

Synthesis of Nickel Nanoparticles Supported on Boehmite for Selective Hydrogenation of *p*-Nitrophenol and *p*-Chloronitrobenzene

Hao Liu · Jia Deng · Wei Li

Received: 9 March 2010 / Accepted: 27 April 2010 / Published online: 14 May 2010
© Springer Science+Business Media, LLC 2010

Abstract Nickel nanoparticles supported on boehmite were prepared by a modified electroless nickel-plating method and a direct reduction method. We mainly studied the catalyst synthesized by the direct reduction method. The as-prepared nickel catalyst was characterized by X-ray diffraction and high-resolution transmission electron microscopy. The catalytic behavior in selective hydrogenation of *p*-nitrophenol to *p*-aminophenol and *p*-chloronitrobenzene to *p*-chloroaniline was studied and compared with Ni-B/ γ -Al₂O₃ catalyst prepared by incipient-wetness impregnation and Ni-B/Al₂O₃·xH₂O catalyst synthesized by a coprecipitation method. The Ni-B/boehmite catalysts were found to be more reactive than the Ni-B/ γ -Al₂O₃ and Ni-B/Al₂O₃·xH₂O catalysts. The superior activity of the Ni-B/boehmite catalyst was attributed to the small Ni-B particles and large amount of structural water, which enhanced the hydrophilicity of the catalyst.

Keywords Ni-B · Boehmite · *p*-Nitrophenol · *p*-Chloronitrobenzene · Hydrogenation

1 Introduction

Aromatic nitro-group compounds are important intermediates and fine chemicals in the chemistry of pharmaceuticals, dyes, drugs, pesticides and so on [1]. *p*-Aminophenol and *p*-chloroaniline are of great commercial importance [2–6]. The traditional synthesis routes are usually harmful

to the environment. Direct catalytic hydrogenation of aromatic nitro-group compounds could be the best choice for preparation of the corresponding aromatic amine compounds. Previously, many studies have reported that liquid phase hydrogenation is a simple way to improve the conversion and selectivity.

Selective hydrogenation of aromatic nitro-group compounds to the corresponding amino-group compounds over various metal catalysts, such as Pt, Pd, Ru, Ag and Ni [7–17], has been investigated extensively. Nickel-based catalysts have been of great interest, because of applications such as hydrogenation, hydrodechlorination, and hydrotreating reactions [18]. Amorphous Ni-B catalyst has a characteristic unique structure that is ordered at short range but disordered at long range [19]. This catalyst shows higher catalytic activity and selectivity than the corresponding crystalline counterparts. Aluminas are used extensively as catalyst supports in industrial hydrogenation. It is well known that the catalyst supports play an important role in the catalytic activity [20]. The catalytic performance of alumina-supported catalysts is largely dependent on the textural properties of the alumina supports [21]. Wang et al. [22] prepared colloidal RuB/Al₂O₃·xH₂O catalyst for liquid phase hydrogenation of benzene to cyclohexene. The superior selectivity of benzene hydrogenation was attributed to the high content of structure water and hydroxyl groups on RuB/Al₂O₃·xH₂O, which enhanced greatly the hydrophilicity of the catalyst. In this paper, a simple method was developed to prepare Ni-B catalyst using boehmite as a support in order to improve the hydrophilicity of the catalyst and consequently the selectivity to *p*-aminophenol (PAP) and *p*-chloroaniline (*p*-CAN). The catalytic performance of Ni-B in the hydrogenation of *p*-nitrophenol (PNP) and *p*-chloronitrobenzene (*p*-CNB) was examined and compared with that of Ni-B/ γ -Al₂O₃ prepared by impregnation and Ni-B/Al₂O₃·xH₂O synthesized by

H. Liu · J. Deng · W. Li (✉)
Key Laboratory of Advanced Energy Materials Chemistry,
Ministry of Education, College of Chemistry, Nankai University,
Tianjin 300071, China
e-mail: weili@nankai.edu.cn

coprecipitation. It has been found that the Ni–B/boehmite catalysts prepared by modified electroless nickel-plating and direct reduction methods are more reactive than the Ni–B/ γ -Al₂O₃ and Ni–B/Al₂O₃·*x*H₂O catalysts. The period of reaction was greatly shortened, and the conversion and selectivity were significantly improved. The Ni–B/boehmite catalyst synthesized by direct reduction was much simpler to prepare, and had similar activity to catalyst prepared by electroless nickel-plating. We tend to favor the direct reduction method and mainly studied the Ni–B/boehmite catalyst prepared by this method.

2 Experimental

2.1 Catalyst Preparation

Boehmite was prepared according to a published procedure [23]. The boehmite-supported NiB catalysts (NiB/boehmite¹) were prepared by the direct reduction method as follows. To a solution of nickel acetate containing 2 mmol Ni in 20 mL deionized water, a certain amount of boehmite dispersed in deionized water was added. The solids content of boehmite was 20 wt%. The weight percentage *x* of nickel in the catalyst was given by $x = \text{Ni}/(\text{Ni} + \text{support}) \times 100\%$. The resulting solution was stirred at 293 K and then reduced by addition of 1 mol/L potassium borohydride solution under a 40 mL/min Ar flow. The molar ratio of BH₄[−]:Ni²⁺ was 3:1. The reaction was allowed to continue until no bubbles were observed. The product was washed thoroughly with distilled water and anhydrous ethanol in series and then isolated by centrifugation. The NiB catalysts synthesized by electroless nickel-plating (NiB/boehmite²) were prepared according to procedures in the literature [24–26]. Ag/boehmite was synthesized as a reference compound [25, 26], and the loading of silver on the support was controlled at 0.20 wt%. The Ag/boehmite could be directly treated with Ni–B electroless plating solution without 4.0 h stirring, washing and drying. The theoretical nickel loading was controlled at 15 wt%.

The Ni–B/Al₂O₃·*x*H₂O was synthesized according to the following procedure. At 323 K, 29 mL of 3.0 M ammonia was added dropwise to 150 mL of a mixed aqueous solution of Al(NO₃)₃ (13.2 mmol) and Ni(CH₃COO)₂ (2 mmol). After addition, agitation was maintained for 0.5 h in order to complete hydrolysis. The precipitate was aged in the mother liquor overnight. The aged precipitate was then washed until neutral and injected into an autoclave for crystallization with 100 mL deionized water at 453 K for 2 h to obtain the catalyst precursor. The catalyst precursor was reduced using 10 mL of aqueous KBH₄ solution containing 0.1 g NaOH. The molar ratio of KBH₄:Ni was 3:1. The product was washed thoroughly

with distilled water and anhydrous ethanol in series and then isolated by centrifugation.

γ -Al₂O₃ was obtained by baking boehmite for 2 h at 393 K and calcining for 4 h at 823 K. The 15% Ni–B/ γ -Al₂O₃ catalyst was prepared by incipient impregnation–chemical reduction. The γ -Al₂O₃ support was impregnated with nickel acetate solution for 4 h and dried at 393 K and then reduced by adding potassium borohydride solution at a fixed speed of 2 mL/min under flowing Ar at 293 K. The molar ratio of KBH₄:Ni was 3:1. The resulting black precipitate was washed thoroughly with water and anhydrous ethanol in series and then isolated by centrifugation.

2.2 Catalyst Characterization

X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Focus diffractometer (Cu *K* α , $\lambda = 1.54178 \text{ \AA}$) at a scan rate of 4° min^{−1}. High-resolution TEM (HRTEM) images were acquired using a JEOL-2010 FEF high-resolution transmission electron microscope equipped with an EDX system (EDAX) and a Philips EM400ST transmission electron microscope. To prepare TEM specimens, a small amount of sample was dispersed in deionized water, and a carbon-coated grid was dipped into the suspension and allowed to dry at room temperature.

2.3 Catalyst Testing

The hydrogenation of *p*-nitrophenol was carried out in a 100 mL autoclave in which the as-prepared catalysts containing 2 mmol Ni, 8 g *p*-nitrophenol, 40 mL ethanol, and 20 mL distilled water were mixed. After replacing the air in the reactor with H₂, the reaction was performed at 373 K and hydrogen pressure of 1.5 MPa with stirring at 800 rpm.

The hydrogenation of *p*-chloronitrobenzene was performed at 373 K and 1.5 MPa of hydrogen pressure with stirring at 800 rpm for 3 h in a 100 mL stainless steel autoclave containing 0.5 g catalyst, 5.0 g *p*-chloronitrobenzene and 60 mL ethanol. The hydrogenation product was analyzed by high-performance liquid chromatography.

The hydrogen consumption during the hydrogenation reactions were supervised with a flowmeter and a flow summarizer. When the instantaneous flow of H₂ was realized, the reaction was timed. The reaction finished until the instantaneous flow of H₂ was zero.

3 Results and Discussion

3.1 Characterization

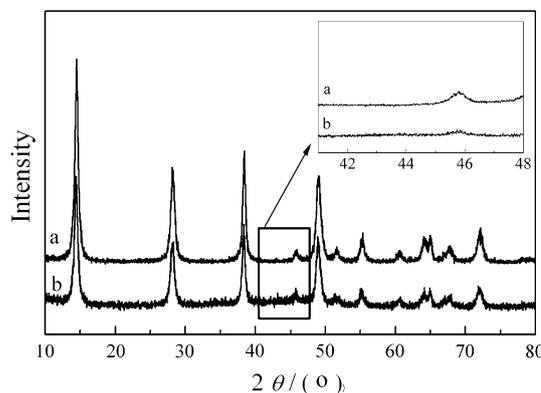
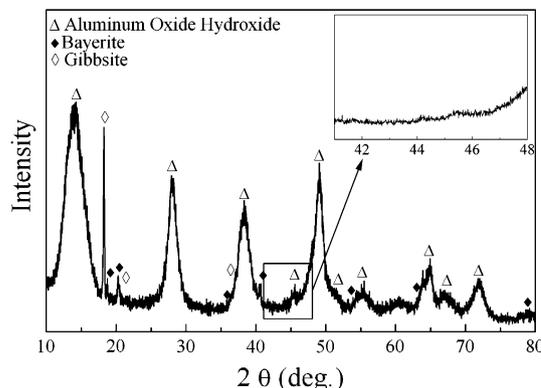
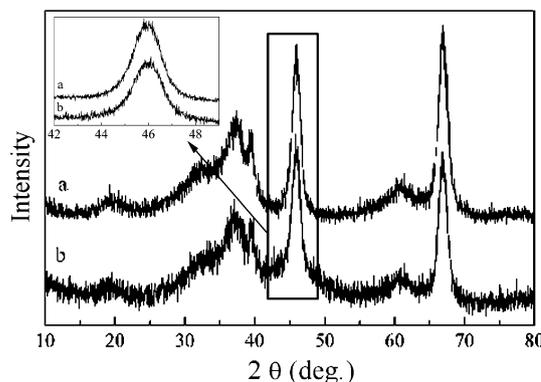
The results of *p*-nitrophenol and *p*-chloronitrobenzene catalytic hydrogenation are shown in Table 1. It can be

Table 1 Hydrogenation activity of *p*-nitrophenol and *p*-chloronitrobenzene over different catalysts

Catalysts	PNP hydrogenation			<i>p</i> -CNB hydrogenation		
	Reaction time (min)	Conversion of PNP (%)	Selectivity for PAP (%)	Reaction time (min)	Conversion of <i>p</i> -CNB (%)	Selectivity for <i>p</i> -CAB (%)
Ni-B/Al ₂ O ₃	85	96	99	90	82	70
Ni-B/boehmite ¹	40	99	99	50	88	96
Ni-B/boehmite ²	36	99	99	60	92	98
Ni-B/Al ₂ O ₃ ·xH ₂ O	45	99	99	63	89	94

seen that the selectivity to *p*-aminophenol was near 100% when Ni-B/boehmite, Ni-B/Al₂O₃·xH₂O and Ni-B/ γ -Al₂O₃ were used as catalysts. The Ni-B/boehmite catalyst exhibited better activity, with the conversion of *p*-nitrophenol and selectivity to *p*-aminophenol exceeding 99% within 40 min (Ni-B/boehmite¹) and 36 min (Ni-B/boehmite²). The duration of the reaction was greatly reduced compared with Ni-B/ γ -Al₂O₃ (85 min) and Ni-B/Al₂O₃·xH₂O catalyst (45 min) catalysts. Similar promoting effects were also observed when Ni-B/boehmite was used for *p*-CNB selective hydrogenation. Using Ni-B/ γ -Al₂O₃ as catalyst, the reaction finished within 90 min, with *p*-CNB conversion of 82% and selectivity to *p*-CAB of 70%. However, when using Ni-B/boehmite as catalyst, both the conversion of *p*-CNB and selectivity to *p*-CAB evidently increased from 82 to 88% and 70 to 96%, respectively. The conversion of *p*-CNB was 89% and selectivity to *p*-CAB was 94% over Ni-B/Al₂O₃·xH₂O after 63 min. Ni-B/boehmite¹ had a similar activity to Ni-B/boehmite², but the catalyst synthesized using the direct reduction method was much simpler. The Ni-B/boehmite¹ catalyst could also be used without posttreatment after reduction of nickel acetate with potassium borohydride. We tend to favor the former, and we mainly studied the Ni-B/boehmite¹ catalyst.

The XRD patterns of as-prepared Ni-B/boehmite¹ and boehmite are shown in Fig. 1. The diffraction pattern in Fig. 1a exhibits the features of boehmite (JCPDS #5-190), with diffraction peaks at 2θ values of 14.5°, 28.2°, 38.4°, 49.1°, 55.1°, 66.2°, 67.6°, and 72.0°. Normally, the Ni-B sample shows only one broad peak around $2\theta = 45^\circ$. There was hardly any difference in XRD patterns between boehmite and the Ni-B/boehmite¹ sample, except that the peak of Ni-B/boehmite¹ between 2θ of 44.0° and 48.0° was wider than that of boehmite. The XRD diffraction pattern of Ni-B/Al₂O₃·xH₂O was complicated (Fig. 2), with diffraction peaks mainly attributed to aluminum oxide hydroxide (AlO(OH), JCPDS #49-133), bayerite (Al₂O₃·3H₂O, JCPDS #3-156) and gibbsite (Al₂O₃·3H₂O, JCPDS #1-264). Figure 3 shows the XRD diffraction pattern of γ -Al₂O₃ (Fig. 3a), which was obtained by calcining boehmite, and 15% Ni-B/ γ -Al₂O₃ (Fig. 3b). It was found that the diffraction pattern of Ni-B/ γ -Al₂O₃ was very similar to that of γ -Al₂O₃, except for the broader diffraction peak between 2θ

**Fig. 1** XRD patterns of boehmite (a) and NiB/boehmite catalyst (b)**Fig. 2** XRD patterns of NiB/Al₂O₃·xH₂O**Fig. 3** XRD patterns of γ -Al₂O₃ (a) and NiB/ γ -Al₂O₃ (b)

of 44.0° and 48.0° , which indicates the amorphous nature of the Ni–B species. Figure 4 presents TEM micrographs of the boehmite and Ni–B/boehmite¹ samples. Compared with boehmite (Fig. 4a), the black spheres in Fig. 4b represent Ni–B clusters. we can observe the morphology of the Ni–B/boehmite, in which the Ni–B cluster is about 20 nm in diameter. Figure 4c shows high-resolution TEM (HRTEM) micrographs of the Ni–B cluster, revealing further details about the morphology of the catalyst. The black spots representing Ni–B nanoparticles are dispersed on the support. The diameters of the particles are around 2 nm in each cluster. The small size of the particles is favorable to enhancing the activity. The better activity of the Ni–B/boehmite catalyst can be attributed to the small Ni–B particles on the Ni–B/boehmite, based on the TEM results, exposing more active sites for hydrogenation.

It is well known that reaction conditions and catalyst supports play an important role in catalytic activity. During the reaction process, the effect of water, either in the solvent or in the structure of the catalysts, on the selective hydrogenation was investigated. Ning et al. [27] found that water was crucial for a high yield of *p*-chloroaniline. Adding appropriate water to the ethanol solvent could markedly improve both activity and selectivity to hydrogenation of *p*-chloronitrobenzene (*p*-CNB). The promoting effect of water was attributed to the existence of water adsorption on the catalyst, which would inhibit the strong adsorption of *p*-CAN (with $-\text{NH}_2$ and halogen groups) and also favor desorption of *p*-CAN because of hydrogen bonding between *p*-CAN and water in the solvent. Wang et al. [22] prepared colloidal RuB/Al₂O₃·*x*H₂O catalyst for liquid phase hydrogenation of benzene to cyclohexene. The RuB/Al₂O₃·*x*H₂O catalyst was prepared by a combined coprecipitation–crystallization reduction method. The superior selectivity in benzene hydrogenation was attributed to the high content of structural water and hydroxyl groups on RuB/Al₂O₃·*x*H₂O, which greatly enhanced the hydrophilicity of the catalyst. In the selective hydrogenation of PNP and *p*-CNB, water might perform a similar function. In our work, the Ni–B/boehmite catalyst had an activity similar to Ni–B/Al₂O₃·*x*H₂O. The superior activity of the Ni–B/boehmite catalyst relative to Ni–B/ γ -Al₂O₃ could be attributed to the presence of boehmite. Boehmite has many properties that γ -Al₂O₃ lacks. Boehmite is the precursor of the alumina, and its structure has been studied extensively [28]. Boehmites are oxide–hydroxides of aluminum with differing water content and crystallite size [29, 30]. γ -Al₂O₃ is obtained by calcination of boehmite above 750 K [29, 31]. The decomposition of boehmite involves elimination of water molecules by condensation of hydrogen atoms and hydroxyl groups. Boehmite is composed of

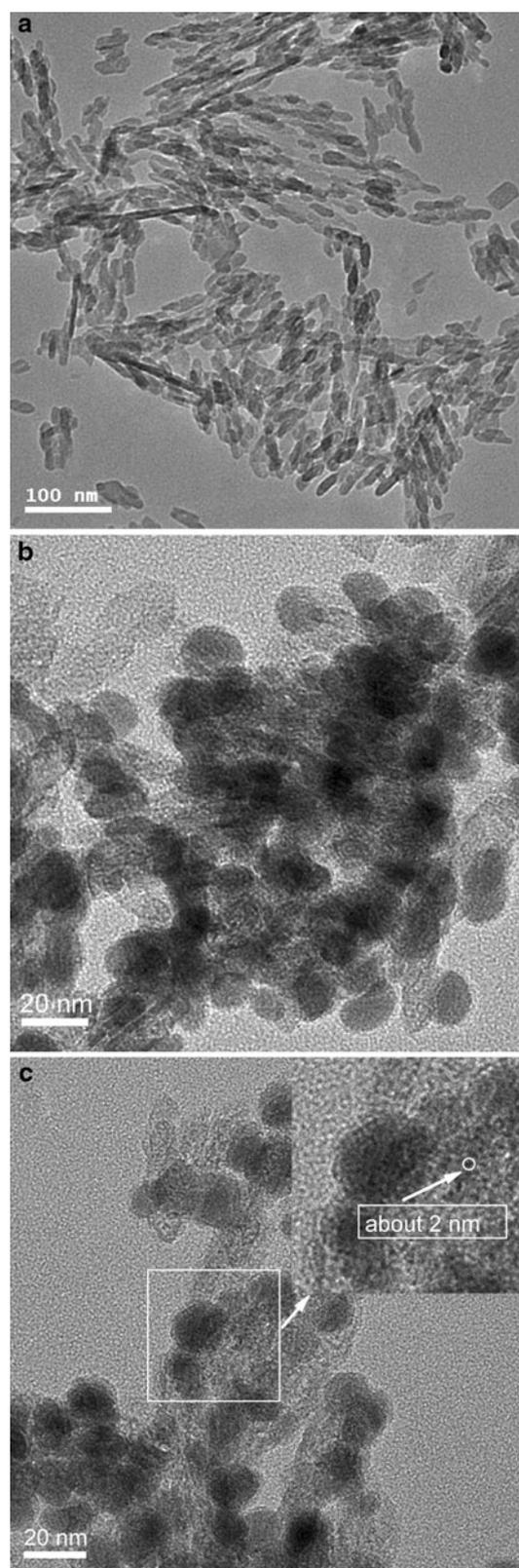


Fig. 4 TEM morphologies of boehmite (a), 15% NiB/boehmite (b), and HRTEM of 15% NiB/boehmite (c)

Table 2 Stability studies of 15% NiB/boehmite¹ catalyst

Catalyst	PNP hydrogenation			<i>p</i> -CNB hydrogenation		
	Reaction time (min)	Conversion of PNP (%)	Selectivity for PAP (%)	Reaction time (min)	Conversion of <i>p</i> -CNB (%)	Selectivity for <i>p</i> -CAB (%)
15% NiB/boehmite ¹						
First	40	99	99	50	88	96
Recycle 1	35	99	99	30	87	96
Recycle 2	50	98	99	60	81	92
Recycle 3	105	91	99	120	76	89

Al–O double layers connected by hydrogen bonds between the hydroxyl groups [32]. Fitzgerald et al. [33] proposed that in the temperature range 323–423 K, reversible elimination of physisorbed water takes place, followed between 423 and 773 K by irreversible dehydration caused by condensation of H-bonded basal OH groups. Above 773 K, additional dehydration and dehydroxylation occurs. The structural water and hydroxyl groups might effectively stabilize the water shell on the Ni–B/boehmite catalyst surface by hydrogen bonding. Compared with the Ni–B/ γ -Al₂O₃ catalyst, Ni–B/boehmite contained greater amounts of structural water and surface hydroxyl groups, which are expected to enhance the hydrophilicity of the catalyst. The hydrophilic surface of Ni–B/boehmite was more favorable for desorption of PAN and *p*-CAB because strong adsorption of PAN (–NH₂ group) and *p*-CAN (–NH₂ and halogen groups) was inhibited. As a result, the rate of hydrogenation evidently increased. The superior activity is attributed to the small Ni–B particles and greater content of structural water. The conversion of PNP was 91% and the conversion of *p*-CNB was 76% over the Ni–B/boehmite catalyst after recycling three times (Table 2). This suggests that the Ni–B/boehmite catalyst exhibited excellent catalytic activity and stability.

4 Conclusion

In this work, Ni–B/boehmite catalysts were prepared by a modified electroless nickel-plating method and a direct reduction method. We mainly studied the direct reduction method. A simple method for preparing a highly active Ni–B catalyst was provided. The Ni–B catalyst prepared by this method was characterized as ultrafine particles with amorphous structure. The as-prepared catalysts exhibited excellent catalytic activity in the selective hydrogenation reactions of *p*-nitrophenol to *p*-aminophenol and *p*-chloronitrobenzene to *p*-chloroaniline. The Ni–B/boehmite catalyst is much more reactive than the Ni–B/ γ -Al₂O₃ catalyst and has similar activity to the Ni–B/Al₂O₃·*x*H₂O catalyst. The superior activity of the Ni–B/boehmite

catalyst is attributed to the small Ni–B particles and greater content of structural water, which enhanced the hydrophilicity of the catalyst.

Acknowledgment The authors acknowledge financial support from the Research Fund for the Doctoral Program of Higher Education (20090031110015), and the Program for New Century Excellent Talents in University.

References

- Han XX, Chen Q, Zhou RX (2007) *J Mol Catal A Chem* 277:210
- Kratky V, Kralik M, Mearova M, Stolcova M, Zalibera L, Hronec M (2002) *Appl Catal A* 235:225
- Du Y, Chen HL, Chen RZ, Xu NP (2006) *J Chem Eng* 125:9
- Chen RZ, Du Y, Xing WH, Xu NP (2006) *Chin J Chem Eng* 14:665
- Du Y, Chen HL, Chen RZ, Xu NP (2004) *Appl Catal A Gen* 277:259
- Sunil PB, Sudhirprakash BS (2005) *Appl Catal A Gen* 293:162
- Komatsu T, Hirose T (2004) *Appl Catal A* 276:95
- Rode CV (2001) *Chem Eng Sci* 56:1299
- Ichikawa S, Tada M, Iwasawa Y, Ikariya T (2005) *Chem Commun* 924
- Han X, Zhou R, Lai G, Zheng X (2004) *Catal Today* 93–95:433
- Han X, Zhou R, Zheng X, Jiang H (2003) *J Mol Catal A Chem* 193:103
- Yu Z, Liao S, Xu Y, Yang B, Yu D (1995) *J Chem Soc Chem Commun* 1155
- Chen YY, Wang C, Liu HY, Qiu JS, Bao XH (2005) *Chem Commun* 42:5298
- Zhang J, Wang Y, Ji H, Wei Y, Wu N, Zuo B, Wang Q (2005) *J Catal* 229:114
- Wang C, Qiu JS, Liang CH, Li X, Yang XM (2008) *Catal Commun* 9:1749
- Liu YC, Huang CY, Chen YW (2006) *J Nanopart Res* 8:223
- Wang WJ, Shen JH, Chen YW (2006) *Ind Eng Chem Res* 45:8860
- Nishimura S (2001) *Handbook of heterogeneous catalytic hydrogenation for organic synthesis*. Wiley, New York
- Li H, Li HX, Dai WL, Wang W, Fang Z, Deng JF (1999) *Appl Surf Sci* 152:25
- Lu HH, Yin HB, Liu YM, Jiang TS, Yu LB (2008) *Catal Commun* 10:313
- Sataporn K, Okorn M, Piyasan P, Joongjai P (2008) *Catal Commun* 10:86
- Wang JQ, Guo PJ, Yan SR, Qiao MH, Li HX, Fan KN (2004) *J Mol Catal A Chem* 222:229

23. Li W, Zhang MH, Tao KY, Wang GL (2008) Chin Pat ZL200610014389.0
24. Wu ZJ, Zhang MH, Ge SH, Zhang ZL, Li W, Tao KY (2005) *J Mater Chem* 15:4928
25. Ge SH, Wu ZJ, Zhang MH, Li W, Tao KY (2006) *Ind Eng Chem Res* 45:2229
26. Wu ZJ, Ge SH, Zhang MH, Tao KY, Li W (2009) *J Colloid Interface Sci* 330:359
27. Ning JB, Xu J, Liu J, Miao H, Ma H, Chen C, Li XQ, Zhou LP, Yu WQ (2007) *Catal Commun* 8:1763
28. Armaroli T, Minoux D, Gautier S, Euzen P (2003) *Appl Catal A Gen* 251:241
29. Mishra D, Anand S, Panda RK, Das RP (2000) *Mater Lett* 42:38
30. Baker BR, Pearson RM (1974) *J Catal* 33:265
31. Lippens BC, Steggerda JJ (1970) In: Linsen BG (ed) *Physical and chemical aspects of adsorbents and catalysts*, Academic Press, London and New York, p. 171
32. Sergio B, Sandrine MT, Gardette JL, Giovanni C (2007) *Polym Degrad Stab* 92:1847
33. Fitzgerald JJ, Pedra G, Dec SF, Seger M, Maciel GE (1997) *J Am Chem Soc* 119:7832