高活性三维花型 Co-Ni/C 双金属催化剂用于邻氯硝基苯选择性加氢反应

解雅玲, 肖 南, 凌 铮, 柳 月, 于 畅, 邱介山*

大连理工大学辽宁省能源材料化工重点实验室, 大连理工大学精细化工国家重点实验室, 辽宁大连 116024

摘要: 采用简单的水热/溶剂热法, 经后续在氮气气氛中的热处理合成了三维花型 Co-Ni/C 双金属催化剂, 它由交织炭片构成, 金属纳米颗粒高度分散其中。随着 Co/Ni 摩尔比的增加, 金属颗粒的粒径逐渐从 26 nm 减至 4 nm 左右。将该催化剂用于邻氯硝基苯选择性加氢制备邻氯苯胺反应, 其催化活性最高为单金属催化活性的 2 倍。这是由于 Co 和 Ni 物种之间存在协同效应。氢气程序升温脱附结果显示, Co/Ni 合金的生成使得 Co₅₀Ni₅₀/C 催化剂产生了新的催化活性位, 因而其活性显著提高。

关键词: 钴; 镍; 纳米碳材料; 双金属催化剂; 协同效应; 邻氯硝基苯; 加氢反应

中图分类号: O643

文献标识码: A

收稿日期: 2012-07-20. 接受日期: 2012-08-16.

*通讯联系人. 电话: (0411)84986024; 传真: (0411)84986080; 电子信箱: jqiu@dlut.edu.cn

基金来源: 国家自然科学基金 (20836002); 大连市科技局 (2011A15GX023).

本文的英文电子版(国际版)由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

Flower-Like Co-Ni/C Bimetallic Catalysts for the Selective Hydrogenation of *o*-Chloronitrobenzene

XIE Yaling, XIAO Nan, LING Zheng, LIU Yue, YU Chang, QIU Jieshan*

Carbon Research Laboratory, Liaoning Key Lab for Energy Materials and Chemical Engineering, State Key Lab of Fine Chemicals, Dalian University of Technology, Dalian 116024, Liaoning, China

Abstract: Three dimensional flower-like Co-Ni/C bimetallic catalysts composed of interlaced carbon flakes with highly dispersed metal nanoparticles were synthesized by a facile hydrothermal/solvothermal process followed by a heat treatment in flowing N₂. The sizes of the metal nanoparticles were from 26 to 4 nm, which became smaller as the Co/Ni molar ratio increased. The catalytic activities for the selective hydrogenation of *o*-chloronitrobenzene to *o*-chloroaniline were tested. The conversion of *o*-chloronitrobenzene over the bimetallic Co-Ni/C catalysts was increased by up to 200% compared with that over a mono-metallic Co/C catalyst, which was due to a synergistic interaction between the Co and Ni species. Hydrogen temperature-programmed desorption results showed that new active sites were formed in the Co₅₀Ni₅₀/C catalyst due to the formation of a Co-Ni alloy, which gave the improved activity of the Co₅₀Ni₅₀/C catalyst.

Key words: cobalt; nickel; carbon nanomaterials; bimetallic catalyst; synergistic effect; *o*-chloronitrobenzene; hydrogenation

Received 20 July 2012. Accepted 16 August 2012.

*Corresponding author. Tel: +86-411-84986024; Fax: +86-411-84986080; E-mail: jqiu@dlut.edu.cn

This work was supported by the National Natural Science Foundation of China (20836002) and Dalian Bureau of Science and Technology (2011A15GX023).

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

The design and synthesis of functional bimetallic alloys are of great interest because their structures and properties can be tuned by adjusting the elemental clusters [1,2]. Bimetallic alloys have been widely tested as catalysts in reactions such as selective hydrogenation [3], oxygen reduction

reaction (ORR) [4], alcohol oxidation [5], and ammonia oxidation [6] with exciting and promising results, and strategies have been introduced for fabricating bimetallic alloys with tuned structures and properties. A bimetallic alloy can have its properties tuned via two effects, namely,

the electronic or ligand effect [7] and the geometric or ensemble effect [8]. The electronic effect results from the formation of heteroatom bonds that change the electronic environment of the metal surface. The geometric effect results from incorporating atoms with different activities on a bimetallic surface that not only gives strain effects but also reduces the number of available multiple adsorption sites. As such, the chemisorption and reaction properties of bimetallic catalysts can be effectively modified [2,9,10]. In most cases, this is due to combined ensemble and electronic effects [11].

Carbon materials have been widely used as supports for making highly active bimetallic catalysts [12–15]. Some work on carbon-supported Co-Ni bimetallic catalysts with much more remarkable catalytic activities than monometallic Co or Ni catalysts have been reported [16–20]. The catalytic activities of the Co-Ni bimetallic catalysts are closely related to their structure and chemical compositions, and these can be controlled to some degree by changing the parameters in the preparation process [21]. It is noteworthy that nanomaterials with 3D flower-like structures have better catalytic, electrochemical, and magnetic properties, which is due to the highly anisotropic shape of the plate-like subunits and open structures [22–25].

Our previous work has shown that flower-like Co/C nanocatalysts exhibited excellent catalytic properties for the selective hydrogenation of *o*-chloronitrobenzene (*o*-CNB) to *o*-chloroaniline (*o*-CAN), which was due to the unique structures and high dispersion of Co nanoparticles [25]. Here, we report the one-pot synthesis of 3D flower-like Co-Ni/C bimetallic catalysts in an improved hydrothermal/solvothermal process. The Co-Ni/C bimetallic catalysts showed high activities for the hydrogenation of *o*-CNB to *o*-CAN, which was due to a synergistic effect between the Co and Ni species in the alloys and the high dispersion of the Co-Ni alloys on the carbon substrate.

1 Experimental

1.1 Catalyst preparation

The precursors of the Co-Ni/C catalysts with different Co/Ni molar ratios were prepared by an improved hydrothermal/solvothermal method [25]. For a typical run, 64 ml of a mixture of deionized water and ethylene glycol ($v/v = 1:1$) was mixed with $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with a total metal amount of 2.4 mmol. Furfural (1 ml) was also added. The mixture was stirred for 30 min at room temperature (r.t.) before it was transferred into a 100 ml Teflon-lined stainless steel autoclave. The autoclave was sealed and kept in an oven at 453 K for 15 h, and then cooled down to r.t. naturally. The solid product

was collected and washed with deionized water and absolute alcohol several times to remove inorganic ions and other impurities, and then dried at 353 K for 3 h. The samples were heated in a quartz tube to 973 K at a rate of 2 K/min and held at 973 K for 3 h in flowing N_2 to yield the final Co-Ni/C catalysts.

1.2 Catalyst characterization

X-ray diffraction (XRD) patterns of the Co-Ni/C catalysts were recorded using a Rigaku D/MAX 2400 diffractometer ($\text{Cu } K_\alpha$ X-ray source operated at 40 kV and 50 mA). N_2 adsorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 instrument. The morphology of the Co-Ni/C catalysts was characterized by scanning electron microscope (SEM, KYKY-2800B) and transmission electron microscopy (TEM, Philips Tecnai G2 20). H_2 temperature-programmed desorption (H_2 -TPD) measurements were conducted on a Quantachrome Autosorb instrument. Prior to the measurement, 50 mg of the catalyst was treated at 753 K in a flowing mixture of H_2/Ar (10:90 v/v) for 30 min. This was then cooled to 323 K before switching to a pure Ar flow of 25 ml/min. The temperature was increased at a rate of 10 K/min to 973 K. The desorbed H_2 was measured by a thermal conductivity detector.

1.3 Hydrogenation of *o*-CNB

Selective hydrogenation of *o*-CNB was conducted at 413 K and 2.0 MPa H_2 pressure in a 100 ml Parr autoclave. The catalysts were used without any pretreatment. Typically, the autoclave was charged with 0.05 g of Co-Ni/C catalyst, 1.00 g (about 6.3 mmol) of *o*-CNB, and 50 ml of absolute alcohol. Before the reaction, the autoclave was flushed four times with H_2 . The hydrogenation products were then analyzed by gas chromatography (GC, Agilent 6890N, SE-54 capillary column, flame ionization detector).

2 Results and discussion

2.1 Structure and morphology of the Co-Ni/C catalysts

The N_2 adsorption isotherms of the Co-Ni/C bimetallic catalysts with different Co/Ni molar ratios are shown in Fig. 1. These were typical type IV curves, indicating a mesoporous structure. The Co-Ni/C catalysts have specific surface areas in the range of 329–408 m^2/g with average pore sizes of 10.6–30.7 nm. These data are summarized in Table 1.

Figure 2 shows the XRD patterns of the Co-Ni/C catalysts with different metal compositions. As the Co loading increased, the intensity of the diffraction peaks became weaker, implying that the metal particles became smaller.

Fig. 1. N_2 adsorption isotherms of the Co-Ni/C catalysts with different Co/Ni molar ratios. For clarity, the isotherms of $Co_{33}Ni_{67}/C$, $Co_{50}Ni_{50}/C$, $Co_{67}Ni_{33}/C$, and Co_{100}/C are vertically offset by 120, 240, 360, and 480 $cm^3(STP)/g$, respectively.

Table 1 Textural parameters of the Co-Ni/C catalysts with different Co/Ni molar ratios

Sample	$A_{BET}/(m^2/g)$	Pore diameter (nm)	Average metal particle size (nm)
Ni_{100}/C	397	10.6	22
$Co_{33}Ni_{67}/C$	330	18.5	18
$Co_{50}Ni_{50}/C$	392	18.7	9
$Co_{67}Ni_{33}/C$	408	30.7	7
Co_{100}/C	329	11.0	5

The particle size decreased from 22 to 5 nm according to the Scherrer equation. The diffraction peak positions of the (111) crystallographic plane of $Co_{33}Ni_{67}/C$, $Co_{50}Ni_{50}/C$, and $Co_{67}Ni_{33}/C$ were 44.47° , 44.44° , 44.32° , respectively, which were between those of Ni_{100}/C (44.50°) and Co_{100}/C (44.23°), and these were shifted towards smaller angles with increased Co content. This was consistent with the results of Takanabe et al. [16]. This change was probably due to the incorporation of Co atoms into the Ni crystal lattice and the partial substitution of Ni atoms to form a Co-Ni alloy during the co-reduction-precipitation of Co^{2+} and Ni^{2+} in the hydrothermal/solvothermal process [20,27]. This would result in the different lattice spacings of the crystal face, and which can be attributed to a geometric effect between the Co and Ni species in the Co-Ni/C bimetallic catalyst.

Typical SEM images of the Co-Ni/C catalysts are shown in Fig. 3. These showed that the Co-Ni/C catalysts with different Co/Ni molar ratios were all flower-like microspheres consisting of interlaced nanoflakes. The voids between the nanoflakes in the net-like structure were about tens of nanometers.

TEM images of the Co-Ni/C catalysts are shown in Fig.

Fig. 2. XRD patterns of the Co-Ni/C catalysts with different Co/Ni molar ratios (a) and zoom of the diffraction peak of the (111) crystallographic plane (b). (1) Ni_{100}/C ; (2) $Co_{33}Ni_{67}/C$; (3) $Co_{50}Ni_{50}/C$; (4) $Co_{67}Ni_{33}/C$; (5) Co_{100}/C .

4. These showed clearly that the metal nanoparticles were highly dispersed in the carbon flakes of the flower-like microspheres. The average metal particle size of the Ni_{100}/C , $Co_{33}Ni_{67}/C$, $Co_{50}Ni_{50}/C$, $Co_{67}Ni_{33}/C$, and Co_{100}/C catalysts measured from the TEM images were 26, 12, 6, 4, and 5 nm, respectively, which is in agreement with the XRD results. The metal nanoparticles became slightly smaller with increasing Co contents in the Co-Ni/C catalysts. This was likely due to an interaction between the Co and Ni species in the formation and growth of the Co-Ni alloys.

2.2 Catalytic activity of the Co-Ni/C catalysts

The catalytic activities of the Co-Ni/C catalysts for the selective hydrogenation of *o*-CNB are shown in Table 2. With the increase of Co content, the conversion of *o*-CNB had a maximum of 99.8% at a Co/Ni molar ratio of 50:50. At this composition, the *o*-CAN selectivity was 98.0%, which was the highest among the five catalysts. The conversion of *o*-CNB over the $Co_{33}Ni_{67}/C$ catalyst was 89.0%, which was a little higher than the 85.0% conversion over the

Fig. 3. SEM images of Co-Ni/C catalysts with different Co/Ni molar ratios. (a) Ni₁₀₀/C; (b) Co₃₃Ni₆₇/C; (c) Co₅₀Ni₅₀/C; (d) Co₆₇Ni₃₃/C; (e) Co₁₀₀/C.

Fig. 4. TEM images of the Co-Ni/C catalysts with different Co/Ni molar ratios. (a) Ni₁₀₀/C; (b) Co₃₃Ni₆₇/C; (c,d) Co₅₀Ni₅₀/C; (e) Co₆₇Ni₃₃/C; (f) Co₁₀₀/C.

Co₆₇Ni₃₃/C catalyst. The *o*-CAN selectivity was 97.0% for the Co₃₃Ni₆₇/C catalyst, and 95.0% for the Co₆₇Ni₃₃/C catalyst. For the mono-metallic catalysts, however, the conversion of *o*-CNB over Ni/C was only 64.0% with a corresponding *o*-CAN selectivity of 96.0%, and the conversion of *o*-CNB over the Co/C catalysts was only 47.0% with a *o*-CAN selectivity of 94.0%.

The differences in catalytic activities shown in Table 2 can be attributed to an interaction between the Co and Ni species of the Co-Ni alloys with different Co/Ni molar ratios. In order to examine the contributions of the interaction

Table 2 *o*-CNB conversion and *o*-CAN selectivity over Co-Ni/C catalysts with different Co/Ni molar ratios and Co-Ni/C-M

Sample	<i>o</i> -CNB conversion (%)	<i>o</i> -CAN selectivity (%)
Ni ₁₀₀ /C	64.0	96.0
Co ₃₃ Ni ₆₇ /C	89.0	97.0
Co ₅₀ Ni ₅₀ /C	99.8	98.0
Co ₆₇ Ni ₃₃ /C	85.0	95.0
Co ₁₀₀ /C	47.0	94.0
Co-Ni/C-M	48.0	98.0

Reaction conditions: 1.00 g of *o*-CNB, 0.05 g of catalyst, 413 K, 2.0 MPa, 2 h.

between the Co and Ni species, equal amounts of Co/C and Ni/C catalysts were mixed mechanically, which was denoted as Co-Ni/C-M. This was tested for *o*-CNB hydrogenation under identical conditions. Over the Co-Ni/C-M catalyst, the conversion of *o*-CNB was only 48.0%, which was much lower than that of the Co₅₀Ni₅₀/C alloy catalyst. This further demonstrated a synergistic interaction between the Co and Ni species in the Co-Ni/C alloy catalyst that resulted in new active sites with improved hydrogenation activity.

To further understand the origin of the active sites and the improved catalytic activity of the bimetallic catalysts, the Co-Ni/C alloyed catalysts were characterized by H₂-TPD. As shown in Fig. 5, all of the TPD profiles showed a low temperature peak at 350 K that can be attributed to the de-

sorption of H₂ molecules on the surface of the Co-Ni/C catalysts. The peaks at 700 and 850 K were due to the desorption of dissociated H atoms that were strongly chemisorbed on the catalyst surface [23]. Interestingly, for the Co₅₀Ni₅₀/C catalyst, one new H₂ desorption peak at 486 K appeared in addition to the three peaks above, as can be seen in Fig. 5(c). This was evidenced that new active sites were formed on the Co₅₀Ni₅₀/C catalyst, and that this resulted in the extra H₂ adsorption and led to the enhanced catalytic activity of the Co₅₀Ni₅₀/C catalyst. The new active sites could be created by the formation of a Co-Ni alloy with an electron density different from that of the Co and Ni single metals [28], which was the main factor for the improved performance of the Co₅₀Ni₅₀/C catalyst in the selective hydrogenation of *o*-CNB.

Fig. 5. H₂-TPD profiles of Co-Ni/C catalysts with different Co/Ni molar ratios. (a) Ni₁₀₀/C; (b) Co₃₃Ni₆₇/C; (c) Co₅₀Ni₅₀/C; (d) Co₆₇Ni₃₃/C; (e) Co₁₀₀/C; (f) Co-Ni/C-M.

3 Conclusions

Three-dimensional flower-like Co-Ni/C bimetallic catalysts with tuned Co/Ni molar ratios were prepared using an improved hydrothermal/solvothermal process followed by a heat treatment. The Co-Ni/C bimetallic catalysts obtained were flower-like microspheres composed of interlaced nanoflakes. In comparison with the Co/C or Ni/C mono-metallic catalyst or their mechanical mixture, the bimetallic Co-Ni/C catalysts showed much higher *o*-CNB conversion and better *o*-CAN selectivity. This was attributed

to the formation of Co/Ni alloys in addition to the tuned size and high dispersion of the alloy metal particles in the carbon matrix and the unique 3D structure. This work demonstrated that the hydrothermal/solvothermal method provides an alternative, simple yet efficient technique to produce Co-Ni/C bimetallic nanocatalysts with enhanced catalytic performances.

References

- 1 Ferrando R, Jellinek J, Johuston R L. *Chem Rev*, 2008, **108**:

- 845
- 2 Zafeiratos S, Piccinin S, Teschner D. *Catal Sci Technol*, 2012, **2**: 1787
- 3 Sun K Q, Hong Y C, Zhang G R, Xu B Q. *ACS Catal*, 2011, **1**: 1336
- 4 Lim B, Jiang M J, Camargo P H C, Cho E C, Tao J, Lu X M, Zhu Y M, Xia Y N. *Science*, 2009, **324**: 1302
- 5 Francis S A, Bergens S H. *J Power Sources*, 2011, **196**: 7470
- 6 Yao K, Cheng Y F. *J Power Sources*, 2007, **173**: 96
- 7 Burc R. *Acc Chem Res*, 1982, **15**: 24
- 8 Maroun F, Ozanam F, Magnussen O M, Behm R J. *Science*, 2001, **293**: 1811
- 9 Li H S, Xu H, Wang J F. *J Nat Gas Chem*, 2011, **20**: 1
- 10 Xiang M L, Wu D D, Zou J, Li D B, Sun Y H, She X C. *J Nat Gas Chem*, 2011, **20**: 520
- 11 孙海杰, 郭伟, 周小莉, 陈志浩, 刘仲毅, 刘寿长. 催化学报 (Sun H J, Guo W, Zhou X L, Chen Zh H, Liu Zh Y, Liu Sh Ch. *Chin J Catal*), 2011, **32**: 1
- 12 Yang B, Lu Q Y, Wang Y, Zhuang L, Lu J T, Liu P F, Wang J B, Wang R H. *Chem Mater*, 2003, **15**: 3552
- 13 Nashner M S, Frenkel A I, Adler D L, Shapley J R, Nuzzo R G. *J Am Chem Soc*, 1997, **119**: 7760
- 14 He C N, Zhao N Q. *J Mater Chem*, 2012, **22**: 1297
- 15 李海涛, 陈昊然, 张因, 高春光, 赵永祥. 催化学报 (Li H T, Chen H R, Zhang Y, Gao Ch G, Zhao Y X. *Chin J Catal*), 2011, **32**: 111
- 16 Takanabe K, Nagaoka K, Nariai K, Aika K. *J Catal*, 2005, **232**: 268
- 17 严新焕, 孙军庆, 徐颖华, 杨建峰. 催化学报 (Yan X H, Sun J Q, Xu Y H, Yang J F. *Chin J Catal*, 2006, **27**: 119
- 18 Hossain M M, Sedor K E, de Lasa H I. *Chem Eng Sci*, 2007, **62**: 5464
- 19 Ishihara T, Eguchi K, Arai H. *Appl Catal*, 1987, **30**: 225
- 20 Ishihara T, Horiuchi N, Inoue T, Eguchi K, Takita Y, Arai H. *J Catal*, 1992, **136**: 232
- 21 Li P, Liu J, Nag N, Crozier P A. *J Catal*, 2009, **262**: 73
- 22 Xu L P, Ding Y S, Chen C H, Zhao L L, Rimkus C, Joesten R, Suib S L. *Chem Mater*, 2008, **20**: 308
- 23 Guan J G, Liu L J, Xu L L, Sun Z G, Zhang Y. *Cryst Eng Comm*, 2011, **13**: 2636
- 24 Ren Y, Gao L. *J Am Ceram Soc*, 2010, **93**: 3560
- 25 Xing L, Qiu J S, Liang C H, Wang C, Mao L. *J Catal*, 2007, **250**: 369
- 26 Abdelsayed V, Aljarash A, El-Shall M S, Al Othman Z A, Alghamdi A H. *Chem Mater*, 2009, **21**: 2825
- 27 周敏, 林国栋, 张鸿斌. 催化学报 (Zhou M, Lin G D, Zhang H B. *Chin J Catal*), 2007, **28**: 210
- 28 Zhang J G, Wang H, Dalai A K. *J Catal*, 2007, **249**: 300