



Preparation and catalytic properties of amorphous alloys in hydrogenation of sulfolene

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Abstract

A series of NiB(P) and NiCoB amorphous alloys were prepared by chemical reduction. Their catalytic activities in hydrogenation of sulfolene were evaluated in a 250 ml stainless autoclave. Influences of solvent and preparation temperature on the catalytic activity of NiB amorphous alloy were studied. Effects of reaction temperature and stirring rate on the catalytic properties of NiB amorphous alloy were researched; Raney Ni properties were also studied. The relationship between particle size of NiB, NiP and NiPB amorphous alloys and their catalytic behaviors has been discussed according to SEM, TEM and ICP results. Comparing the activities of NiCoB amorphous alloys with NiB, CoB and Raney Ni catalysts, we found that, NiCoB amorphous alloys with mole ratio of Ni/Co at 2.4 have much higher activity in hydrogenation of sulfolene.

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Keywords: Sulfolene; Hydrogenation; Sulfolane; NiB(P) amorphous catalyst; NiCoB amorphous catalyst

1. Introduction

Sulfolane is an important solvent. Most organic compounds and polymers can be dissolved in it. The industrial production of sulfolane began in England in 1940s: butadiene reacted with sulfuric dioxide to synthesize sulfolene, then hydrogenation of sulfolene on Ni-based catalyst can produce sulfolane. The most frequently used Ni-based catalyst is Raney Ni. As Raney Ni has some severe disadvantages such as environmental pollution, scientists must find a new type of catalyst that has high activity and does not pollute environment to take its place.

Amorphous alloys represent a new class of catalytic materials. Since Smith's first report using amorphous alloy as catalysts in 1980 [1], more and more research

work have been done on hydrogenation reactions over amorphous alloys. Up to now, amorphous alloy catalysts have been used in hydrogenation of olefins [2], selective hydrogenation of diene [3–5], selective hydrogenation of benzene [6–9], selective hydrogenation of acetylene in a large excess of ethene [10], hydrogenation of aldehyde and alcones such as furfural [11], glucose [12–14] and cinnamaldehyde [15], hydrogenation of nitrobenzene [16,17], selective hydrogenation of nitriles [18–20] and hydrogenation of carbon monoxide [21]. In the above reactions, amorphous alloys showed unique catalytic performance, and in many cases they were more active than Raney Ni catalyst.

Here, we report hydrogenation of sulfolene over a series of NiB(P) and NiCoB amorphous alloy catalysts. These amorphous alloys showed high catalytic performance in proper reaction conditions, and they were easy to prepare and did not pollute the

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environment. In comparison with Raney Ni, NiCoB amorphous alloys with a mole ratio of Ni/Co at 2.4 were more active in some reaction conditions.

2. Experimental

2.1. Catalyst preparation

The NiP-1 sample was prepared as in [22]. The NiP-2 sample was prepared by stirring an aqueous solution that consists of 240 g/l nickel hypophosphite, 20 g/l sodium acetate and 40 g/l sodium citrate at 300 K. The pH value of the solution was adjusted to 8 using 2 M NaOH aqueous solution. The black precipitate was washed with distilled water and soaked in ethanol. The NiPB-1 (NiPB-2) amorphous powder was prepared by adding dropwise 25 ml (50 ml) of 2 M KBH_4 aqueous solution to 50 ml of 1 mol/l nickel hypophosphite aqueous solution under vigorous stirring at 300 K. The black precipitate was washed with distilled water and soaked in ethanol. The NiB amorphous alloy powder was prepared by adding dropwise 2 M KBH_4 aqueous solution to 0.1 mol/l nickel nitrate aqueous solution under vigorous stirring in nitrogen atmosphere. For NiB-1, the preparation temperature was 273 K. For NiB-2 and NiB-3, the temperature was

268 K. The mole ratio of KBH_4 and $\text{Ni}(\text{NO}_3)_2$ was 5:1 for NiB-1 and NiB-2 and 2.5:1 for NiB-3. The preparation methods of CoB or NiCoB amorphous alloys were the same as NiB-3, except that cobalt nitrate or the mixture of cobalt nitrate and nickel nitrate was used instead of nickel nitrate.

2.2. Catalyst characterization

The compositions of the as-prepared samples were analyzed by inductively coupled plasma analysis (ICP, TJA ICP-9000(N + M)). The amorphous characters of these samples were determined by X-ray powder diffraction (XRD, Rigaku Dmax-2500 with $\text{Cu K}\alpha$ radiation). The surface morphology and particle size of the samples were observed by a scanning electron micrograph (SEM, HitachiX-650) and a transmission electron micrograph (TEM, Philips EM400ST).

2.3. Activity test

The hydrogenation of sulfolene was performed at 328–333 K and 3.0 MPa of hydrogen pressure in a 250 ml stainless autoclave containing 0.6 g catalyst, 10 g sulfolene and 100 ml distilled water. The reaction mixture was stirred at 250 rpm at reaction temperature for 2 h. The reaction product was analyzed by a

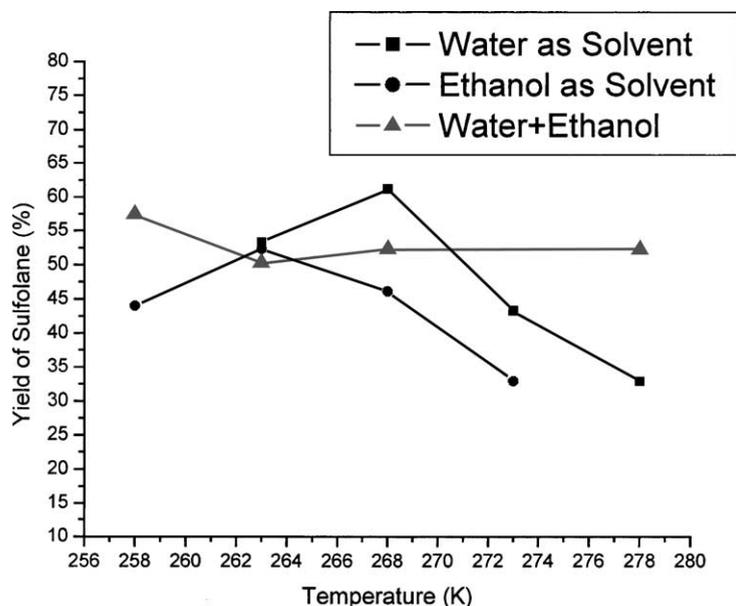


Fig. 1. Dependence of catalytic activity of NiB amorphous alloy on preparation temperature in different solutions.

gas chromatograph (SP 502) with a flame ionization detector.

3. Results and discussion

3.1. Influence of reaction conditions on catalytic activity of NiB amorphous alloy

In the hydrogenation of sulfolene, sulfolane was the only product, so it can be concluded that the selectivity of the sulfolane is almost 100%. With the reaction temperature decrease, the sulfolane yield first increased and then decreased (Table 1). The optimum reaction temperature is 323 K. This is because this hydrogenation reaction is an exothermic reaction. Table 1 shows that the hydrogenation activity of NiB amorphous catalyst approached 100% with the diffusion effect eliminated and the stirring rate being 400 rpm at 323 K. It can be seen that both NiB amorphous alloy and Raney Ni can exhibit excellent catalytic activity on sulfolene hydrogenation reaction, when the diffusion effect has been eliminated.

Because the stirring rate was relatively low in the actual industrial production, the catalytic activity of as-prepared samples were evaluated at 250 rpm in

Table 1

Influence of reaction temperature and stirring rate on activity of NiB amorphous catalyst and Raney Ni

Reaction temperature (K)	Stirring rate (rpm)	Yield of sulfolane (%)	
		NiB-2	Raney Ni
335	250	57.7	67.7
328	250	61.7	85.5
323	250	88.6	95.7
318	250	85.7	92.5
323	300	93.1	98.7
323	350	99.3	98.8
323	400	99.4	99.1

order to find a proper catalyst to replace Raney Ni. Reaction temperature was chosen as 335 or 328 K in our studies.

3.2. Effect of preparation conditions (solvent or temperature) on the catalytic performance of NiB amorphous alloy

Ethanol, a mixture of ethanol and water, or water was chosen as solvent of Ni(NO₃) and KBH₄. Ethanol was only used as solvent of Ni(NO₃). The volume ratio of mixture of ethanol and water was 1:9. The dependence of catalytic activity of the NiB amorphous

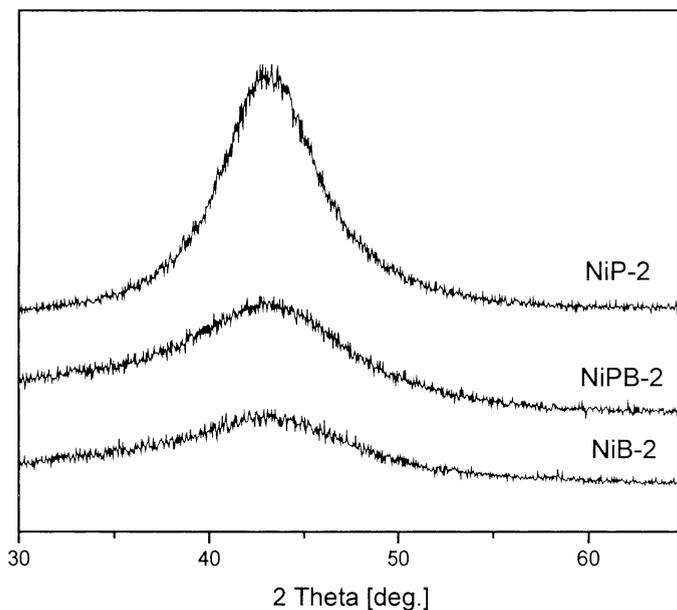


Fig. 2. XRD patterns of NiB, NiP and NiBP amorphous alloys.

alloy powder prepared from these three systems on preparation temperature is illustrated in Fig. 1.

In aqueous solution, the preparation mixture was easy to freeze when the preparation temperature was lower than 260 K, so the lowest temperature approached 258 K. With the decreasing of preparation temperature, the catalytic activity of the NiB amorphous powder from the three systems increased. The

best preparation condition was at 258 K in aqueous solution.

3.3. Activity of NiB, NiP and NiBP amorphous catalysts

The XRD patterns of NiB(P) amorphous alloys shown in Fig. 2 gave only a broad peak around

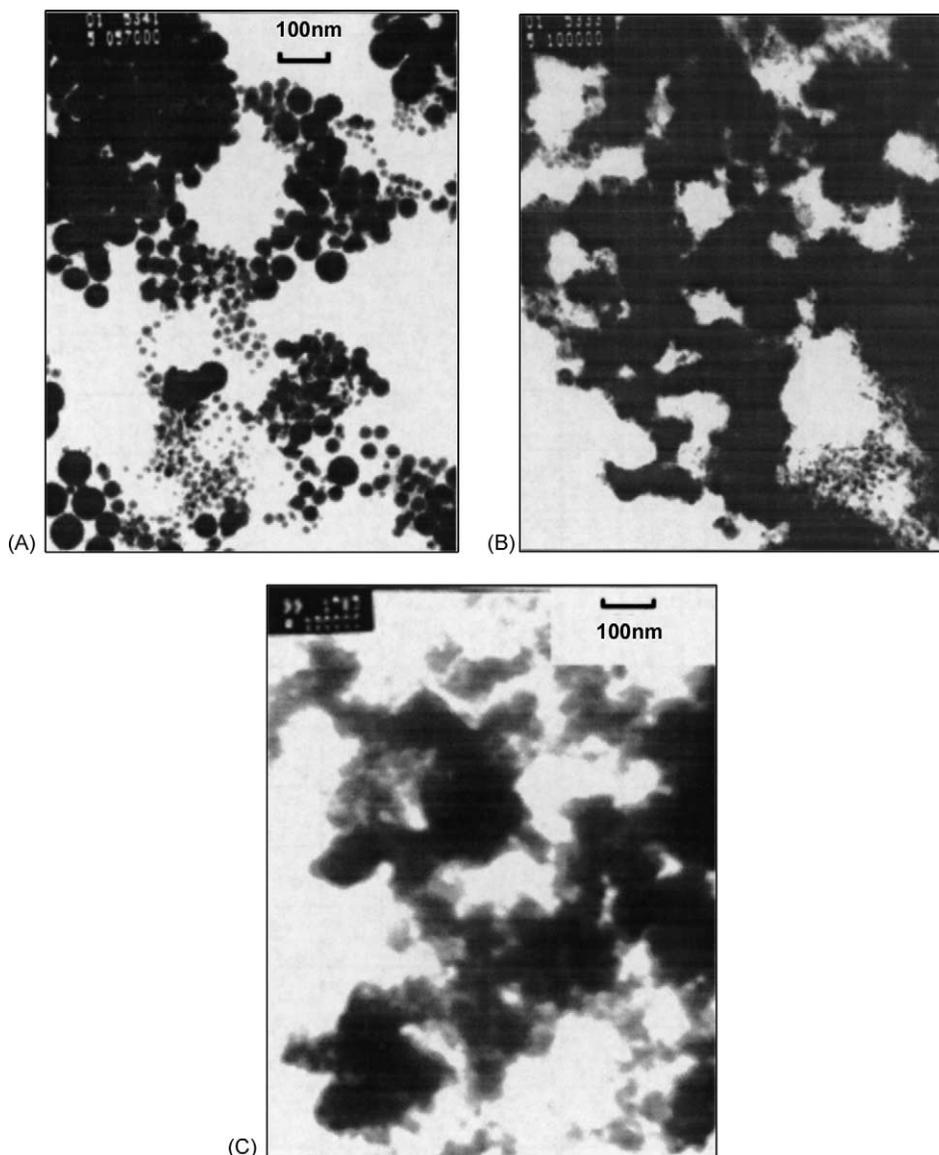


Fig. 3. TEM micrograph of NiP, NiBP and NiB amorphous alloy (A: NIP-2; B: NIPB-2; C: NIB-2).

$2\theta = 45^\circ$. This was assigned to the amorphous state of nickel–metalloid alloy [23]. Notably, the patterns contained no distinct peak corresponding to a crystalline phase. The obvious differences in the peak intensity in the XRD patterns of the three samples showed that the NiB powder has a wider disorder range than NiBP powder, and the NiBP powder has a wider disorder range than NiP powder [17]. The distinct differences

of the morphology and particle size among these three samples were observed in the SEM and TEM micrographs. The NiP-2 sample has a spherical morphology (Fig. 3A). The particle size ranges from 5 to 70 nm. The NiBP-2 amorphous powder has an irregular morphology (Fig. 3B), and the particle size ranges from 5 to 30 nm. The NiB samples exhibit different morphologies in different preparation conditions. NiB-1



Fig. 4. SEM micrograph of NiB amorphous alloys (A: NiB-1; B: NiB-2).

Table 2

Composition, average particle size and catalytic activities of NiB, NiBP and NiP amorphous catalyst^a

Sample	Composition (at.%)	Average particle size (nm)	Yield of sulfolane (%)
NiP-1	Ni ₇₄ P ₂₆	70	6.2
NiP-2	Ni ₆₅ P ₃₅	35	20.0
NiPB-1	Ni ₅₄ P ₃₃ B ₁₃		36.3
NiPB-2	Ni ₆₉ P ₁₁ B ₂₀	20	36.0
NiB-1	Ni ₆₉ B ₃₁	20	32.9
NiB-2	Ni ₆₅ B ₃₅	<5	57.7

^a Sulfolene hydrogenation reaction temperature was 333 K.

sample prepared at 273 K has an approximately spherical morphology (Fig. 4A) and the average particle size is about 20 nm. NiB-2 sample prepared at 268 K has a net-like morphology (Fig. 4B); one can see from the TEM micrograph (Fig. 3C) that the net is formed by many interconnected fine particles with sizes <10 nm.

Table 2 lists the composition, average particle size and catalytic activities of NiB, NiBP and NiP amorphous catalysts. Though Ni was the active component, the activity for the hydrogenation of sulfolene increased with metalloid content increases for the same Ni–metalloid amorphous alloy. This is in accordance

with the studies of Okamoto et al. [24] There exists an obvious correlation between the particle size and the catalytic activity of these samples. With the particle size decreasing (NiB-2 < NiB-1~NiBP-2 < NiP-2 < NiP-1), the catalytic activity of the samples increased (NiB-2 > NiBP-2~NiB-1 > NiP-2 > NiP-1).

The differences of the catalytic activities among different Ni–metalloid alloys can be explained from two points of views. The first viewpoint attributed the differences to the differences of the electron densities on the nickel metal among NiP, NiB and NiBP catalysts [17,24,25]. In NiB powder, boron donates electrons to the nickel metal, whereas phosphorus accept electrons from nickel metal in NiP powder. In NiBP powder, these two cases are existing at the same time. The differences of electron densities on the nickel metal results in the markedly different hydrogenation activity of these catalysts. The second viewpoint attributed the differences to the difference of the particle sizes or active site numbers [26,27]. Both factors can affect the catalytic performance of the amorphous alloys, but in different cases the dominant one is different. In our research work, the second one may be dominant.

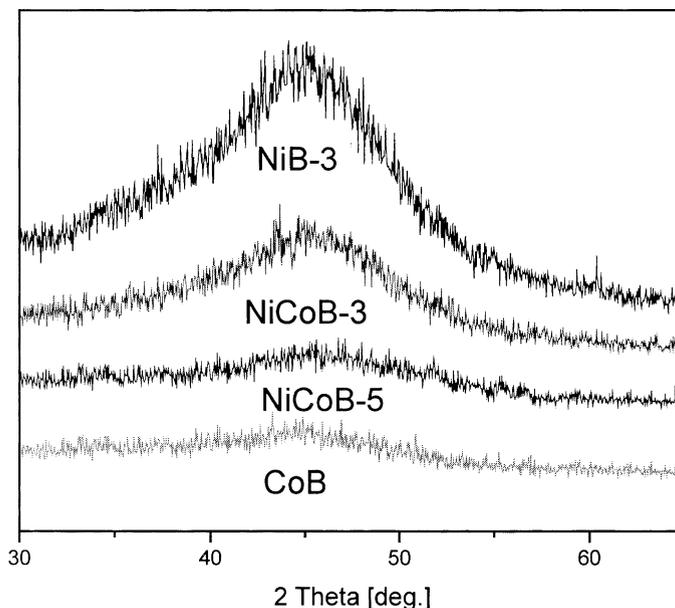


Fig. 5. XRD patterns of NiB, CoB and NiCoB amorphous alloys.

Table 3
Composition and activity of NiB, CoB and NiCoB amorphous alloys^a

Sample	Preparation condition		Composition (at.%)	Mole ratio of Ni/Co	Yield of sulfolane (%)
	Concentration of M ²⁺ (mol/l)	Mole ratio of Ni ²⁺ /Co ²⁺			
NiB-3	0.1	–	Ni ₅₁ B ₄₉	–	77.6
CoB	0.1	–	Co ₅₈ B ₄₂	–	46.1
NiCoB-1	0.1	4:1	Ni ₄₂ Co ₁₂ B ₄₆	3.5:1	63.3
NiCoB-2	0.1	3:1	Ni ₄₁ Co ₁₇ B ₄₂	2.4:1	96.1
NiCoB-3	0.1	2:1	Ni ₃₈ Co ₂₂ B ₄₀	1.7:1	84.3
NiCoB-4	0.1	1:1	Ni ₃₁ Co ₃₄ B ₃₅	1:1.1	69.9
NiCoB-5	0.1	1:2	Ni ₂₂ Co ₃₇ B ₄₁	1:1.7	59.1
NiCoB-6	0.7	3:1	Ni ₃₅ Co ₁₅ B ₅₀	2.3:1	98.1
NiCoB-7 ^b	0.7	3:1	Ni ₄₇ Co ₁₈ B ₃₅	2.6:1	97.1
Raney Ni					85.5

^a Sulfolene hydrogenation temperature was 328 K.

^b Mole ratio of KBH₄ and M²⁺ was 5:1.

3.4. Activity of NiB, CoB and NiCoB amorphous alloys

The XRD patterns of Co(Ni)B amorphous alloys as shown in Fig. 5 also gave only a broad peak around $2\theta = 45^\circ$, which was assigned to the amorphous state of cobalt (nickel)–metalloid alloy [23]. Also the patterns did not contain any distinct peak corresponding to a crystalline phase. The obvious difference in the peak intensity in the XRD patterns of the samples showed that CoB powder has a wider

disorder range than NiCoB powder, and NiCoB powder has a wider one than NiB powder. Moreover, the extent of the wider disorder range increased with an increase of cobalt content in NiCoB amorphous samples.

Table 3 lists the composition and catalytic activity of NiB, CoB and NiCoB amorphous alloys with different mole ratios of Ni/Co. The mole ratios of Ni/Co in NiCoB samples could be changed with the initial mole ratio of Ni²⁺/Co²⁺ in the reactants. Therefore, the compositions of the NiCoB amorphous alloys could

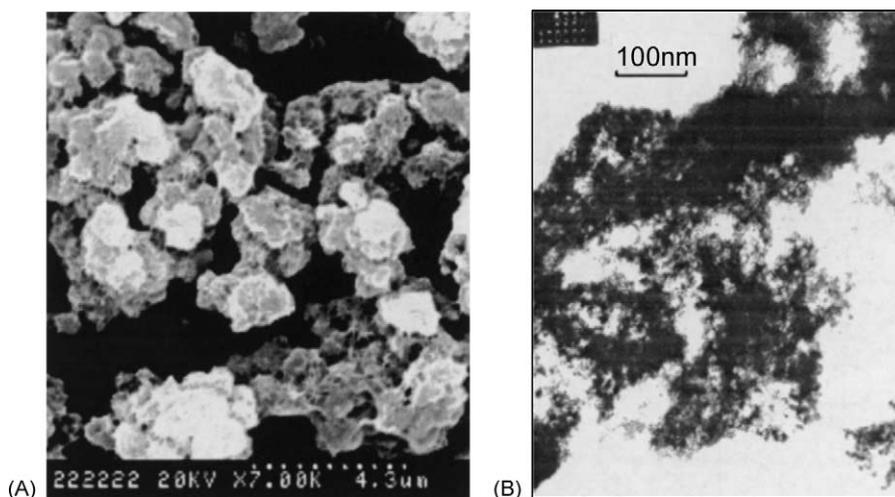


Fig. 6. SEM and TEM micrograph of NiCoB-6 sample (A: SEM; B: TEM).

be easily adjusted by changing the initial contents of the metallic salts.

Both NiB and CoB amorphous alloys were active in hydrogenation of sulfolene, but the hydrogenation activity of NiB amorphous catalyst was higher than that of the corresponding CoB. Furthermore, both the Ni and the Co elements in NiCoB catalysts may be the active sites during the hydrogenation of sulfolene. This differs from the hydrogenation of benzene over NiCoB amorphous alloys [6]. Catalytic activities of all as-prepared NiCoB samples were higher than that of CoB sample. But only two NiCoB samples, with mole ratios of Ni/Co at 1.7 and 2.4, respectively, showed higher activities than that of NiB, indicating that the collaboration of Ni and Co element only takes place in these cases. With the mole ratio of Ni/Co decreasing, the activity of NiCoB samples first increased, then decreased. The optimum mole ratio of Ni/Co is 2.4:1. During the initial concentration of metal salts and the mole ratio of metal salt/ KBH_4 changed, respectively at above ratio, the activities of NiCoB-6 and NiCoB-7 were high all the same, and all higher than that of Raney Ni. SEM and TEM micrographs of NiCoB-6 (Fig. 6A and B) showed its morphology to be analogous to that of NiB-2; the particle size is about 5 nm.

4. Conclusions

In this research, a series of NiB(P) and Ni(Co)B amorphous alloys were prepared by chemical reduction method. Their catalytic activities of sulfolene hydrogenation have been measured.

- When the diffusion effect was eliminated, both NiB amorphous alloy and Raney Ni can exhibit excellent catalytic activity on sulfolene hydrogenation reaction.
- The differences of the particle sizes of NiB, NiBP and NiP amorphous catalysts had a direct correlation with the differences of their hydrogenation activity.
- Both NiB and CoB amorphous alloy catalysts were active in hydrogenation of sulfolene; the collaboration effect of Ni and Co element took place when mole ratio of Ni/Co ranged from 1.7 to 2.4.
- For NiCoB amorphous catalysts, the optimum mole ratio of Ni/Co is 2.4. And its catalytic activity was higher than that of Raney Ni in all reaction conditions.

Acknowledgements

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