huayi (Group) Company, Natural Science Foundation of Science and Technology Department of Jilin Province (20130101015JC), the Innovation Project of Frontiers of Science and New Interdiscipline of Jilin University (2012), the open subject of State Key Laboratory of Inorganic Synthesis and Preparative Chemistry (2012–15) and the National Science Foundation of China (Grant NO. 20973080).

References

1. Meyer C I, Regenhardt S A, Marchi A J and Garetto T F 2012 *Appl. Catal. A: Gen*. **417–418** 59
2. Xu J, Sun K-P, Zhang L, Ren Y-L and Xu X-L 2005 *Catal. Commun*. **6** 462
3. Li J, Tian W-P and Shi L 2011 *Catal. Lett*. **141** 565
4. Pillai U R, Demessie E S and Young D 2003 *Appl. Catal. B: Environ*. **43** 131
5. Li J, Tian W-P, Wang X and Shi L 2011 *Chem. Eng. J*. **175** 417
6. Zhang R-C, Yin H-B, Zhang D-Z, Qi L and Lu H-H 2008 *Chem. Eng. J*. **140** 488
7. Yu Y, Guo Y-L, Zhan W-C, Guo Y and Wang Y-Q 2011 *J. Mol. Catal. A: Chem*. **337** 77
8. Herrmann U and Emig G 1998 *Ind. Eng. Chem. Res*. **37** 759
9. Lu W-J, Lu G-Z, Guo Y, Guo Y-L and Wang Y-S 2003 *Catal. Commun*. **4** 177
10. Wang Q, Cheng H-Y, Liu R-X, Hao J-M, Yu Y-C and Zhao F-Y 2009 *Catal. Today* **148** 368
11. Liu P, Liu Y and Yin Y 1999 *J. Mol. Catal. A: Chem*. **138** 129
12. Feng Y-H, Yin H-B, Wang A-L, Xie T and Jiang T-S 2012 *Appl. Catal. A: Gen*. **425–426** 205
13. Meyer C I, Marchi A J, Monzon A and Garetto T F 2009 *Appl. Catal. A: Gen*. **367** 122
14. Wilson O M, Knecht M R, Martinez J C G and Crooks R M 2006 *J. Am. Chem. Soc*. **128** 4510
15. Yoswathananont N, Nitta K, Nishiuchi Y and Sato M 2005 *Chem. Commun*. **1** 40
16. Numwong N, Luengnaruemitchai A, Chollacoop N and Yoshimura Y 2012 *Chem. Eng. J*. **210** 173
17. Toshima N, Hrarda M and Asakurat K 1992 *J. Phys. Chem*. **96** 9927
18. Harada M, Asakura K and Toshima N 1993 *J. Phys. Chem*. **97** 5103
19. Toshima N and Wang Y 1994 *Langmuir* **10** 4574
20. Lu P, Teranishi T, Asakura K, Miyake M and Toshima N 1999 *J. Phys. Chem. B* **103** 9673
21. Li S-Y, Liu G, Lian H-L, Jia M-J and Zhao G-M 2008 *Catal. Commun*. **9** 1045
22. An N-H, Yu Q-S, Liu G, Li S-Y, Jia M-J and Zhang W-X 2011 *J. Hazard. Mater*. **186** 1392
23. Wang Y, Ren W-J, Deng K, Gui L-L and Tang Y-Q 2000 *Chem. Mater*. **12** 1622
24. Teranishi T and Miyake M 1999 *Chem. Mater*. **11** 3414
25. Jung S M, Godard E, Jung S Y, Park K-C and Choi J U 2003 *J. Mol. Catal. A: Chem*. **198** 297
26. Usami Y, Kagawa K, Kawazoe M, Yasuyuki M, Sakurai H and Haruta M 1998 *Appl. Catal. A: Gen*. **171** 123
27. Hu T-J, Yin H-B, Zhang R-C, Wu H-X, Jiang T-S and Wada Y J 2007 *Catal. Commun*. **8** 193
28. Li K-T, Hsu M-H and Wang I 2008 *Catal. Commun*. **9** 2257
29. Wang R, Liao S and Ji S 2008 *J. Power Sources* **180** 205
30. Xu J, Sun K-P, Zhang L, Ren Y-L and Xu X-L 2006 *Catal. Lett*. **107** 5
31. Xu Y, Du L, Liao S-J, Li Y-X and Song H-Y 2012 *Catal. Commun*. **17** 29
32. Xu Y, Chen D, Liao S-J, Song H-Y and Li Y-W 2012 *J. Catal*. **291** 36
33. Li H-X, Li H, Zhang J, Dai W-L and Qiao M-H 2007 *J. Catal*. **246** 301