

## Effect of Metallic Additives on Structure and Catalytic Properties of Supported NiPB/SiO<sub>2</sub> Catalyst

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**Abstract:** A new preparation method was proposed to deposit amorphous alloys containing NiP and metallic additives such as Fe, Co, and Cu. The different effects of metallic additive on structure and catalytic properties of supported amorphous NiMPB/SiO<sub>2</sub> (M=Fe, Co, Cu) catalysts were observed, and the improvement of catalytic activity due to heating pretreatment in hydrogen was found.

**Keywords:** Amorphous alloy, catalyst, hydrogenation, acetylene, ethene.

Supported amorphous alloy catalysts have received much attention in recent years because they show larger surface area, higher thermal stability and superior catalytic properties<sup>1-7</sup> as compared with ultra-fine or rapidly quenched metal metalloid amorphous alloys. Preparation, characterization and catalytic performance of supported NiB catalyst have been reported by several research groups, however, only one preparation method of supported amorphous alloy catalyst containing NiP was proposed<sup>1,2</sup> which was found by us to be unable to deposit NiP sufficiently onto support. Furthermore, metallic additives have been reported to be essential to improve the thermal stability and catalytic activity of rapidly quenched amorphous alloy, but their effect for supported amorphous alloy catalyst containing NiP has not been revealed because of the preparation problem. In this paper, the preparation of supported amorphous alloy catalysts containing NiP and metallic additive by a new method is reported. The structure and catalytic property of the catalysts are studied.

### Experimental

*Sample preparation:* Firstly, a small amount (0.5wt.%) of NiB was deposited onto silica gel support (401m<sup>2</sup>/g, pore volume 0.95ml/g, 80~120 mesh) to prepare NiB/SiO<sub>2</sub> according to the method described in literature<sup>8</sup>. Secondly, 5 grams of NiB/SiO<sub>2</sub> was added into 40 ml of an aqueous solution containing NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O (=0.7mol/L), Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (=0.1mol/L) and one metallic additive salt (=0.025mol/L) of CuSO<sub>4</sub>·5H<sub>2</sub>O, Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O or FeSO<sub>4</sub>·7H<sub>2</sub>O, and immediately, the chemical

reduction started, accompanied by hydrogen releasing from solution. After the reaction finished, the sample was washed by distilled water and then anhydrous ethanol. The sample is denoted as NiMPB/SiO<sub>2</sub> where M represents Cu, Co or Fe. NiPB/SiO<sub>2</sub> was also prepared according to above method when metallic additive salt was not used.

#### *Characterization*

A D-Max-2A X-ray diffractometer with a copper target and a nickel filter was used to investigate the structure. The surface area were measured with a Micromeritics ASAP 2400 using BET method from N<sub>2</sub> adsorption isotherms at 77K. Transmission electron micrograph (TEM) was performed on a Japan JEM-2000 FX electron microscope. Differential scanning calorimetry (DSC) was conducted on an America Du Pont 2100 Differential Scanning Calorimeter under high pure N<sub>2</sub> atmosphere at the heating rate of 10°C/min.

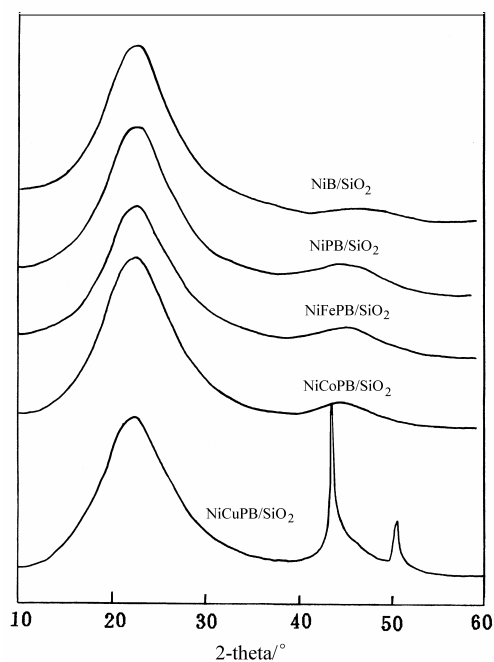
#### *Catalytic performance evaluation*

The catalytic experiments were carried out in a microcatalytic flow reactor under  $9.8 \times 10^5$  Pa at 383K and  $90000 \text{ h}^{-1}$  GHSV. An on-line GC was employed to analyze the reactants and products. The feed gas contained 1.65% C<sub>2</sub>H<sub>2</sub>, 2.56% H<sub>2</sub> and 95.79% C<sub>2</sub>H<sub>4</sub>.

### **Results and Discussion**

It has been found that only 20% of amorphous NiP alloy produced during the reduction of Ni<sup>2+</sup> was loaded onto support by using the method described in literature<sup>1</sup>. This is because the reduction of Ni<sup>2+</sup> can take place not only around support but also anywhere in the solution. However, almost all alloys produced by using the method of this paper were deposited onto support because of the existence of NiB which can catalyze the reduction of Ni<sup>2+</sup> by H<sub>2</sub>PO<sub>2</sub><sup>-</sup> and thus make the reduction merely occur around NiB particles.

The XRD patterns of NiB/SiO<sub>2</sub>, NiPB/SiO<sub>2</sub> and NiMPB/SiO<sub>2</sub> samples are presented in **Figure 1**. For NiB/SiO<sub>2</sub> sample, a broad peak around  $2\theta=22^\circ$  due to the silica gel and one broad peak around  $2\theta=45^\circ$  corresponding to amorphous NiB were observed. After the deposition of NiMP or NiP, the peak intensity around  $2\theta=45^\circ$  was increased, indicating the increment of amorphous alloy. Because no other XRD peak appeared in the XRD spectra of NiFeBP/SiO<sub>2</sub>, NiCoPB/SiO<sub>2</sub> and NiPB/SiO<sub>2</sub> samples, NiFeP, NiCoP and NiP were deposited onto support as amorphous alloy. In the XRD spectra of NiCuPB/SiO<sub>2</sub>, however, except above broad peaks, there appeared two sharp peaks at  $2\theta=43^\circ$  and  $2\theta=51^\circ$  resulting from crystalline Cu. Therefore, Ni<sup>2+</sup> was reduced to amorphous NiP but Cu<sup>2+</sup> to crystalline Cu in NiCuPB/SiO<sub>2</sub> sample.

**Figure 1.** XRD patterns of supported amorphous alloy catalysts**Table 1.** Catalytic properties of catalysts in the selective hydrogenation of acetylene in a large excess of ethene

Catalyst	X <sup>a</sup> , %	S <sup>b</sup> , %
NiB/SiO <sub>2</sub>	10	60
NiPB/SiO <sub>2</sub>	30	68
NiFePB/SiO <sub>2</sub>	55	67
NiCoPB/SiO <sub>2</sub>	60	69
NiCuPB/SiO <sub>2</sub>	19	41

<sup>a</sup> Acetylene conversion.<sup>b</sup> Ethene selectivity.**Table 2.** Effect of pretreatment temperature on structure and catalytic property of NiFePB/SiO<sub>2</sub>

T, K	Structure	D <sup>a</sup> , nm	X, %
323	A <sup>b</sup>	13	55
423	A	13	59
523	A	13	64
610	A+C <sup>c</sup>	15	69
800	C	26	15

<sup>a</sup> Average NiFePB particle size.<sup>b</sup> Amorphous.<sup>c</sup> Crystalline

The catalytic activity and selectivity in the selective hydrogenation of acetylene in a large excess of ethene over different samples are given in **Table 1**. Clearly, activity was promoted by Fe and Co, but impaired by Cu. Enrichment of surface Ni and change of microstructure due to the addition of Fe and Co are considered to be responsible for the promotion effect of Fe and Co. However, the investigation of inhibition effect of Cu is under way.

The effect of pretreatment in hydrogen on the structure and catalytic activity of NiFePB/SiO<sub>2</sub> was also investigated and some results are listed in **Table 2**. As can be seen from Table 2, when pretreatment temperature is lower than the crystallization temperature (617K) of NiFePB/SiO<sub>2</sub>, the average size of NiFePB particles remains constant but catalytic activity increases with the temperature. This activity increment may be due to the reduction of oxide species containing nickel and iron on the surface of NiFePB particles. It has been noticed that partially crystalline sample shows even higher activity than the totally amorphous one, implying that amorphous alloy might be a precursor of some better catalysts. After pretreatment at 800K, the alloy of the catalyst becomes crystalline and thus the catalytic activity becomes poor. It should be pointed out that the severe sintering of NiFePB particles has not been observed, which may be ascribed to the interaction of support with alloy particles and the dispersion function of the support.

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### References

1. J. F. Deng, X. P. Zhang, E. Z. Min, *Appl. Catal.*, **1989**, *37*, 339.
2. H. X. Li, W. L. Dai, C. Shen, S. Y. Zhou, J. F. Deng, *Chem. Lett.*, **1997**, 133.
3. W. J. Wang, M. H. Qiao, H. X. Li, W. L. Dai, J. F. Deng, *Appl. Catal.*, **1998**, *168*, 151.
4. W. J. Wang, M. H. Qiao, J. Yang, S. H. Xie, J. F. Deng, *Appl. Catal.*, **1997**, *163*, 101.
5. T. X. Li, H. M. Li, S. Cui, M. Li, S. J. Li, *Chinese J Catal.*, **1991**, *12*(6), 483.
6. X. P. Zhang, D. J. Liu, J. F. Deng, *Chinese J Catal.*, **1990**, *11*(3), 173.
7. R. Yang, B. Zhong, T. D. Hu, T. Liu, *Chinese J Mol. Catal.*, **1998**, *12*(4), 241.
8. E. Z. Min, W. Z. Lu, J. F. Deng, A. Z. Ma, *U.S.09/061,081*, **1998**.

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