Journal of New Materials for Electrochemical Systems 18, 231-235 (2015)

Preparation of an Active Ni_2B/SBA-15 Catalyst to Improve $NaBH_4$ Hydrolysis for Hydrogen Generation

Fei Wu[1,2], Ting Li[1], Jindan Chen[1], Xiu Ru Yang[1], Cheng Ming Li[1] , Mei Qiang Fan[*,1] and Kang Ying Shu[†,1]

[1]Department of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, P R China
[2]Zhejiang Tianneng Energy Technology Co., Ltd., Changxing County, Zhejiang Province 313100, China

Received: September 27, 2015, Accepted: November 20, 2015, Available online: December 05, 2015

Abstract: *Ni_2B nanoparticle distributed on ordered SBA-15 mesoporous silica was prepared in situ and its catalytic activity for $NaBH_4$ hydrolysis was investigated in the presented paper. The problem of Ni_2B aggregation is resolved and the catalytic activity of Ni_2B is also improved due to the effect of SBA-15. The catalytic activity increases with Ni_2B/SBA-15 weight ratio increased from 1:4 to 2:1 and the catalyst with Ni_2B/SBA-15 weight ratio of 2:1 has high catalytic activity close to that of Ni_2B. The sintered experiment shows that the catalytic activity comes from amorphous Ni_2B, not crystalline Ni_2B. High sintering temperature leads to the conversion from amorphous Ni_2B to crystalline Ni_2B and damages the nanostructure of amorphous Ni_2B framework.*

Keywords: Hydrogen generation; Ni_2B nanoparticles; ordered SBA-15 mesoporous silica

1. INTRODUCTION

Sodium boron hydride ($NaBH_4$) is a good hydrogen source for fuel cell as it has high hydrogen capacity (10.8 wt%), safety, pure hydrogen generation and mild hydrolysis temperature[1]. $NaBH_4$ is stable in dry air or alkaline solution. Its hydrolysis rate can be controlled via the addition of suitable catalysts, that is, a highly active catalyst is a key center for $NaBH_4$ hydrolysis [2]. Lots of catalysts including various noble metals, non-noble metal nanoclusters, and their derivatives have been developed to accelerate the hydrolysis rate of $NaBH_4$ [3]. Hydrogen generation is accelerated by applying metal-metal oxide catalysts such as Pt, PtRu disposed on TiO_2, CoO and $LiCoO_2$ [4, 5]. In order to reduce catalyst cost, the non-notable catalyst, especially that cheap Co-B and Ni-B catalysts are used to replace the notable metal. An effective method to improve the catalytic activity of Co-B and Ni-B catalysts is doped with other elements including Cr, P, Cu [6-8]. However, using chemical reduction of metal salt and sodium borohydride often leads to the aggregation and lowers down the specific surface area, which decreases the catalyst activity of the catalyst [9]. Now, the active site scattered on the surface of high-surface-area supporting materials is effective to increase the contact area with the reactants sufficiently and prevent the aggregation and destabilization of catalyst nanoparticles [10, 11]. Finding a cheap, high-specific-surface-area catalyst carrier is necessary to improve and keep the catalyst activity. Order SBA-15 mesoporous silica is considered as a good catalyst carrier as it has a large specific area, good chemical and physical properties, unique chemical stability and environmental friendliness [12]. The active sites such as Pt, Ni, Co deposit on the surface of SBA-15 and present high catalytic activity [13, 14].

Ni_2B-based catalyst has been widely investigated as a catalyst for $NaBH_4$ hydrolysis owing to its low cost. Its catalytic activity can be potentially improved by applying Ni_2B distributed on some oxide particles due to the so-called dispersion effect [15]. But so far, Ni_2B/SBA-15 catalyst with different nanostructures has seldom been reported. In the presented study, a nanostructure of Ni_2B distributed on the surface of SBA-15 was prepared and its catalytic activity for $NaBH_4$ hydrolysis was investigated. The microstructure analysis will be used to reveal the catalytic behavior of Ni_2B for future catalyst design.

2. EXPERIMENTAL

2.1. Materials and preparation for Ni_2B/SBA-15 catalyst

The main materials used in the experiment, including nickel salt (analytical reagent), sodium boron hydride (analytical reagent), cetyltrimethylammonium bromide (CTAB, analytical reagent), were purchased from Aladdin reagent company. SBA-15 (100-500

To whom correspondence should be addressed:
Email: *fanmeiqiang@126.com, †kangyingshu@163.com

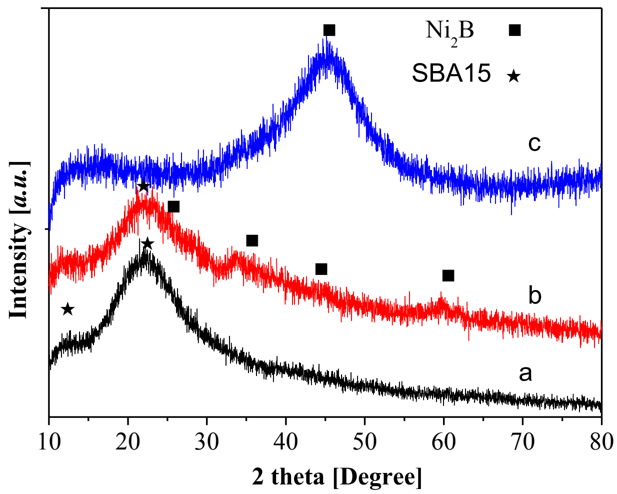

Figure 1. XRD patterns of SBA-15(a), Ni_2B/SBA-15 catalyst (b) and Ni_2B (c).

nm) was bought from Xianfeng nano Company in NanJing P. R. China. The materials were used without any pretreatments.

Ni_2B/SBA-15 catalyst was prepared though the followed process. First, 0.1 g of SBA-15, 0.091 g of cetyltrimethyl ammonium bromide (CTAB, analytical reagent), and different mass of nickel salt were added to 250 ml of deionized water, and the mixture was stirred for 5 h. Thereafter, sodium borohydride solution was added dropwise to the mixture, which was stirred continuously at room temperature. The molar ratio of nickel salt and sodium borohydride was set at 1.05. The weight ratio of Ni_2B/SBA-15 was set at 1:4, 1:3, 1:2, 1:1, 2:1.

2.2. Measurement of hydrolysis kinetics

Hydrolysis experiments were performed in a sealed reactor attached to a condenser and a graduated cylinder at 25 °C and 1 atm. The detailed hydrolysis conditions were similar to those in our pervious studies [16]. The hydrolysis experiments were carried out at 50 °C unless otherwise stated.

2.3. Microstructure analysis

Powder X-ray diffraction patterns of the prepared samples were obtained using an X-ray diffractometer (Thermo ARL X'TRA, Switzerland). Scanning electron microscopy observations were collected with a JSM-5610LV (JEOL Co.) equipped with an INCA energy-dispersive X-ray spectrometer.

3. RESULTS AND DISCUSSION

3.1. Characterization of Ni_2B/SBA-15 catalyst

Fig. 1 shows the XRD patterns of SBA-15, Ni_2B/SBA-15 catalyst and Ni_2B. Peaks at 24^0 and 45^0 corresponding to SBA-15 and Ni_2B (JCPD 25-0576), respectively, are observed in the XRD patterns of SBA-15 and Ni_2B. The large wide peaks reflected small grain size of SBA-15 and Ni_2B. However, only wide peaks at 24^0 corresponding to SBA-15 and other weak peaks at 25^0, 36^0,45^0 and 60^0 corresponding to amorphous Ni_2B are identified in the XRD patterns of Ni_2B/SBA-15 catalyst. Fig. 2 shows morphologies of

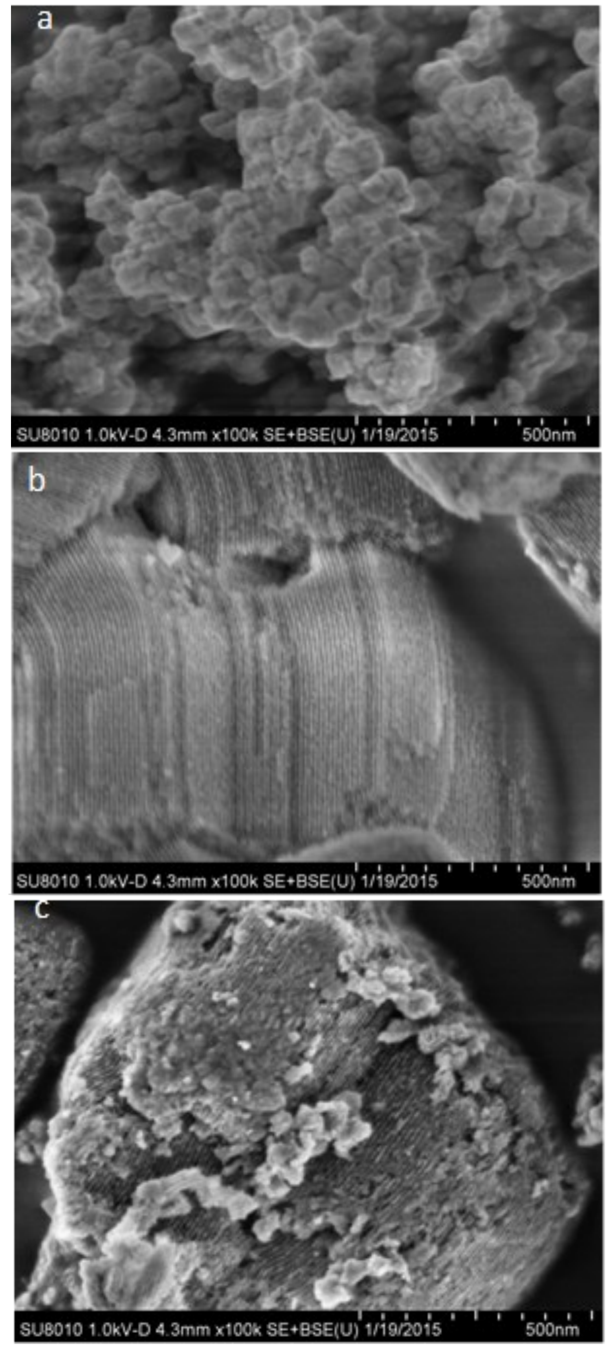

Figure 2. Morphologies of Ni_2B (a), SBA-15(b) and Ni_2B/SBA-15 catalyst (c).

Ni_2B, SBA-15 and Ni_2B/SBA-15 catalyst. Ni_2B presents framework structure with loose sphere piled together. The particle size ranges in hundreds of nm. SBA-15 exhibits layer structure with lots of fine slit distributed on its surface. After Ni_2B deposited on the surface of SBA-15, lots of fine particles with tens of nm are observed and many fine slits disappears in Fig. 2c. The Ni_2B distributed on SBA-15 surface has smaller particle size than pure Ni_2B.

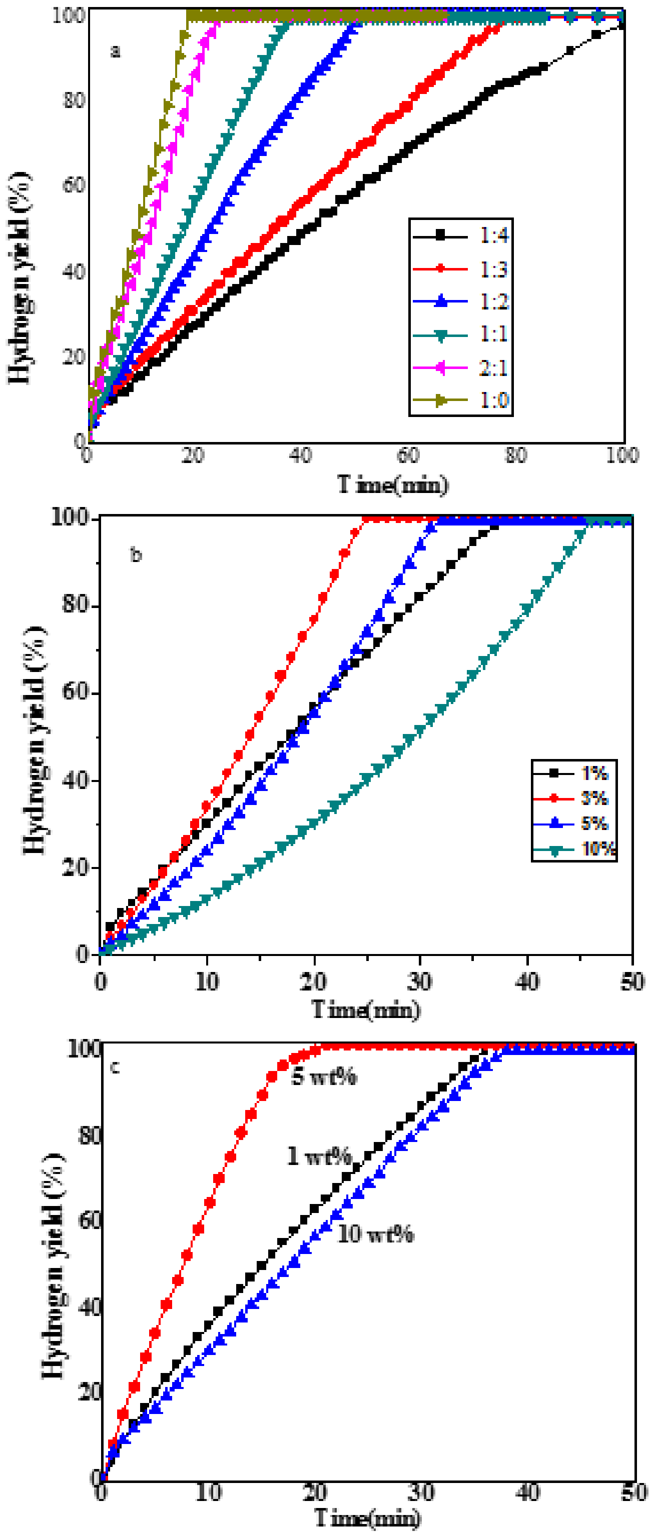

Figure 3. Hydrogen generation curves of $NaBH_4$ hydrolysis catalyzed by Ni_2B/SBA-15 catalyst. a, effect of Ni_2B/SBA-15 weight ratio; b, effect of $NaBH_4$ concentration; c, effect of NaOH concentration.

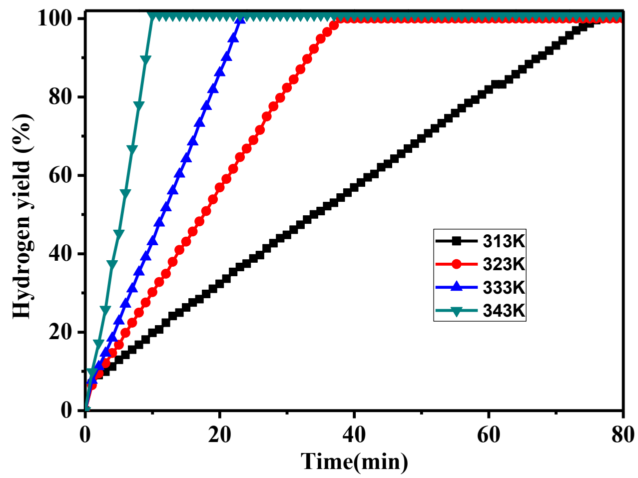

Figure 4. Hydrogen generation curves of $NaBH_4$ hydrolysis catalyzed by Ni_2B/SBA-15 catalyst with different temperatures.

3.2. Composition design on hydrogen generation

Fig. 3 shows hydrogen generation curves of $NaBH_4$ hydrolysis catalyzed by Ni_2B/SBA-15 catalyst. Ni_2B is a catalyst for $NaBH_4$ hydrolysis and 100% of hydrogen yield is obtained within 100 min in 1 wt% $NaBH_4$-10 wt% NaOH solution. The hydrogen generation rate increases with the increase of Ni_2B/SBA-15 weight ratio. Reaching 100% of hydrogen yield needs 105, 78, 53, 38, 25 and 20 min when Ni_2B/SBA-15 weight ratio increases 1:4 to 1:3, 1:2, 1:1, 2:1 and 1:0 in Fig. 3a. The catalytic activity increases with the increase of Ni_2B/SBA-15 weight ratio. But the catalyst with Ni_2B/SBA-15 weight ratio of 2:1 has almost similar catalytic activity to that of Ni_2B, reflecting that the nanostructure of Ni_2B distributed on SBA-15 improved catalytic activity of Ni_2B.

The effect of $NaBH_4$ concentration on hydrogen generation is shown in Fig. 3. The hydrogen yield up to 100% needs different time when $NaBH_4$ hydrolysis is catalyzed by Ni_2B/SBA-15 catalyst. About 38, 25, 32 and 47 min correspond to 1, 3, 5 and 10 wt% of $NaBH_4$ concentration. The results show that Ni_2B/SBA-15 catalyst has good catalytic activity for $NaBH_4$ hydrolysis and hydrogen generation rate increases with $NaBH_4$ concentration increasing from 1 to 3 wt%, but decreases with $NaBH_4$ concentration further increased. It was due to low diffusion rate at high $NaBH_4$ concentration because the increase of hydrolysis byproduct $NaBO_2$ concentration increases the viscosity in the hydrolysis process.

The effect of NaOH concentration is shown in Fig. 3c. The hydrogen generation rate increases with increasing in NaOH concentration and reaches a maximum at 5 wt%, then decreases with further increasing in NaOH concentration. It was due to that hydroxyl ion was involved in the hydrolysis of $NaBH_4$. But excessive concentration of NaOH will lead to decrease the solubility of $NaBO_2$ and the subsequent precipitation from the solution and adherence on the catalyst surface, which lower the catalytic activity of the catalyst.

3.3. Effect of hydrolysis temperature

Fig. 4 shows hydrogen generation curves of $NaBH_4$ hydrolysis catalyzed by Ni_2B/SBA-15 catalyst at different temperatures. Hy-

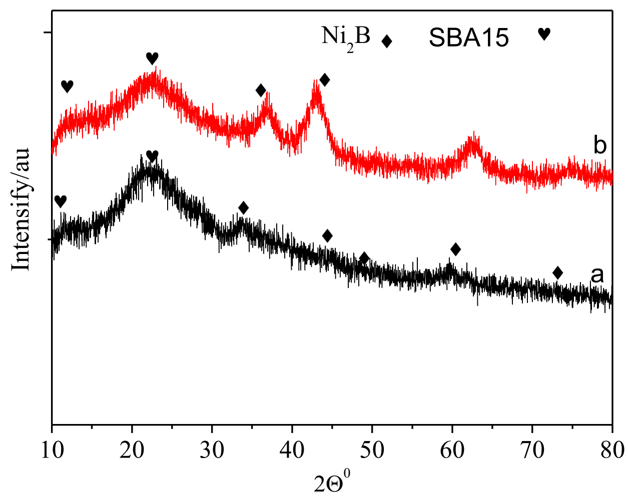

Figure 5. XRD patterns of Ni_2B/SBA-15 catalyst before and after sintered at 300 ^{0}C.

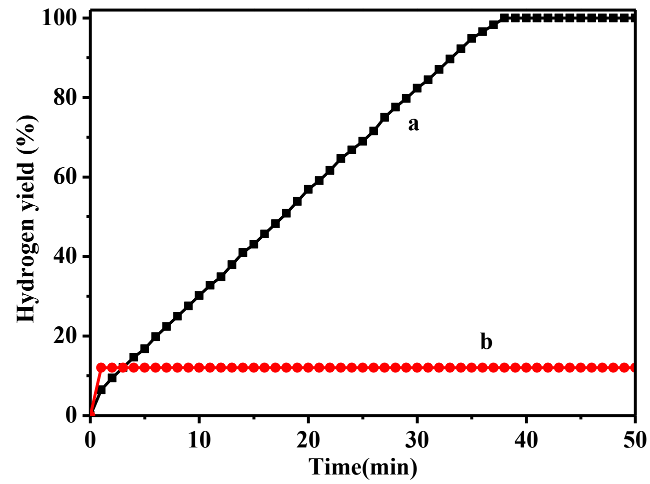

Figure 7. Hydrogen generation curves of $NaBH_4$ hydrolysis catalyzed by Ni_2B/SBA-15 catalyst before and after sintered at 300^{0}C. a, unprepared; b, sintered at 300^{0}C.

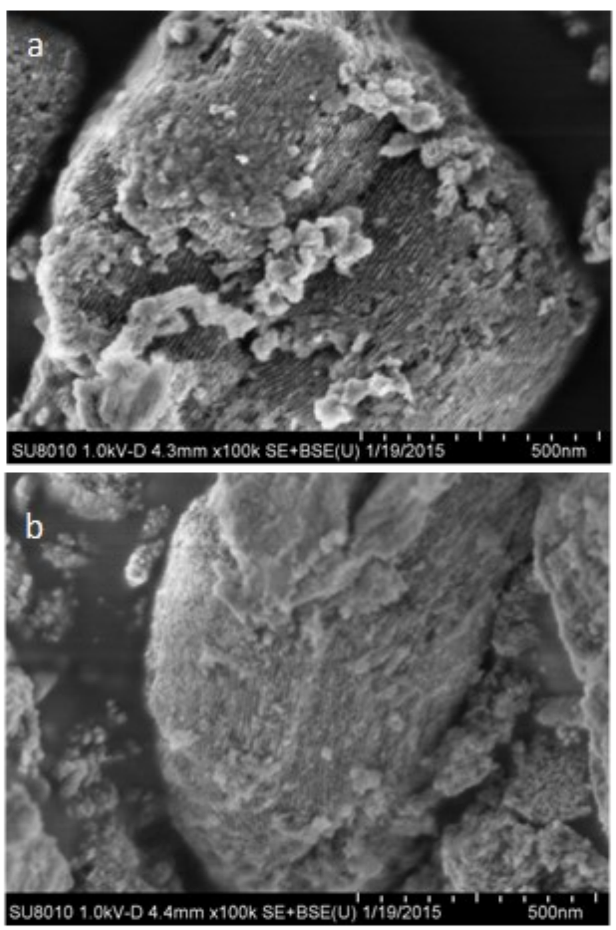

Figure 6. Morphologies of Ni_2B/SBA-15 catalyst before and after sintered at 300 ^{0}C. a, unprepared; b, sintered at 300^{0}C.
z at 300^{0}C.

drogen yield up to 100% for $NaBH_4$ hydrolysis were obtained at 313, 323, 333 and 343 K. It is known that the higher the hydrolysis temperature, the higher the hydrogen yields percentage and the shorter the hydrolysis time. The hydrogen generation rate increases with temperature increase. The average hydrogen generation rate can be calculated in the first 10 min. Their value is 1.98, 3.01, 4.31 and 10.08 corresponding to 313, 323, 333 and 343 K, respectively. The relative apparent activation energy (Ea) is calculated to be 46.89 kJ mol^{-1}.

3.4. Effect of sintering temperature

Fig. 5 shows XRD patterns of Ni_2B/SBA-15 catalyst before and after sintered at 300 ^{0}C. In comparison with amorphous Ni_2B, broadened peaks for crystalline Ni_2B significantly occurred at 36, 42 and 62 ^{0} after Ni_2B/SBA-15 catalyst was sintered at 300 ^{0}C. It can also be observed that the peak lines for SBA-15 and Ni_2B become wider, reflected that the grain size decreases. The phenomena can be further confirmed in Fig. 6, which shows morphologies of Ni_2B/SBA-15 catalyst before and after sintered at 300 ^{0}C. The unprepared Ni_2B/SBA-15 catalyst presents Ni_2B layer distributed on the surface of SMA-15, including some Ni_2B particles with hundreds of nm diameter are observed in Fig. 6a. After sintered at 300 ^{0}, the Ni_2B layer disappear and fine loose particles with ten of nm diameter are observed. The results shows that fine Ni_2B particles were generated on the Ni_2B layer when amorphous Ni_2B was converted to crystalline Ni_2B at 300 ^{0}C.

The catalytic activity of Ni_2B/SBA-15 catalyst before and after sintered at 300 ^{0}C. The unprepared Ni_2B/SBA-15 catalyst has high catalytic activity for $NaBH_4$ hydrolysis, 100 % of hydrogen yield can be obtained within 40 min. However, the sintered Ni_2B/SBA-15 catalyst has worsened catalytic activity for $NaBH_4$ hydrolysis, only approximate 12% of hydrogen yield is obtained in the initial one minute of hydrolysis process and then there is no hydrogen generated in the following time. The results shows that the catalytic activity of Ni_2B/SBA-15 catalyst is seriously worsened due to the effect of sintering at 300 ^{0}C. Combined with the XRD, SEM results, the catalytic of Ni_2B/SBA-15 catalyst come from amorphous.

4. CONCLUSION

The Ni_2B/SBA-15 was prepared in situ and its catalytic activity for $NaBH_4$ hydrolysis was investigated. The catalytic activity came from amorphous Ni_2B, not crystalline Ni_2B. It increases with Ni_2B/SBA-15 weight ratio increased from 1:3 to 2:1. The catalyst with Ni_2B/SBA-15 weight ratio of 2:1 was close to that of Ni_2B, reflected that the nanostructure of amorphous Ni_2B deposited on SBA-15 surface improved the catalytic activity of Ni_2B.

5. ACKNOWLEDGMENTS

This work was financially supported by the Scientific Research Foundation for the Returned Scholars, postdoctoral support of P. R China (2015M581910), postdoctoral preferential support of Zhejiang province (BSH1502029), the National Science Foundation of China (Project No. 51501175), and the Guangxi Key Laboratory of Information Materials (Guilin University of Electronic Technology, project No. 1210908-02-K).

REFERENCES

[1] Demirci U.B., Akdim O., Miele P., Int. J. Hydrogen Energy, 34, 2638 (2009).
[2] Liu B.H., Li Z.P., J. Power sources, 187, 527 (2009).
[3] Kim J.H., Kim K.T., Kang Y.M., Kim H.S., Song M.S., Lee Y., Int J Hydrogen Energy, 29, 263 (2004).
[4] Yoshitsugu K., Suzuki K., Fukumoto K., Sasaki M., Yamamoto T., Kawai Y., Hayashi H., Int J Hydrogen Energy, 27, 1029 (2002).
[5] Krishnan P., Yang T., Lee W.Y., Kim C., J Power Sources, 143, 17 (2005).
[6] Patel N., Fernandes R., Miotello A., J Power Sources, 188, 411 (2009).
[7] Ding X.L., Yuan X., Jia C., Ma Z.F., Int. J. Hydrogen Energy, 20, 11077 (2010).
[8] Fernandes R., Patel, N., Miotello A., Applied Catalysis B: Envi-romental, 92, 68 (2009).
[9] Xu D., Wang H., Guo Q., Ji S., Fuel Process Technol., 92, 1606 (2011).
[10]Umegaki T., Yan J.M., Zhang X.B., Shioyama H., Kuriyama N., Xu Q., J. Power Sources, 191, 209 (2009).
[11]Tian H., Guo Q., Xu D., J. Power Sources, 195, 2136 (2010).
[12]Rioux R.M., Song H., Hoefelmeyer J.D., Yang P., Somorjai G. A., J. Phys. Chem. B., 109, 2192 (2005).
[13]Song H., Rioux R., James D.H., Komor R., Niesz K., Grass M., Yang P., Gabor A.S., J. Am. Chem. Soc., 128, 3027 (2006).
[14]Carrero A., Calles J. A., Vizcaino A., Applied Catalysis A: General, 327, 82 (2007).
[15]Chen Y., Kim H., Fuel Process Technol., 89, 966 (2008).
[16]Fan M.Q., .Sun L.X., Xu F., Int. J. Hydrogen energy, 37, 4571 (2012).