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Research Note

A new approach to high performance Co/C catalysts for selective hydrogenation of chloronitrobenzenes

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Abstract

We report a facile solvothermal method for producing Co/C microspheres composed of nanosheet structures in a mixture of water and ethylene glycol. The morphology and cobalt loading of the Co/C microspheres can be controlled by adjusting the solvent composition. The Co/C microspheres obtained in the water–ethylene glycol mixture and calcined at 700 °C were very active for the hydrogenation of chloronitrobenzene (CNB), with 98% CNB conversion and 97% selectivity to *o*-chloroaniline at 2.0 MPa and 140 °C. In the hydrogenation of *p*-CNB and *m*-CNB, the catalyst showed a conversion of ⩾97% and a selectivity of 99% to the corresponding chloroanilines.

Keywords: Co/C microsphere; Solvothermal synthesis; Selective hydrogenation

1. Introduction

The selective hydrogenation of chloronitrobenzenes (CNB) to make the corresponding chloroanilines (CAN) is one of the most important reactions in the synthesis of various fine chemicals, such as dyes, urethanes, agro-chemicals, and pharmaceuticals [1]. For this type of hydrogenation reaction, numerous catalysts, such as palladium, platinum, rhodium, nickel, and copper-chromite catalysts, have been extensively studied [2–10]. It is not uncommon that the hydrogenation process is accompanied by hydrogenolysis of the carbon–halogen bond over these catalysts [11]. Therefore, it remains a challenge to overcome this problem, and many efforts have been made over the past decades, including introducing special additives (promoters and inhibitors) [12–14], modifying the support, and tuning the particle sizes of the catalysts [4,15,16]. Meanwhile, attempts also have been made to exploit cheaper catalysts to replace expensive noble metals [17].

Cobalt-based catalysts have been found to be highly active in Fischer–Tropsch synthesis and selective hydrogenation of α,β-unsaturated aldehydes [18–20]. Raja et al. reported that Co nanoparticles supported on silica displayed exceptionally high turnover frequencies and high selectivity for the hydrogenations of nitro-substituted aromatics such as nitrobenzene, 3-nitrophenol, and 3-nitro-*o*-cresol [21]. To the best of our knowledge, little work has been done on CNB hydrogenation over the cheap iron group metals. Here, we report for the first time that Co/C catalysts that perform very well in CNB hydrogenation can be prepared by a simultaneous co-reduction–precipitation of Co^{2+} under mild solvothermal conditions, followed by controlled calcination in flowing N_2. We found that the Co/C catalyst calcined at 700 °C is very active for CNB hydrogenation, exhibiting high CNB conversion and high selectivity to CAN.

2. Experimental

The precursor of the Co/C catalyst was prepared in a mixture of H_2O and ethylene glycol (EG) under solvothermal condition, with furfural as the carbon source and cobalt acetate tetrahydrate ($Co(AC)_2{\cdot}4H_2O$) as the cobalt source. First, 0.3 g of $Co(AC)_2{\cdot}4H_2O$ was introduced to 30 ml of a mixed H_2O and

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EG solution (v/v = 1:1). About 0.5 ml of furfural was added under stirring, resulting in a reddish-brown solution. The solution was then transferred into a 40-ml Teflon-lined stainless-steel autoclave that was sealed and heated at 180 °C for 15 h before being cooled to room temperature. The resulting solid material was collected from the autoclave, centrifuged, washed with deionized water and ethanol to remove the ions, and finally dried at 80 °C for 3 h in vacuum. The as-obtained sample was heated to 300–900 °C at a rate of 2 °C/min and kept at the final temperature for 3 h in flowing N_2. The samples obtained hydrothermally in water, and solvothermally in ethylene glycol were heated at 2 °C/min to 700 °C and kept at 700 °C for 3 h in flowing N_2. For comparison, a commercial activated carbon (Beijing Activated Carbon Co., Ltd.; BET surface area 1009 m^2/g)-supported Co (10 wt%) catalyst also was prepared by wet impregnation of cobalt acetate. The as-made samples are designated Co/C(W + EG), Co/C(W), Co/C(EG), and Co/AC.

Nitrogen adsorption and desorption isotherms were measured at −196 °C using a Micromeritics ASAP 2020 instrument. The cobalt loading was determined by an ICP apparatus (Optima 2000DV). X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX 2400 diffractometer equipped with a Cu$K\alpha$ X-ray source operating at 40 kV and 50 mA. The as-made Co/C catalysts were examined by scanning electron microscopy (SEM) using a KYKY-2800B device, and by transmission electron microscopy (TEM), using a Philips Tecnai G^2 20 device. H_2 chemisorption measurements were conducted at 40 °C in a Quantachrome Autosorb instrument.

CNB hydrogenation was carried out at 140 °C and 1.0–3.0 MPa hydrogen pressure in a 100-ml Parr autoclave. Typically, the autoclave was charged with 0.1 g of Co/C catalyst (about 0.17 mmol of cobalt), 3.2 mmol of *o*-CNB, and 50 ml of ethanol. Before the reaction, the autoclave was flushed 4 times with hydrogen. The hydrogenation products were analyzed by gas chromatography (GC) using an Agilent 6890N chromatograph equipped with a SE-54 capillary column and a flame ionization detector.

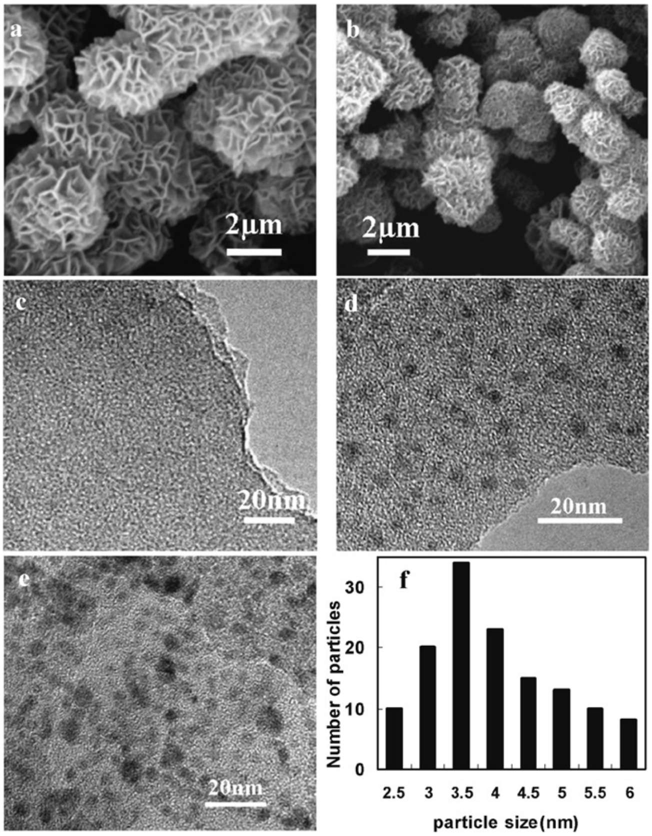

Fig. 1. SEM images of the precursor of the Co/C(W + EG) catalyst (a) and the Co/C(W + EG) catalyst calcined at 700 °C (b), TEM image of the uncalcined Co/C(W + EG) precursor (c), TEM images of the Co/C(W + EG) catalyst calcined at 600 °C (d), 700 °C (e), and the particle size distribution of the Co/C(W + EG) catalyst calcined at 700 °C (f).

Table 1
Effect of solvents on the properties of Co/C catalysts

Catalyst	Co loading (%)	BET (m^2/g)	Conv. (%)	Sel. (%)
Co/C(W)	6.1	339	49	99
Co/C(W + EG)	9.3	385	98	97
Co/C(EG)	11.7	309	91	99

Reaction conditions: 0.1 g catalyst, 0.5 g substrate, 50 ml ethanol, 140 °C, 2.0 MPa.

3. Results and discussion

Typical SEM images of the precursors of the Co/C catalysts made in the mixed H_2O and EG solvent are shown in Fig. 1a. The precursor consists of a sphere-shaped network structure with many flower-like flakes. The spheres range from 4 to 6 μm in diameter, and the flakes are about 40 nm thick. Fig. 1b shows the SEM image of the Co/C catalyst made in H_2O and EG after heat treatment at 700 °C for 3 h in N_2. The morphology of the precursor can be maintained during the subsequent calcination step, even though their diameters become small after heat treatment. The Co/C catalyst precursors created in H_2O are mainly hard, solid microspheres with few irregular fragments ranging in diameter from 2 to 4 μm. Some microspheres with peanut-like morphology also can be seen, likely due to the coalescence of two microspheres. The Co/C catalyst precursors created in the EG solvothermal process are composed mainly of nanospheres with diameters of several hundred nanometers. Obviously, the morphology of the Co/C catalyst precursors can be controlled by using different solvents. Table 1 summarizes the effect of the solvents on BET surface area, Co loading, and catalytic activity for the hydrogenation of *o*-CNB over the Co/C catalysts calcined at 700 °C for 3 h. The cobalt loadings of the Co/C catalysts increased in the order Co/C(W) < Co/C(W + EG) < Co/C(EG). The BET surface area of the Co/C(W) catalyst with a precursor created in H_2O is 339 m^2/g, that for the Co/C(W + EG) catalyst with the precursor created in H_2O and EG is 385 m^2/g, and that for the Co/C(EG) catalyst with the precursor created in EG is 309 m^2/g. The catalytic activity of the Co/C catalysts has been tested in the selective hydrogenation of *o*-CNB. The selectivity to *o*-CAN is >97% over the three catalysts, with *o*-CNB conversions of 49% over Co/C(W), 98% over Co/C(W + EG), and 91% over Co/C(EG). The low activity over Co/C(W) may be due to the low Co loading and its morphology. The Co/C(EG)

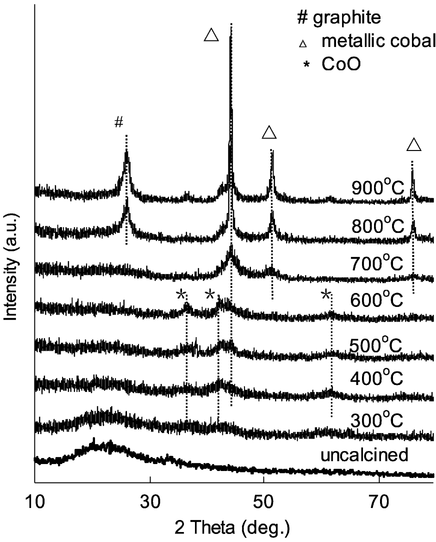

Fig. 2. XRD patterns of the Co/C(W + EG) precursor and Co/C(W + EG) catalysts calcined from 300 to 900 °C.

catalyst with high Co loading showed a reasonable conversion for *o*-CNB. Only the Co/C(W + EG) catalyst showed superior conversion and selectivity in the reaction. It would be of interest to understand the structural changes and the catalytic performance of Co/C(W + EG) catalysts created under different conditions in the preparation steps.

The calcination temperature is critical to the formation and growth of metal particles. Fig. 2 shows the XRD patterns of the Co/C(W + EG) precursor and the Co/C(W + EG) catalysts created at different temperatures. No diffraction peaks of cobalt compounds are detected in the precursor, indicating that the size of cobalt species is too small and below the detection limits of XRD. The cobalt species consist mainly of β-$Co(OH)_2$, with only a small amount of metallic cobalt obtained by furfural reduction. For Co/C(W + EG) catalysts heated below 600 °C, the XRD pattern displays very broad diffraction peaks corresponding to CoO and metallic cobalt. When the calcination temperature is above 600 °C, only peaks corresponding to metallic cobalt are present. These peaks become sharp with further increases in calcination temperature, while the peaks corresponding to CoO disappear. This means that the average size of the Co particles in the Co/C(W + EG) catalysts increases. The average size of the corresponding cobalt nanoparticles in the Co/C(W + EG) catalysts is calculated to be about 4 nm at a precursor calcination temperature of 700 °C, 20 nm at 800 °C, and 27 nm at 900 °C according to Scherrer's equation.

A typical TEM image of the precursor of the Co/C(W + EG) catalyst is shown in Fig. 1c. No cobalt species particles can be seen, probably because the metal species are small and/or embedded in the matrix. After the precursor is calcined at 300 °C, small nanoparticles (ca. 2 nm) aggregated in the carbon matrix can be seen uniformly dispersed in the carbon matrix. As the calcination temperature increases from 300 to 600 °C, the size of these nanoparticles increases gradually; however, they are still small even when the composite precursor is calcined at 600 °C (Fig. 1d). The TEM image of Co/C(W + EG) catalyst calcined at 700 °C shows spherical Co clusters dispersed homogeneously on the carbon matrix (Fig. 1e). The size distribution of these spherical Co clusters ranges from 2.5 to 6 nm (mean, 3.5 nm) (Fig. 1f). When the precursor is calcined at 800 °C, which results in some irregular onion-like holes in the flakes, the average size of the cobalt particles is 20–30 nm. The particle size increases further when the calcination temperature is increased to 900 °C, resulting in more onion-like holes in the flakes. The particle size from the TEM examination is consistent with that from the XRD measurements.

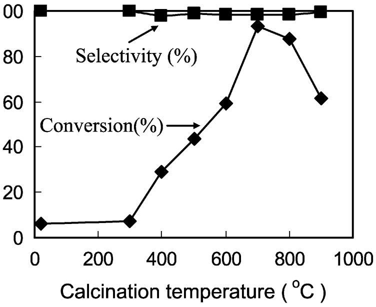

Fig. 3. Hydrogenation of *o*-CNB over Co/C(W + EG) catalysts calcined at different temperatures. Reaction conditions: *o*-CNB, 0.5 g; catalyst, 0.12 mmol Co; temperature 140 °C; time 3 h; pressure 3 MPa.

To determine how much cobalt can be accessed, the H_2 chemisorption on the microsphere-like Co/C catalyst calcined at 700 °C was measured. The H_2 chemisorption results show that the cobalt surface area is ca. 8.0 m^2/g, with a dispersion of ca. 13%. Based on the H_2 chemisorption results, the average particle size of the cobalt particles is calculated to be ca. 7.8 nm, slightly larger than that obtained from the XRD and TEM studies, indicating that most of the Co particles can be accessed.

The variable catalytic performance of Co/C(W + EG) catalysts created at different calcination temperatures is demonstrated by the *o*-CNB conversion and selectivity to *o*-CAN shown in Fig. 3. The activity of the Co/C catalysts calcined at 300–900 °C increases when the calcination temperature for the composite precursor is below 700 °C and passes through a maximum at a calcination temperature of 700 °C, then decreases with further increases in calcination temperature to 800 and 900 °C. The catalyst calcined at 700 °C shows the highest *o*-CNB conversion of 93% and a high selectivity to *o*-CAN (about 99%). The improved catalytic activity of the Co/C catalyst when the calcination temperature is below 700 °C is believed to be due mainly to the formation and improved dispersion of metallic cobalt particles, whereas the deteriorated catalytic performance of the Co/C catalysts at calcination temperatures above 700 °C is believed to be due to the aggregation of the cobalt particles as revealed by the TEM and XRD studies discussed above.

The effect of the reaction temperature and pressure on the CNB hydrogenation over the Co/C(W + EG) catalyst calcined at 700 °C also was addressed. The reactions were conducted at 140 °C for 3 h with 0.1 g of Co/C catalyst, 0.5 g of substrate (0.17 mmol of Co), and 50 ml of ethanol. At the initial reaction pressure of 1 MPa, the conversion of *o*-CNB was only 68% with about 99% selectivity to the *o*-CAN, with nitrobenzene and aniline as byproducts. When the reaction pressure was increased to 2.0 MPa, the *o*-CNB conversion increased dramatically to 98%, the selectivity to the *o*-CAN decreased slightly to 97%, with aniline the only byproduct. Further increasing the reaction pressure to 3.0 MPa, little changes in the *o*-CNB conversion and the selectivity to *o*-CAN were observed. When the reaction temperature was decreased from 140 to 120 °C, the conversion of *o*-CNB dropped to 69%, with a selectivity to *o*-chloroaniline of 94%. Meanwhile, nitrobenzene, a dechlorinated byproduct, was formed with a selectivity of 5.4%. The possible reason for this is that hydrogenation of the nitro group is more sensitive to temperature compared with hydrogenolysis of the C–Cl bond and is mostly accelerated at 140 °C, and thus the selectivity to *o*-chloroaniline is improved significantly [22]. When the reaction time was decreased to 1.5 h, only 77% conversion of *o*-CNB was obtained under similar conditions. The CNB hydrogenation over the Co/AC catalyst was conducted at 140 °C and 2 MPa for 3 h. The conversion of *o*-CNB was only 69%, lower than that over Co/C(W + EG) catalyst, whereas the selectivity of *o*-CAN over both catalysts remained at the same level.

Another advantage of the Co/C catalysts is that they can be easily separated and recovered magnetically after the hydrogenation reaction. The recycled Co/C(W + EG) catalyst exhibited a good *o*-CNB conversion of 94% and a high selectivity to *o*-CAN of 99% at the reaction pressure of 3 MPa. Compared with the fresh catalyst, no obvious loss in activity and selectivity for the recovered Co/C catalysts was observed, indicating that the Co/C catalyst is stable in the reaction and can be reused.

The catalytic performance of the Co/C(W + EG) catalyst for the hydrogenation of the *o*-CNB isomers (*m*-CNB and *p*-CNB) was also studied. The conversions of *m*-CNB and *p*-CNB reached 97% and 100%, respectively, and the selectivities to *m*-CAN and *p*-CAN were as high as 99%. Such a high selectivity to CAN is difficult to achieve when using a single noble metal without other transition metals [4]. The detailed catalytic mechanism involved in the *o*-CNB hydrogenation over the Co/C catalyst remains unclear. More detailed studies of the potential and unique catalytic properties of the novel microsphere-like Co/C catalysts are required, which will be demonstrated for other hydrogenation reactions in the future.

4. Conclusions

Highly dispersed Co/C catalysts with superior catalytic performance for the hydrogenation of chloronitrobenzenes were successfully prepared by a combined two-step process involving a simultaneous co-reduction–precipitation of Co^{2+} under furfural solvothermal conditions and controlled calcination in flowing N_2. The morphology, BET surface area, and cobalt loading of the catalysts can be controlled by using different solvents. Co particles of mean size 3.5 nm were homogeneously dispersed on the carbon matrix after the Co/C composite precursors were calcined at 700 °C. The Co/C catalyst showed high activity and high selectivity in the CNB hydrogenation reactions and could be used as magnetic separable catalyst. The novel Co/C catalysts are also of potential use in the hydrogenation of chloronitrobenzenes.

Acknowledgments

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References

[1] V. Kratky, M. Kralik, M. Mecarova, M. Stolcova, L. Zalibera, M. Hronec, Appl. Catal. A 235 (1–2) (2002) 225.
[2] B. Coq, A. Tajani, F. Figuéras, J. Mol. Catal. A Chem. 68 (1991) 331.
[3] S. Ichikawa, M. Tada, Y. Iwasawa, T. Ikariya, Chem. Commun. (2005) 924.
[4] X.X. Han, R.X. Zhou, G.H. Lai, X.M. Zheng, Catal. Today 93–95 (2004) 433.
[5] X.X. Han, R.X. Zhou, X.M. Zheng, H. Jiang, J. Mol. Catal. A Chem. 193 (2003) 103.
[6] B. Coq, A. Tijani, R. Dutartre, F. Figuéras, J. Mol. Catal. A Chem. 79 (1993) 253.
[7] X. Yang, H. Liu, Appl. Catal. A 164 (1997) 197.
[8] Z. Yu, S. Liao, Y. Xu, B. Yang, D. Yu, J. Chem. Soc. Chem. Commun. (1995) 1155.
[9] B.J. Zuo, Y. Wang, Q.L. Wang, J.L. Zhang, N.Z. Wu, L.D. Peng, L.L. Gui, X.D. Wang, R.M. Wang, D.P. Yu, J. Catal. 222 (2004) 493.
[10] J.L. Zhang, Y. Wang, H. Ji, Y.G. Wei, N.Z. Wu, B.J. Zuo, Q.L. Wang, J. Catal. 229 (2005) 114.
[11] A. Tijani, B. Coq, F. Figuéras, Appl. Catal. 76 (1991) 255.
[12] H. Greenfield, F.S. Dovell, J. Org. Chem. 32 (1967) 3670.
[13] G.C. Bond, D.E. Webster, N.Y. Ann, Acad. Sci. 158 (1969) 540.
[14] J.R. Kosak, N.Y. Ann, Acad. Sci. 172 (1970) 175.
[15] B. Coq, A. Tijani, F. Figuéras, J. Mol. Catal. 71 (1992) 317.
[16] B. Coq, A. Tijani, R. Dutartre, F. Figuéras, J. Mol. Catal. 79 (1993) 253.
[17] Y.C. Liu, Y.W. Chen, Ind. Eng. Chem. Res. 45 (2006) 2973.
[18] C. Ando, H. Kurokawa, H. Miura, Appl. Catal. A Gen. 185 (1999) L181.
[19] Y. Nitta, K. Ueno, T. Imanaka, Appl. Catal. 56 (1989) 9.
[20] Y. Nitta, Y. Hiramatsu, T. Imanaka, J. Catal. 126 (1990) 235.
[21] R. Raja, V.B. Golovko, J.M. Thomas, A. Berenguer-Murcia, W.Z. Zhou, S.H. Xie, B.F.G. Johnson, Chem. Commun. 15 (2005) 2026.
[22] Y.Y. Chen, C. Wang, H.Y. Liu, J.S. Qiu, X.H. Bao, Chem. Commun. (2005) 5298.