

Novel Carbon Nanotubes-supported NiB Amorphous Alloy Catalyst for Benzene Hydrogenation

Mei Hua YANG, Rong Bin ZHANG, Feng Yi LI*

Institute of Applied Chemistry, Nanchang University, Nanchang 330047

Abstract: The NiB amorphous alloy catalysts supported on CNTs and alumina were prepared by impregnation and chemical reduction. The gas-phase benzene hydrogenation was used as a probe reaction to evaluate the catalytic activity. The result showed that the NiB amorphous alloy catalyst supported on carbon nanotubes exhibited higher activity than that supported on alumina.

Keywords: Carbon nanotubes, NiB amorphous alloy, benzene hydrogenation.

Carbon nanotubes(CNTs) have developed entirely new field in many natural science since their discovery in 1991. The unique physical and chemical properties make them potential and promising applications in various areas like reinforcement materials and microelectronics devices. Recently, there has been great interest to use CNTs as catalyst support in heterogeneous catalysis, and some meaningful results have been obtained¹⁻³. Additionally, amorphous NiB alloy have attached much attention due to its excellent catalytic properties⁴⁻⁵. Therefore, it is significant work to combine NiB amorphous alloy with CNTs in order to get novel catalyst with high activity. In this paper, we investigated the catalytic activity of CNTs-supported NiB amorphous alloy catalyst for benzene hydrogenation, and compared it with NiB/Al₂O₃ amorphous catalyst. The result indicated that the NiB/CNTs catalyst has higher benzene hydrogenation activity than the NiB/Al₂O₃.

CNTs(Provided by Shenzhen Nanotech Port Co., Ltd) was produced by chemical vapor deposition method. The carbon nanotubes was pretreated by refluxing in 4 mol/L HNO₃ aqueous solution for 12 h at 140 °C to remove other carbon materials and metal particles and decorate the surface. The NiB/CNTs was prepared as the follows: 0.3 g CNTs was vacuumed first and then impregnated with an ethanol solution of 0.05 mol/L Ni(NO₃)₂·6H₂O overnight. The mixture was reduced by adding dropwise the desired amount of the 3 mol/L KBH₄ aqueous solution with vigorous stirring at room temperature for 30 min. The black precipitate formed in the process of reaction was immediately collected on a filter, washed with large amounts of distilled water, followed by an ethanol rinse and dried at room temperature under the protection of pure nitrogen

* E-mail: fy-li@sohu.com

flow and squeezed the wanted sample. A similar procedure was employed to prepare the NiB/Al₂O₃ catalyst. The bulk composition of amorphous alloys and the Ni-loading on the support were determined by inductively coupled plasma(ICP) spectrometry. The special surface area of the sample was measured by N₂ adsorption at 77 K.

Benzene hydrogenation was carried out in a pulse-microcatalytic reactor (stainless steel U-shaped tube, 4 mm i.d.), which was fixed at the inlet of a gas chromatograph (H₂ as carrier gas) for on-line analysis of reaction effluents. The catalyst was reduced *in situ* by H₂(30 mL.min⁻¹) at 473K for 1h before the reaction was performed. A volume of 1μL benzene was injected into the reactor containing 0.05 g catalyst each time.

Figure 1 Benzene conversion over NiB/CNTs(1) and NiB/Al₂O₃(2)

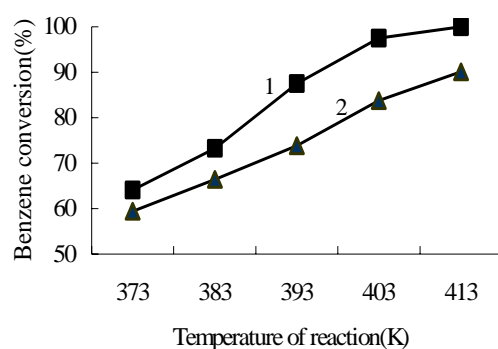
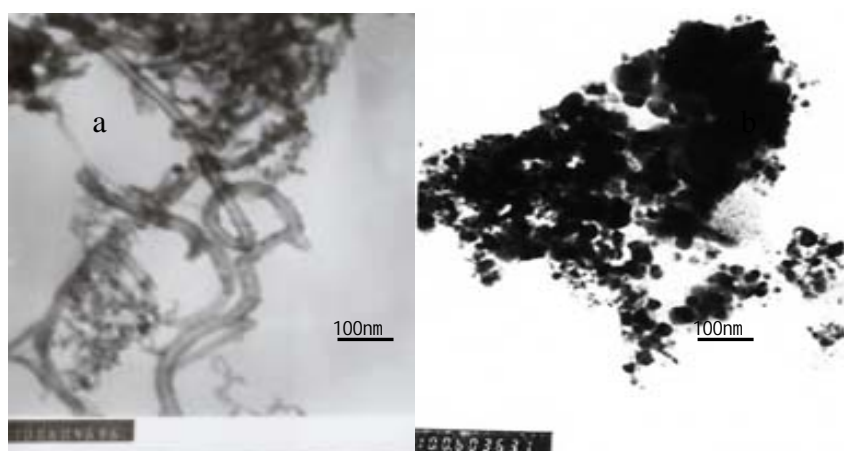


Figure 1 shows the results of benzene hydrogenation over NiB/CNTs and NiB/Al₂O₃ in the temperature range from 373K to 413K. It is obvious that, under the same reaction conditions, the NiB/CNTs catalyst exhibits higher catalytic activity than the NiB/Al₂O₃ catalyst.

Figure 2 TEM images



a) NiB/CNTs amorphous alloy catalyst; b) NiB/Al₂O₃ amorphous alloy catalyst

From **Figure 2**, we can see the difference in the TEM morphologies of the NiB/CNTs sample and the NiB/Al₂O₃ sample. For the NiB/CNTs sample, the NiB amorphous alloy particles are even distributed on the surface of the tubes, and many particles are very small in diameter (about 5 nm). Whereas on the surface of γ -Al₂O₃, the NiB amorphous alloy particles congregated to form cluster-like substance. After acidic oxidation treatment, there are a large number of functional groups (-OH, -COOH) on the nanotubes. These functional groups make the surface of the CNTs more accessible to the solution of the metal precursor or deposits⁶. Therefore, more Ni metallic precursors are attached to the nanotubes and NiB amorphous alloy particle are dispersed more homogeneously on the outer surface of the nanotubes, leading to small diameters on the whole. We think that the higher activity of the NiB/CNTs catalyst closely related to the higher dispersion and smaller particle size of NiB amorphous alloy.

Table 1 Some characteristics of the samples determined by ICP and BET

Samples	Ni-loading(wt.%)	Bulkcomposition(weight ratio)	S _{BET} (m ² g ⁻¹)
NiB/CNTs	8.76	Ni _{90.56} B _{9.44}	107
NiB/Al ₂ O ₃	8.38	Ni _{90.95} B _{9.05}	192

In addition, from **Table 1**, we can learnt that the Ni-loading and bulk composition of the two different catalysts are very close, but the special surface area of the NiB/CNTs catalyst is much lower than that of the NiB/Al₂O₃. It indicates that the special properties of the CNTs support may also play important role in improving the activity of benzene hydrogenation. As we all known, the CNTs possess many unique properties such as excellent electronic conductivity and strong hydrogen storage ability *etc.*, which are very useful for hydrogenation reaction²⁻³. Therefore, we believe that CNTs will be a promising support for amorphous alloy and can improve the properties of the amorphous alloy to make amorphous alloy realistic application. We will continue to research the influence of CNTs on the amorphous alloy catalyst in the future.

Acknowledgments

This work was supported by the National Natural Science Foundation of China(No. 20263003) and the Natural Science Foundation of Jiangxi province(No. 0250009).

References

1. J. M. Planeix, N. Coustel, B. Coq, *et al.*, *J. Am. Chem. Soc.*, **1994**, *116*, 7935.
2. Y. Zhang, H. B. Zhang, G. D. Lin, *et al.*, *Appl. Catal A: General*, **1999**, *187*, 213.
3. J. Z. Luo, L. Z. Gao, Y. L. Leung, C. T. Au, *Catalysis Letters*, **2000**, *66*, 91.
4. R. B. Zhang, F. Y. Li, Q. J. Shi, L. T. Luo. *Appl. Catal A: General*, **2001**, *205*, 279.
5. R. B. Zhang, F. Y. Li, N. Zhang, Q. J. Shi. *Appl. Catal A: General*, **2003**, *239*, 17.
6. C. H. Li, K. F. Yao, J. Liang, *Carbon*, **2003**, *41*, 85.

Received 18 August, 2003