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Short Communication

# Effect of polymers and alkaline earth metals on the catalytic performance of Ni–B amorphous alloy in benzophenone hydrogenation

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ABSTRACT

Soluble polymers are found to be effective in inhibiting the agglomeration of the active Ni particles in Ni–B amorphous alloy catalysts and then increase the catalysts activity in benzophenone hydrogenation. However, the acidic nature of polyethylene glycol 1000 will cause the dehydration of benzhydrol and decrease its yield. Here, we found that the addition of alkaline earth metals can tune the acid–base properties of the catalysts and overcome this shortcoming. Ba and polyethylene glycol 1000 doped Ni–B was found to exhibit excellent activity and selectivity to benzhydrol due to its larger surface areas, more surface active Ni species, and better acidic properties.

## 1. Introduction

Since 1980s, amorphous alloys have attracted much attention because of their interesting intrinsic properties, e.g., short-range order, long-range disorder, and high dispersion, as well as their potential applications in catalysts and hydrogen storage materials [1]. In particular, Ni–B amorphous alloys have exhibited excellent catalytic activity and selectivity equivalent or superior to those of conventional catalysts in various hydrogenations. Since agglomeration of the tiny particles in amorphous alloys usually decreased their activities, many types of modifiers, including metal, organic, and inorganic modifiers, have been used to overcome this shortcoming [2–6]. For example, Li and coworkers have found Ce-doped Ni–B amorphous alloy catalyst exhibiting higher activities than the undoped one for liquid-phase hydrogenation of furfural [6].

Polymers have been widely used in the field of catalysis due to their unique properties of macromolecular structure [7–9]. Though polymers are widely applied as carriers in the catalysts, only a few results have been reported on polymers used as modifiers. Particularly, the role of polymers as modifiers in amorphous alloy has not been reported. On the other hand, the alkaline earth metals have also been applied as effective modifiers to tune the acid–base properties of the catalysts due to their basic nature [10–12]. Yet, the synergistic effect of polymers and alkaline earth metals has never been reported.

In this paper, a series of polymers were first used as modifiers in Ni–B amorphous alloy and tested in benzophenone hydrogenation to benzhydrol, an important pharmaceutical intermediate [13]. It was found that a polyethylene glycol 1000 (PEG(1000)) modified Ni–B catalyst exhibited higher activity than the undoped Ni–B, but the selectivity to benzhydrol was lower due to the dehydration of benzhydrol. We then found that alkaline earth metals can increase the selectivity to benzhydrol effectively. The synergistic effect of polymers and alkaline earth metals on the catalytic performance of Ni–B amorphous alloy was studied and clarified based on necessary characterizations.

## 2. Experimental

### 2.1. Preparation of catalysts

The polymer-modified Ni–B amorphous alloy was prepared by adding 50 mL of a 1.0 M aqueous $KBH_4$ containing 0.2 M NaOH dropwise to 10 mL of a 0.5 M aqueous $NiCl_2 \cdot 6H_2O$ containing 1.0 g polymer with vigorous stirring while cooling in an ice bath to furnish a black precipitate. The precipitate was washed by deoxygenated distilled water until the washings were pH = 7. The catalyst was further washed with absolute ethanol three times to replace residual water and then stored under absolute ethanol. The obtained catalysts were denoted as Ni–B-p (p is the type of the polymer). When $X(NO_3)_2 \cdot nH_2O$ was also added in the $NiCl_2 \cdot 6H_2O$ and polymer solutions during the preparation, the catalysts so obtained were denoted as Ni–X-B-p (X = Mg, Ca, Sr, Ba, molar ratio X:Ni = 1:8, $n = 0$, 4 or 6).

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**Table 1**
Effect of polymers on Ni–B amorphous alloys in benzophenone hydrogenation.

| Catalyst | Conversion of benzophenone (%) | Selectivity to benzhydrol (%) | Selectivity to diphenylmethane (%) | Yield of benzhydrol[b] (%) |
|---|---|---|---|---|
| Ni–B | 57.0 | 81.3 | 14.1 | 46.3 |
| Ni–B-PVP[a] | 79.8 | 73.6 | 21.4 | 58.7 |
| Ni–B-PAA[a] | 63.7 | 72.3 | 22.6 | 46.1 |
| Ni–B-PVA[a] | 24.6 | 92.9 | 3.3 | 22.9 |
| Ni–B-PAM[a] | 8.7 | 92.0 | 4.8 | 8.0 |
| Ni–B-PEG(400) | 74.8 | 84.8 | 9.1 | 63.4 |
| Ni–B-PEG (1000) | 96.1 | 72.3 | 21.3 | 69.5 |
| Ni–B-PEG (2000) | 73.6 | 89.0 | 7.7 | 65.5 |
| Ni–B-PEG (10000) | 60.2 | 89.5 | 7.0 | 53.9 |

Reaction conditions: 6.0 g benzophenone, 0.5 g catalyst, 200 mL methanol, temperature at 403 K, initial P($H_2$) = 2.5 MPa, and reaction time 2 h.

[a] PVP: polyvinylpyrrolidone; PAA: polyacrylic acid; PVA: polyvinyl alcohol; PAM: polyacrylamide.

[b] Yield of benzhydrol=(conversion of benzophenone)×(selectivity to benzhydrol)/100.

### 2.2. Catalysts characterization

Bulk compositions were identified by inductively coupled plasma analysis (ICP) on a VISTA-MPX spectrometer. BET surface area was measured using a Micromeritics Tristar II 3020 surface area and pore analyzer. X-ray diffraction (XRD) patterns were acquired on a Bruker D8-ADVANCE X-ray diffractometer. Scanning electron microscopy (SEM) was carried out on a JEOL JSM-7500 electron microscope. The Fourier transform infrared spectra (FT-IR) were recorded with a Bruker VECTOR 22 Fourier transform spectrophotometer. $H_2$-chemisorption, temperature programmed desorption of $H_2$ ($H_2$-TPD) and temperature programmed desorption of $NH_3$ ($NH_3$-TPD) were performed on a TP-5000 instrument from Xianquan Ltd. X-ray photoelectron spectroscopy (XPS) measurements were recorded with a PHI 1600 spectroscope.

### 2.3. Catalyst activity test

Benzophenone hydrogenation was conducted as follows: benzophenone (6.0 g), catalyst (0.5 g), methanol (200 mL) were mixed in a 500 mL stainless steel autoclave equipped with a mechanical stirrer and electrical heating system. The air in the autoclave was first replaced with $H_2$ three times in succession at room temperature. Then the autoclave was pressurized with $H_2$ to 2.5 MPa, and heated to 403 K at a rate of 4 K/min. On reaching 403 K, hydrogenation was started by stirring the reaction mixture vigorously and proceeded for 2 h. Reaction mixtures were analyzed by a gas chromatography using a 30 m SE-54 capillary column and the product structures were confirmed by a gas chromatograph-mass spectroscopy (GC-MS) on Agilent 5975 C.

## 3. Results and discussion

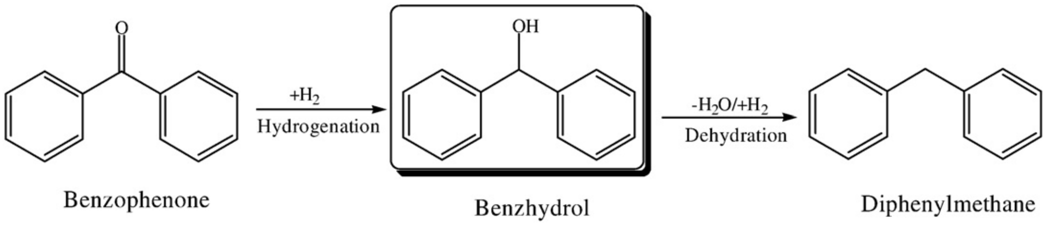
### 3.1. Catalyst selection

Table 1 shows the results of benzophenone hydrogenation over the Ni–B amorphous alloys. The undoped Ni–B exhibited a relatively low conversion (57.0%) and moderate selectivity to benzhydrol (81.3%), together with small amount of diphenylmethane as the major byproduct. Fortunately, most polymers improved the conversion of benzophenone; only polyvinyl alcohol (PVA) and polyacrylamide (PAM) modified amorphous alloys revealed terribly low activity. Considering that both PVA and PAM partly dissolved in precursor solutions, the in-situ prepared Ni–B particles should mostly adsorb on the surface of undissolved polymers and then lower the activity of these modified catalysts. In contrast, soluble polymers improved the dispersion of the active Ni species in the modified Ni–B amorphous alloys and then increased their activities. Interestingly, the conversion of benzophenone first increased and then decreased with the increase of polyethylene glycol (PEG) molecular weight for the PEG-modified Ni–B amorphous alloys. Ni–B-PEG(1000) showed the best conversion, but lower selectivity to benzhydrol (72.3%) compared with the undoped Ni–B. We ascribed this result to the acidic nature of PEG(1000), which will induce dehydration of the obtained benzhydrol to diphenylmethane (Scheme 1). Thus, some alkaline earth metals were added to tune the acid–base properties of Ni–B-PEG(1000) and the results are listed in Table 2.

Just as we have expected, the selectivity to benzhydrol all increased and reached at least 93.8% by the addition of alkaline earth metals. The conversion of benzophenone also increased with the increase of the basic properties of the alkaline earth metals and Ni–Ba-B-PEG(1000) showed the best conversion (96.8%), even a little higher than Ni–B-PEG(1000). Furthermore, the yield of benzhydrol over Ni–Ba-B-PEG(1000) (90.8%) was obviously higher than that of Ni–Ba-B (56.0%) (Table 2). Thus, Ni–Ba-B-PEG(1000) is proven to have the highest yield for the hydrogenation of benzophenone to benzhydrol due to the synergistic effect of PEG(1000) and Ba.

### 3.2. Catalyst characterizations

The results of compositions, BET surface areas and $H_2$-chemisorption of Ni–B, Ni–B-PEG(1000) and Ni–Ba-B-PEG(1000) are summarized in Table 3. From the ICP analysis, it is found that Ni–B-PEG(1000) contains similar B with Ni–B and the B contents increase remarkably with the addition of Ba. With the addition of PEG(1000), the BET surface area and pore volume of Ni–B only increased slightly, whereas both of them increased noticeably with further addition of Ba. Thus, Ni–Ba-B-PEG(1000) has the largest surface area among the catalysts studied, probably owing to the synergistic effect of PEG(1000) and Ba. With respect to $H_2$-chemisorption, the two PEG-modified catalysts show similar values and are both higher than the undoped Ni–B, which means the PEG-modified catalysts have larger number of active Ni species, in accordance with their activities in benzophenone hydrogenation.



**Scheme 1.** Possible mechanism of benzophenone hydrogenation.

**Table 2**
Effect of alkaline earth metals on Ni–B-PEG(1000) and Ni–B amorphous alloys in benzophenone hydrogenation.

| Catalyst | Conversion of benzophenone (%) | Selectivity to benzhydrol (%) | Selectivity to diphenylmethane (%) | Yield of benzhydrol[a] (%) |
|---|---|---|---|---|
| Ni–B | 57.0 | 81.3 | 14.1 | 46.3 |
| Ni–Ba-B | 62.8 | 89.2 | 4.4 | 56.0 |
| Ni–B-PEG (1000) | 96.1 | 72.3 | 21.3 | 69.5 |
| Ni–Mg-B-PEG (1000) | 82.3 | 94.9 | 3.1 | 78.1 |
| Ni–Ca-B-PEG (1000) | 91.7 | 94.4 | 3.9 | 86.6 |
| Ni–Sr-B-PEG (1000) | 92.8 | 94.5 | 3.6 | 87.7 |
| Ni–Ba-B-PEG (1000) | 96.8 | 93.8 | 3.0 | 90.8 |

Reaction conditions: 6.0 g benzophenone, 0.5 g catalyst, 200 mL methanol, temperature at 403 K, initial P($H_2$ ) = 2.5 MPa, and reaction time 2 h.

[a] Yield of benzhydrol = (conversion of benzophenone) × (selectivity to benzhydrol)/100.

**Table 3**
Physicochemical properties of the Ni–B amorphous alloys.

| Catalyst | Composition (atomic ratio)[a] | Surface area $m^2/g$ | Pore volume $cm^3/g$ | $H_2$-chemisorption $cm^3/g$ |
|---|---|---|---|---|
| Ni–B | $Ni_1B_{0.43}$ | 20.7 | 0.059 | 0.28 |
| Ni–B-PEG (1000) | $Ni_1B_{0.42}$ | 20.9 | 0.071 | 0.43 |
| Ni–Ba-B-PEG (1000) | $Ni_1Ba_{0.012}B_{0.58}$ | 37.5 | 0.089 | 0.42 |

[a] Based on ICP results.

Fig. 1 shows the XRD patterns of Ni–B, Ni–B-PEG(1000) and Ni–Ba-B-PEG(1000). The three catalysts were all present in the amorphous structure, as only one broad diffraction peak around $2\theta = 45°$ appeared [14,15], indicating that the addition of PEG(1000) and Ba had not changed the amorphous structure of these Ni–B catalysts.

Fig. 2 shows SEM images of the amorphous alloy catalysts. Each sample displayed approximately spherical morphology, consistent with other reported Ni-based amorphous alloy catalysts [16]. It is obvious that the particle sizes of the PEG-modified samples became smaller than the undoped Ni–B. Particularly, the particle sizes of Ni–Ba-B-PEG(1000) decreased to 30 to 70 nm and were homogeneously dispersed on its surface, explaining the highest surface area and pore volume of this catalyst. On the other hand, no evidence for the existence of PEG(1000) on the surface of the two PEG-modified samples can be found from the SEM results. So we proposed that most of PEG(1000) may be removed during washing in the preparation process and it indeed prevented the agglomeration of the amorphous alloy particles mainly in the reduction process of preparation to attain more active Ni species. The results that no characteristic peaks of PEG(1000) was detectable in the FT-IR spectroscopy and XRD curves of the PEG-modified catalysts proved this assumption.

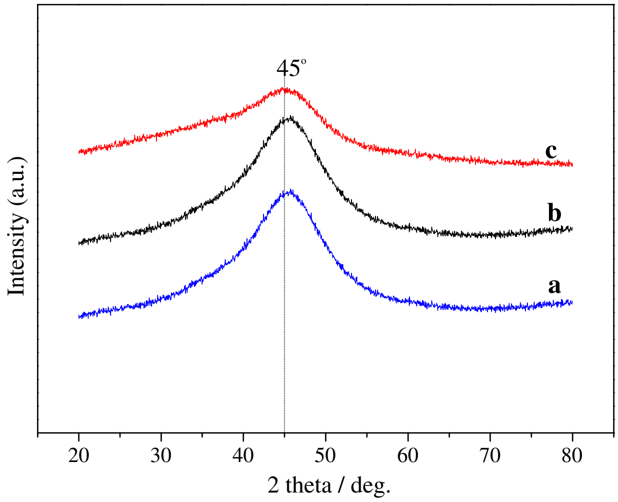


**Fig. 1.** XRD patterns of the amorphous alloy catalysts. (a) Ni–B, (b) Ni–B-PEG(1000), (c) Ni–Ba-B-PEG(1000).

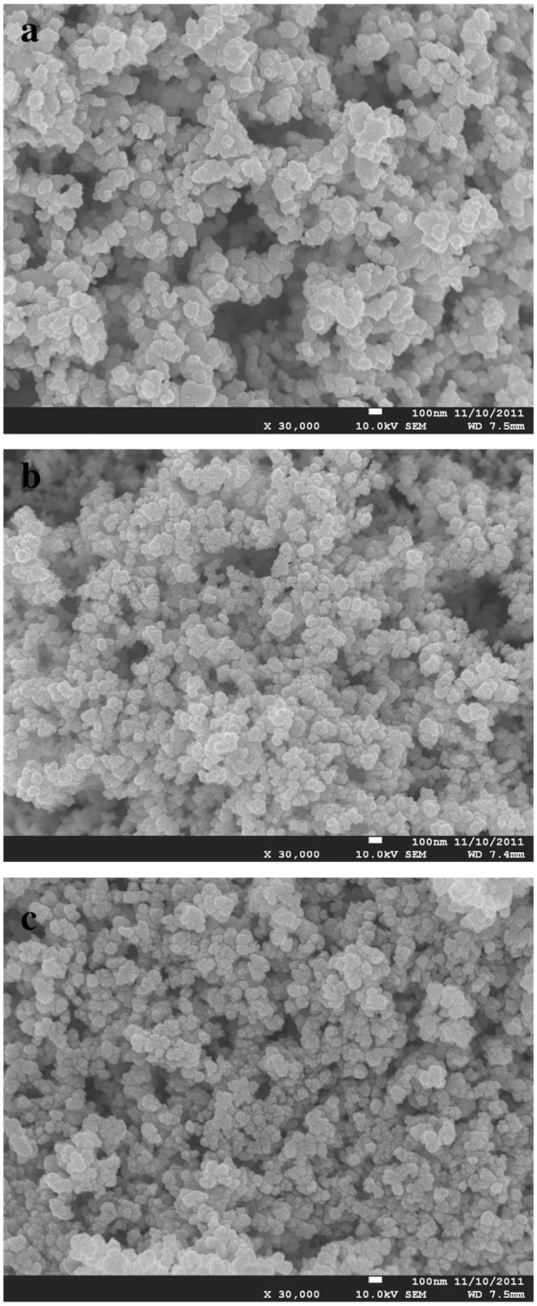


**Fig. 2.** SEM images of the amorphous alloy catalysts. (a) Ni–B, (b) Ni–B-PEG(1000), (c) Ni–Ba-B-PEG(1000).

The electronic states of surface Ni in the three catalysts are determined by XPS (Fig. 3). The characteristic peaks of Ni 2p centered at 853.4 eV and 856.9 eV in all samples can be assigned to metallic and oxidized Ni, respectively. Moreover, the peak areas of metallic Ni 2p in Ni–B-PEG(1000) and Ni–Ba-B-PEG(1000) become much larger

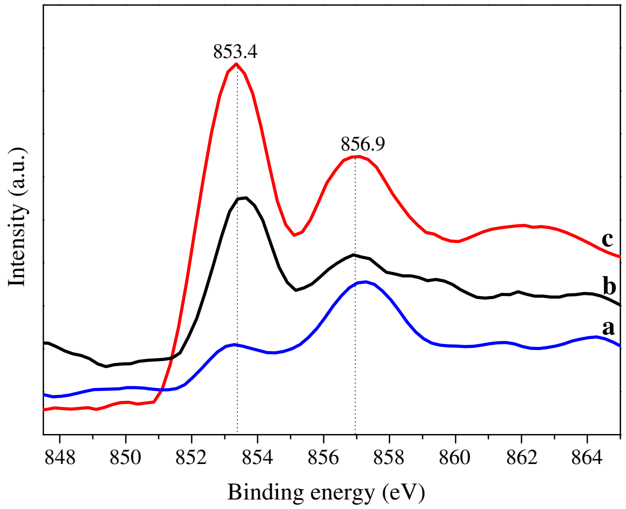


**Fig. 3.** XPS spectra of Ni 2p in the amorphous alloy catalysts. (a) Ni–B, (b) Ni–B-PEG(1000), (c) Ni–Ba-B-PEG(1000).

than that in Ni–B, indicating that more active Ni species were formed on the catalysts surface due to PEG(1000) modification. These conclusions were consistent with the $H_2$-chemisorption results.

Fig. 4 shows the $H_2$-TPD profiles of the three samples. Ni–B exhibits two obvious peaks at about 540 K and 650 K, indicating the presence of two adsorbing sites on its surface [5,15]. In contrast, both Ni–B-PEG(1000) and Ni–Ba-B-PEG(1000) have a sharp peak (at around 550 K), together with a very smooth peak (at around 600–800 K), thus it can be concluded that the active Ni species of the catalysts have a trend to become uniform in the presence of PEG(1000) [2,17].

$NH_3$-TPD curves of the Ni–B amorphous alloy catalysts are presented in Fig. 5. For Ni–B, the peaks centered at 580 K are assigned to the weakly acidic sites and the peaks centered approximately at 660 K are assigned to the moderately-strong acidic sites; whereas, Ni–B-PEG(1000) and Ni–Ba-B-PEG(1000) only showed one strong $NH_3$ desorption peak centered at around 650 K and 670 K, respectively (Fig. 5a). It is apparent that Ni–B-PEG(1000) has more acidic amounts than Ni–B, calculated from their peak areas, which can be ascribed to the acidity of PEG(1000), explaining the lower selectivity to benzhydrol over Ni–B-PEG(1000). Furthermore, Ni–Ba-B-PEG(1000) showed lower acidic amounts than Ni–B-PEG(1000) due to the tuning of Ba, and in turn, exhibited the best selectivity to benzhydrol among them. On the other hand, Ni–Ba-B-PEG(1000) showed the lowest desorption peak and the smallest acidic amounts among the four alkaline earth metals modified Ni–B-PEG(1000) catalysts, which was in good agreement with the basic sequence of the alkaline earth metals (Fig. 5b). Thus, it can be concluded that the basic properties of the alkaline earth metals modified Ni–B-PEG(1000) amorphous alloy catalysts increased with the increase of the basic properties of the alkaline earth metals.

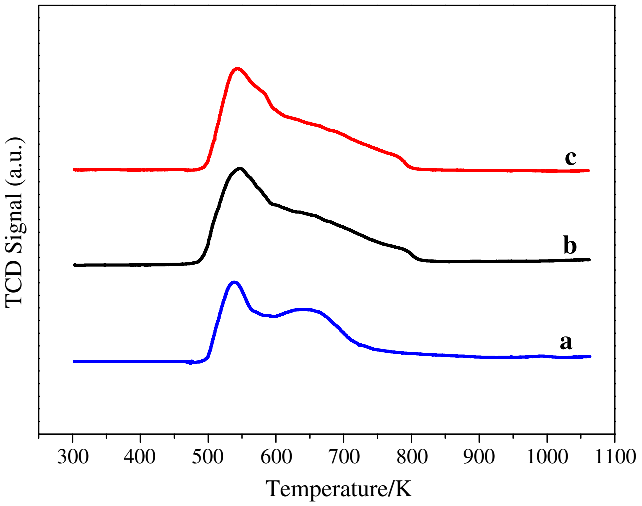


**Fig. 4.** $H_2$-TPD spectra of the amorphous alloy catalysts. (a) Ni–B, (b) Ni–B-PEG(1000), (c) Ni–Ba-B-PEG(1000).

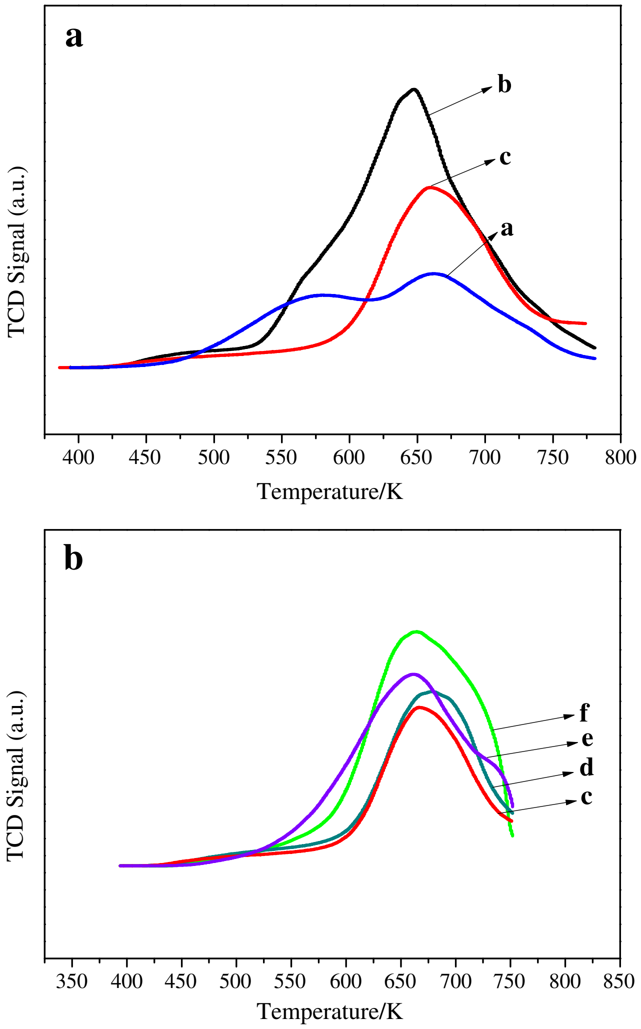


**Fig. 5.** $NH_3$-TPD spectra of the amorphous alloy catalysts (a: undoped and PEG(1000) doped ones; b: alkaline earth metal and PEG(1000) doped ones). (a) Ni–B, (b) Ni–B-PEG(1000), (c) Ni–Ba-B-PEG(1000), (d) Ni-Sr-B-PEG(1000), (e) Ni-Ca-B-PEG(1000), (f) Ni–Mg-B-PEG(1000).

## 4. Conclusion

Soluble polymers are proven to inhibit the agglomeration of the active Ni particles in Ni–B amorphous alloys during the preparation process, thus improving the dispersion of the active Ni species and then increasing the catalysts activity. On the other hand, the acidic nature of PEG(1000) will cause the dehydration of the obtained benzhydrol to diphenylmethane and lower its selectivity. Fortunately, the addition of alkaline earth metals can effectively adjust the acid–base properties of Ni–B-PEG(1000) and increase the selectivity to benzhydrol. It was found that Ni–Ba-B-PEG(1000) showed excellent activity and selectivity for the hydrogenation of benzophenone to benzhydrol due to its larger surface areas, more homogeneously dispersed surface active Ni species, and better acidic properties, demonstrating the synergistic effect of PEG(1000) and Ba.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2012.02.031.

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