Furfural Hydrogenation over Amorphous Alloy Catalysts Prepared by Different Reducing Agents

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The catalytic hydrogenation of furfural was studied over a series of Ni-B, Co-B, and Ni-Co-B amorphous alloy catalysts that were prepared by the chemical reduction method using KBH₄ and NaBH₄ as reducing agents. These catalysts were characterized by N₂ adsorption/desorption, XRD, XPS, FE-SEM, and TEM. The results showed that NaBH₄ had a much stronger reduction ability to enhance the surface concentration of the metallic active sites for furfural hydrogenation and electron transfer capability, leading to much higher hydrogenation activity. In the Ni-Co-B amorphous alloy catalyst, the equilibrium between the isolated Ni-B/Co-B active sites and the combined Ni-Co-B active sites was important in regulating furfural conversion and products distribution.

Keywords: Furfural hydrogenation; Ni-Co-B amorphous alloy; Reducing agent; Synergistic effect; Electron transfer capability

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INTRODUCTION

The diminishing supply of fossil fuels and increasing concern for environmental pollution create a necessity for the development of renewable energy, which can be obtained from alternative sources such as lignocellulosic biomass (Huber et al. 2006; Lin and Huber 2009). Furfural (FUR) is an important chemical platform for the production of lignocellulosic chemicals and biofuels (Li et al. 2016). Furfural hydrogenation has been used industrially to produce different chemicals, namely furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (MF), tetrahydrofuran (THF), and other value-added chemicals, such as cyclopentanol, cyclopentanone, dihydropyran, and 1,4-butanediol (Guo et al. 2014; Yan et al. 2014). In these products, FA can be applied in the production of resins, fine chemicals, lysine, vitamin C, lubricants, dispersing agents, plasticizers, and in the synthesis of fiber (Nagaraja et al. 2007a; Kotbagi et al. 2016). THFA is a green solvent in agricultural application, printing inks, industrial and electronic cleaners, and in the preparation of 1,5-pentanediol (Bhogeswararao and Srinivas 2015). Based on this background, different research groups have attempted to produce FA and THFA via the hydrogenation of FUR (Li et al. 2004; Nagaraja et al. 2007b; Audemar et al. 2015; Fulajtarova et al. 2015; Ghashghaee et al. 2017a).

By changing reaction conditions and catalyst systems, the target product of FUR hydrogenation can be selectively tuned. Liu et al. (1998) reported that, in the initial reaction phase, the formation of FA and tetrahydrofurfural are parallel and competitive, and THFA is the final product of further hydrogenation of FA and tetrahydrofurfural. Therefore, the choice of active component plays an important role in producing FA or THFA. The conventional catalysts used for FUR hydrogenation to FA are copper chromite (Cu-Cr)-based catalysts but their toxicity causes severe environmental pollution (Li et al. 2006). Recently, some chromium-free catalysts were developed (Ghashghaee et al. 2017b; Jiménez-Gómez et al. 2017; O'Driscoll et al. 2017; Tukacs et al. 2017). The metal-metalloid amorphous alloys have short-range ordered and long-range disordered atomic arrangements. They are important catalytic materials due to their unique chemical and structural properties, including broadly adjustable composition, structural homogeneity, and high concentration of coordinately unsaturated sites (Pei et al. 2012). Some amorphous alloy catalysts such as Ni-B (Lee and Chen 1999; Wang et al. 2003), Ni-B modified with different metallic promoter (Fe (Li et al. 2003b), Co (Luo et al. 2001), Ce (Li et al. 2004)), Co-B (Li et al. 2006), and Co-Mo-B (Chen et al. 2002), have been extensively investigated and are expected to be practically applied in liquid-phase FUR hydrogenation due to their high catalytic efficiency and low environmental impact (Li et al. 2004). The reaction mechanism of metal-metalloid amorphous alloys has also been broadly investigated. Pei et al. (2012) proposed that the promotion effect of metallic Co on Ni-B amorphous alloy occurred both electronically and structurally. Co donates electron to Ni, resulting in electron-enriched Ni and electron-deficient Co. Du et al. (2011) reported that the optimum Ni-Co-B catalyst with a Co/(Co+Ni) mole ratio of 0.5 was significantly more active than Ni-B and Co-B catalysts. Luo et al. (2001) also reported that ultrafine Ni-Co-B amorphous catalysts showed higher activity and better selectivity to FA than either Ni-B, or Co-B, or a mixture of Ni-B and Co-B catalysts. Therefore, the Ni-Co-B amorphous alloy catalyst is a promising candidate for effectively adjusting the product distribution of FUR hydrogenation.

During the preparation of metal-metalloid amorphous alloy catalysts *via* the chemical reduction method, KBH₄ and NaBH₄ are all frequently-used reduction agents for the reduction of metallic ions. The generation of molecular hydrogen during the hydrolysis of KBH₄ was less applicable than that of NaBH₄ due to its low gravimetric density of hydrogen, slow kinetics, and high production cost compared to NaBH₄ (Liu and Li 2009; Xu *et al.* 2011). However, it has not been reported whether the difference in reducibility of KBH₄ and NaBH₄ would impact the catalytic properties of Ni-Co-B amorphous alloy catalysts. In this paper, the effects of reduction agents on the structure and catalytic performance of Ni-Co-B amorphous alloy catalysts for FUR hydrogenation was systemically investigated.

EXPERIMENTAL

Catalyst Preparation and Activity Evaluation

The amorphous alloy catalysts were prepared *via* the conventional chemical reduction method (Li *et al.* 2003b). The furfural hydrogenation activity was evaluated in an autoclave. The experimental details are presented in the Supplementary materials.

RESULTS AND DISCUSSION

Bulk Composition and Textural Properties

The bulk composition and textural properties of the amorphous alloy catalysts are shown in Table 1. The reaction mechanism between Ni^{2+} (Co²⁺) and BH₄⁻ can be expressed by the following equations (Shen *et al.* 1993):

$$BH_4^- + 2H_2O = BO_2^- + 4H_2 \uparrow$$
(1)

$$BH_{4}^{-} + 2Ni^{2+}(Co^{2+}) + 2H_{2}O = 2Ni(Co) \downarrow + BO_{2}^{-} + 4H^{+} + 2H_{2} \uparrow$$
(2)

$$BH_4^- + H_2O = B \downarrow + OH^- + 2.5H_2 \uparrow$$
(3)

The relative rates of reduction reactions Eq. 2 and Eq. 3 manipulate the formation of amorphous alloy and influence their formation and electrochemical properties.

Catalysts	SBET	V _P (cm³/g)	D _P (nm)	Bulk comp.	XPS Peak Intensity (%) ^b					
	(m²/g)			(atom%) ^{°a}	I(Ni ^e)/I(Ni ^o)	I(Co ^e)/I(Co ^o)	I(B ^e)/I(B ^o)			
NiB-K	92.3	0.44	18.9	Ni _{63.6} B _{36.4}	Ni _{63.6} B _{36.4} 3.7/96.3 -		2.3/97.7			
Ni₃Co₁B-K	55.1	0.20	14.6	Ni _{48.7} Co _{18.9} B _{32.4}	16.4/83.6	31.5/68.5	7.9/92.1			
Ni₁Co₁B-K	51.0	0.18	13.7	Ni _{29.6} Co _{35.3} B _{35.1}	15.0/85.0	13.0/87.0	7.9/92.1			
Ni₁Co₃B-K	42.3	0.16	14.9	Ni _{14.0} Co _{50.7} B _{35.3}	20.9/79.1	31.8/68.2	12.2/87.8			
CoB-K	16.6	0.08	18.6	Co _{69.8} B _{30.2}	—/—	14.7/85.3	22.4/77.6			
NiB-Na	40.3	0.22	22.2	Ni66.3B33.7	50.1/49.9	—/—	16.5/83.5			
Ni₃Co₁B-Na	18.9	0.08	16.2	Ni _{48.1} Co _{18.7} B _{33.2}	51.0/49.0	51.2/48.8	22.0/78.0			
Ni1Co1B-Na	19.4	0.08	15.8	Ni _{30.5} Co _{35.8} B _{33.7}	22.5/77.5	11.5/88.5	16.7/83.3			
Ni₁Co₃B-Na	44.3	0.16	14.6	Ni14.4C049.4B36.2	36.2/63.8	42.4/57.6	17.9/82.1			
CoB-Na	180.3	0.29	6.3	CO67.7B32.3	—/—	1.0/99.0	10.4/89.6			
^a Determined by ICP-OES; ^b Area ratio of the Ni ^e (Ni ^e 2p _{3/2} and Ni ^e 2p _{1/2}) to Ni ^o (Ni ^o 2p _{3/2} and										
Niº2p1/2) peaks, Coe (Coe2p3/2 and Coe2p1/2) to Coo (Coo2p3/2 and Coo2p1/2) peaks, and Be to Bo										
peaks (main peak excluding satellite peak).										

Table 1. Textural Properties and Composition of Amorphous Alloy Catalysts

The change of B content in the catalysts prepared with NaBH₄ as a reduction agent showed a similar trend with those prepared with KBH₄. However, the highest B content belonged to Ni₁Co₃B instead of NiB. According to the above-mentioned reaction mechanism, the occurrence of BH₄⁻ hydrolysis to oxidized B species was unavoidable (Li *et al.* 1999). In addition, some oxidized metallic species also existed due to the poor reducing ability of BH₄⁻ when using ethanol as a preparation solvent (Li *et al.* 2000).

As can be seen in Table 1, the incorporation of Co into NiB had a large influence on the structural properties. Though there are some errors in the pore size distribution (PSD) calculated from different models (Rege and Yang 2000; Ghashghaee and Karimzadeh 2011), the conventional Barrett-Joyner-Halenda (BJH) model is reliable to obtain the PSD curve of those catalysts with similar characters. For the catalysts prepared by KBH₄, S_{BET} and V_P decreased gradually as the increase of Co/Ni ratio. For the NiB-K catalyst, the large surface area might be attributed to the presence of oxidized B species, which have promoted the dispersing of NiB particles (Li *et al.* 2006). This could be explained by the large H1 hysteresis loop on the N₂ adsorption/desorption isotherms (Fig. S1a). The increase of Co/Ni ratio might have improve the reduction between metallic ions and BH_4^- (Eq. 2), leading to the nonlinear decrease of S_{BET} . It also can be seen that NiB-K and CoB-K had more mesopores and macropores, which can be attributed to the aggregation of magnetic NiB and CoB particles (Fig. S2a).

For the catalysts prepared by NaBH₄, as the increase of Co/Ni ratio, the S_{BET} and V_P first increased and subsequently decreased. However, the D_P decreased nonlinearly, which is similar to the change of S_{BET} and V_P in the catalysts prepared by KBH₄. Due to the stronger reduction ability of NaBH₄ relative to KBH₄ (Akira *et al.* 1981), the sharp decrease in S_{BET} and V_P of NiB-Na relative to those of NiB-K can be ascribed to the higher disorder of NiB-Na. With the introduction of Co, the reduction of BH₄⁻ might be improved (Eq. 3). Much more electron transfer was achieved from B to Ni (Co) compared to NiB-Na catalyst. As a result, the disorder of Ni-Ni (Co) coordination and Co-Co (Ni) coordination was enhanced, thus decreasing the S_{BET} and V_P of the Ni₃Co₁B-Na catalyst. The further increase of Co content might have more oxidized Co species generated which served as a spacer, preventing the catalyst particles from aggregating and increasing surface area (Chen and Chen 2006). Therefore, the CoB-Na catalyst had the highest S_{BET} and V_P (Table 1) and showed the largest H1 hysteresis loop (Fig. S1b).

Morphology and Surface Composition

The morphology of all catalysts was characterized by Field Emission Scanning Electron Microscope (FE-SEM) and High Resolution Transmission Electron Microscope (HRTEM) as shown in Fig. 1 and Fig. S3, respectively. The NiB-K catalyst showed an inhomogeneous particle size of 7.6 ± 10 nm and presented some white gel-like substances which were ascribed to the oxidized B species (Fig. S3) (Li *et al.* 2003b). With the introduction of Co, Ni₃Co₁B-K mainly showed a "cauliflower" shape. The further increase in Co content promoted the gradual transformation of "cauliflower"-shaped particles into spherically-shaped particles.



Fig. 1. FE-SEM images of different amorphous alloy catalysts

Many small particles with a mean size of 3.9 nm were located on the middle part. For the CoB-K catalyst, the particle size increased to 5.3 ± 4.0 nm. When NaBH₄ was used as the reduction agent, NiB-Na displayed a "cauliflower" shape similar to Ni₃Co₁B-K with a homogeneous particle size distribution of 7.5 ± 3.1 nm (Fig. S3), indicating that the intensity and disorder of the NiB-Na amorphous alloy were promoted (Chen 1998).

The transformation of the morphology to a spherical shape with the introduction of a small quantity of Co indicates that the electron transfer between B and Ni might have been changed. When the Co/Ni ratio increased to 3/1, the dispersion of catalyst particles was further improved. Furthermore, CoB-Na displayed many big clusters surrounded with whiskers. Consequently, the amorphous alloy particles were difficult to be observed due to the formation of oxide crystals.

The XPS spectra of the amorphous alloy catalysts obtained from different reduction agents are shown in Fig. 2.



Fig. 2. Ni 2p, Co 2p, and B 1s XPS spectra of different amorphous alloy catalysts

As shown in Fig. 2 and Table 1, the peak intensity and surface density of elemental nickel (Ni^e) and elemental cobalt (Co^e) of the catalysts prepared by NaBH₄ were much higher than those of the catalysts prepared by KBH₄, which indicates that NaBH₄ had much stronger reduction ability than KBH₄. For those catalysts prepared by NaBH₄, the introduction of Co resulted in a slight increase in the surface concentration of Ni^e and elemental boron (B^e) without a shift in Binding Energy (BE), suggesting that the reduction between Ni²⁺ and BH₄⁻ was improved. The increase of the Co/Ni ratio from 1/3 to 1/1 led to obvious decrease in the surface density of Ni^e and B^e and a moderate increase in Co^e. Considering the results of BET and HRTEM investigations, it can be concluded that Ni and Co have a synergistic effect in manipulating the structure of the bimetallic Ni-Co-B amorphous alloys by improving the M-B (M= Ni and Co) interaction and increasing the structural disordering factors of Ni-Co-B (Wei et al. 2014). When the Co/Ni ratio gradually increased to 3/1, the Ni^e and Co^e of the catalysts all showed an increased surface concentration, especially for the Co^e, providing more active sites for FUR hydrogenation. However, for the CoB-Na catalyst, the strong heat release during the reduction process caused the easy oxidation of Co^e, resulting in the nearly undetected Co^e and the large amount of oxidized Co (Co^o) species which are visible in Fig. 1 and Fig. S3. Consequently, the very low Co^e/Co^o peak intensity ratio was due to the decreased surface concentration of Co^e.

Catalytic Activity and Reaction Mechanism

Table 2 summarizes the FUR hydrogenation properties of all catalysts. Ethanol was used as the reaction solvent and did not participate in the FUR hydrogenation reaction to form other byproducts. A blank experiment showed nearly no conversion of FUR.

Cotolyata	R _H ^m b	$R_{\rm H}^{\rm S}$	Con.	Sel. (%)			Yield (%)			
Calalysis	(mmol/h⋅g _M)	(mmol/h·m²)	(mole%)	MF	THFA	FA	MF	THFA	FA	
No catalyst	0	0	1.2	0	0	100	0	0	1.2	
NiB-K	2.9	0.1	53.4	0.4	14.9	84.7	0.2	8.0	45.2	
Ni₃Co₁B-K	70.2	1.3	89.0	0.5	28.4	71.1	0.4	25.3	63.3	
Ni₁Co₁B-K	76.5	1.5	93.1	0.1	22.2	77.7	0.1	20.7	72.3	
Ni₁Co₃B-K	110.6	2.6	100.0	1.0	75.2	23.9	0.9	75.2	23.9	
CoB-K	8.3	0.5	98.3	0.4	1.3	98.3	0.4	1.3	96.6	
NiB-Na	67.7	1.9	79.6	0.1	27.9	72.0	0.1	22.2	57.3	
Ni₃Co₁B-Na	64.7	3.5	83.9	0.1	24.2	75.7	0.1	20.3	63.5	
Ni₁Co₁B-Na	81.8	4.2	98.6	0.5	31.0	68.6	0.5	30.5	67.6	
Ni₁Co₃B-Na	99.7	2.3	99.8	1.1	87.0	11.9	1.1	86.9	11.8	
CoB-Na	120.6	0.7	99.8	1.3	11.8	87.0	1.3	11.7	86.8	
^a Reaction condition: Furfural (5 mL, 0.06 mol), ethanol (25 mL) as reaction solvent, catalyst (0.25										
g), $T = 373$ K, $p(H_2) = 3.0$ MPa, stirring rate = 800 rpm, 3 h; ^b The initial hydrogenation rate within										
the first 0.5 h reaction.										

Table 2. Furfural Hydrogenation Results over Amorphous Alloy Catalysts a

It can be seen that NiB-K and CoB-K showed extremely low initial hydrogenation rate ($R_{\rm H}^{\rm m}$) due to the low surface concentration of metallic Ni and Co. With the introduction and increase of Co, the $R_{\rm H}^{\rm m}$ showed a nonlinear increase. As demonstrated by BET and XPS results, the electron transfer from the alloying B to Ni remained at a low level over the NiB-K catalyst, which showed a low FUR conversion of 53.4% after reaction for 3 h. However, the FUR conversion and FA selectivity of CoB-K catalyst were much higher than those of NiB-K, indicating that the isolated Co-B active sites showed better hydrogenation activity of the C=O bond on the carbonyl group of the furfural molecule than the isolated Ni-B active sites. The increase of Co/Ni molar ratio has improved the activity of the NiCoB-K catalysts because the Ni active sites became more electron-enriched due to the increase of B^e content (Li *et al.* 2003a), which was favorable for electron donation to the π^* -orbital.

The FA selectivity in the NiCoB-K catalysts was lower than that of NiB-K and CoB-K, while the THFA selectivity was higher. Since the tetrahydrofurfural generated from the direct furan ring hydrogenation of FUR was not observed, it can be concluded that the interaction between Ni and Co enhanced the further hydrogenation of FA to THFA (Liu *et al.* 1998; Chen 1998). Ni₁Co₃B-K had the highest selectivity and yield of THFA. On one hand, the electron-enriched isolated Co-B active sites could facilitate the formation of H⁻ species (Noller and Lin 1984) and the activation of the adsorbed C=O group through an electron back-donation from the $d_{x^2-y^2}$ orbital of Co to the $\pi^*_{C=0}$ antibonding orbital of the C=O group, possibly promoting the hydrogenation conversion of FUR to FA. On the other hand, there is a strong electronic interaction in the combined Co-Ni-B active sites. The increase of Co content caused an increase of B content (Table 1), which made Ni active sites more electron-rich due to the electron-donation of the alloying B (Luo *et al.* 2001).

The catalytic properties of various catalysts prepared by NaBH₄ are also shown in Table 2. The FUR conversion showed a similar change trend to that of those catalysts prepared by KBH₄. However, NiB-Na and CoB-Na showed a higher $R_{\rm H}^{\rm m}$ than NiB-K and CoB-K, implying that they have more surface metallic active sites (Table 1). Ni₁Co₁B-Na showed the highest $R_{\rm H}^{\rm S}$ of 4.2 mmol/h·m² due to the optimum synergistic effect between Ni and Co. The change trend of FA and THFA selectivity in the NiCoB-Na catalysts could be explained by the proposed mechanism of the NiCoB-K catalysts as mentioned above. Though the CoB catalyst showed the highest selectivity and yield of FA whether the reduction agent was KBH₄ or NaBH₄, it was liable to be oxidized according to the XPS results (Fig. 2). The best catalyst for FUR hydrogenation to FA was Ni₁Co₁B-K and the best catalyst for FUR hydrogenation to THFA was Ni₁Co₃B-Na.

The evolution of the FUR conversion and the products selectivity versus reaction time over these two catalysts are provided in Fig. 3. The FUR conversion of Ni₁Co₁B-K catalyst showed a linear increase before 150 min reaction and a facile increase to the maxima of 92.1% during the latter 90 min reaction. However, the products selectivity did not obviously change. THFA and FA were simultaneously generated from FUR hydrogenation throughout the whole reaction process. In the case of Ni₁Co₃B-Na catalyst, the FUR conversion showed a sharp increase and achieved almost complete transformation in the foregoing 90 min reaction. The fast hydrogenation of FUR by the saturation of C=O bond on the carbonyl group of FUR molecule to FA obviously increased the FA selectivity to the summit of 95.1% during the front 30 min reaction due to much more electron-enriched isolated Co-B active sites. Afterwards, the THFA selectivity sharply increased at the cost of the decrease of FA selectivity, indicating that FA was further hydrogenated into THFA by the saturation of C=C bond on the furan ring of FA molecule as mentioned above. After reaction for 4 h, the selectivity of FA and THFA was 7.6% and 90.4%, respectively. The reaction kinetics was measured as shown in Fig. 4. It is evident that the change of Ni/Co molar ratio had a large effect on the plot. The Ni₁Co₁B-K catalyst showed a steady ability for FA production with the highest yield of 75.8% due to the undiminished surface Ni^e and Co^e after reaction as showed in Fig. 5. The Inductively Coupled Plasma (ICP) analysis showed that there was a mass loss of 7.8 wt% of the NiCoB total content in the recycled catalyst, indicating that the stability of NiCoB amorphous alloy catalysts needed to be improved which will be conducted in our following work. The Ni₁Co₃B-Na catalyst showed the highest THFA yield of 90.3% with a FUR conversion of 99.9%, which is superior to the bimetallic Cu-Ni catalysts under more severe conditions (Liu *et al.* 2016).



Fig. 3. Effects of reaction time on FUR hydrogenation properties over different catalysts: (a) Ni₁Co₁B-K; (b) Ni₁Co₃B-Na. Reaction conditions: Furfural (12 mL, 0.144 mol), ethanol (60 mL) as reaction solvent, catalyst (0.60 g), T = 373 K, $p(H_2) = 3.0$ MPa, stirring rate = 800 rpm



Fig. 4. Kinetics profile of THFA and FA production from FUR hydrogenation over different

catalysts: (a) Ni1C01B-K; (b) Ni1C03B-Na. Reaction conditions were the same as Fig. 3



Fig. 5. Ni 2p and Co 2p XPS spectra of Ni₁Co₁B-K catalyst before and after FUR hydrogenation reaction. Reaction conditions were the same as Fig. 3

A plausibly dominant furfural adsorption model and corresponding hydrogenation performances over different Ni-Co-B amorphous alloy catalyst are shown in Fig. 6. When the Co/Ni ratio was 1/1, the equilibrium between the isolated Ni-B/Co-B active sites and the combined Ni-Co-B active sites was achieved to optimize the synchronous production of FA and THFA. When the Co/Ni ratio was 3/1, much more isolated Co-B active sites facilitated the prompt deep hydrogenation of FA to THFA.



Fig. 6. A plausibly dominant furfural adsorption model and corresponding hydrogenation performance over Ni₁Co₁B and Ni₁Co₃B amorphous alloy catalysts

CONCLUSIONS

- 1. The difference in reduction ability of reduction agents and the Ni/Co molar ratio had obvious effects on the formation, disorder, and dispersion of amorphous alloy particles, leading to a great change in the activity and products selectivity of NiCoB amorphous alloy catalysts during the furfural (FUR) hydrogenation reaction.
- 2. Compared with KBH₄, the catalysts prepared using NaBH₄ as the reduction agent has much higher intrinsic activity due to much more surface metallic active sites for furfural adsorption and hydrogenation and better electron transfer capability.
- 3. The isolated Co-B active sites showed better hydrogenation activity of the C=O bond on the carbonyl group of furfural molecule than the isolated Ni-B active sites. The combined Ni-Co-B active sites with much more electron transfer promoted the deep hydrogenation of the C=C bond on the furan ring of furfuryl alcohol molecule.

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APPENDIX

S1. EXPERIMENTAL

Materials

Furfural (99%), furfuryl alcohol (98%), NaBH₄ (98%), and KBH₄ (97%) were purchased from Aladdin (Shanghai, China). Tetrahydrofurfuryl alcohol (99%) was purchased from Adamas-beta (Shanghai, China). 2-Methylfuran (98%) was purchased from TCI (Shanghai, China). Nickel acetate (C₄H₆O₄Ni·4H₂O), cobalt acetate (C₄H₆O₄Co·4H₂O), and absolute ethyl alcohol (EtOH) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All reagents were directly used without further treatment.

Catalyst Preparation

The amorphous alloy catalysts were prepared by the conventional chemical reduction method according to the reported procedure (Li *et al.* 2003): 48 mL 2.0 M KBH₄ or NaBH₄ aqueous solution containing 0.2 M NaOH was dropwise added into 30 mL ethanol solution containing some content of C₄H₆O₄Ni·4H₂O, C₄H₆O₄Co·4H₂O or the mixture of C₄H₆O₄Ni·4H₂O and C₄H₆O₄Co·4H₂O with different Ni/Co molar ratio (3/1, 1/1 and 1/3) under vigorous stirring. The total molar amount of metallic ions was 0.024. The reaction was performed at 273 K for about 3.0 h in an ice-water bath under consecutive nitrogen flow of 50 mL/min. The resulting black solid was washed with deionized water several times until pH \sim 7 was achieved. It was further washed with EtOH and finally, it was stored in EtOH to avoid oxidation by air until the time of use. The catalysts with different Ni/Co molar ratio were marked as NiB, Ni₃Co₁B, Ni₁Co₁B, Ni₁Co₃B, and CoB and the "K" or "Na" was close behind to indicate the specific reducing agent.

Catalyst Activity Evaluation

Liquid phase furfural hydrogenation was carried out in a 100 mL YZPR-100 (M) stainless steel autoclave equipped with an electrical heating jacket and a mechanical stirrer, containing 0.25 g of catalyst, 5 mL of FUR and 25 mL of ethanol. The air in the autoclave was excluded completely by repetitive filling with N₂ four times and H₂ three times. Then the autoclave was filled with H₂ up to 3.0 MPa. Then, the reactor was heated to a desired temperature (373 K) with a stirring rate of 200 rpm. When the hydrogen pressure reached a steady state, the hydrogenation was started immediately by adjusting the stirring rate to 800 rpm. According to the drop of H₂ pressure within the first 0.5 h, the initial hydrogenation rate (the H₂ uptake rate per gram of M (M= Ni, or Co, or the mixture of Ni and Co), $R_{\rm H}^{\rm m}$ in mmol·h⁻¹·gM⁻¹) was calculated according to the ideal gas equation (Li et al. 2006). The areal activity (the H₂ uptake rate per m^2 of the surface area, $R_{\rm H}^{\rm S}$ in mmol·h⁻¹·m⁻²) was also calculated, which could be roughly considered as the intrinsic activity (Li et al. 2006). After reaction for 3 h, the liquid product was detected by a gas chromatographic analysis (GC 9900, Jiafen, Beijing; Column: FFAP, 30 m \times 0.25 mm \times 0.25 µm) equipped with a flame ionization detector (FID). The FUR conversion and the selectivity to different product was calculated according to the study of Sharma et al. (2013). All results were reproduced, and the errors were limited within $\pm 5\%$.

Catalyst Characterization

The bulk compositions of the catalyst samples were determined by the OPTIMA 8000 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, PerkinElmer). The Brunauer-Emmet-Teller surface area (S_{BET}), pore volume (V_p), and average pore diameter (D_p) of the catalysts were detected by the N₂ adsorption/desorption isotherms at 77 K using a ASIQMO002-2 analyzer (Quantachrome, US). The samples were degassed under vacuum at 353 K for 6 h prior to measurement. Powder X-ray diffraction (XRD) patterns were measured at $2\theta = 5$ to 80° using a D/max-RA X-ray diffractometer (Rigaku, Japan) with Cu K α radiation ($\lambda = 0.154$ nm) operated at 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS) measurement was carried out on an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific Inc., US) with the Al Ka radiation to determine the surface atomic ratios and valence states of elements of the fresh samples. In order to subtract the surface charging effect, the C1s peak has been fixed at binding energy of 284.6 eV. The morphology of the fresh catalysts was observed by a Hitachi S-4800 high resolution Field Emission Scanning Electron Microscope (FE-SEM, Hitachi, Japan) operated at 1.0 kV and 10 µA. High Resolution Transmission Electron Microscope (HRTEM) analysis and selected area electron diffraction (SAED) were performed on a JEM-2100F microscope (JEOL, Japan) operating at 200 kV. Samples for TEM were prepared by dispersing the samples in ethanol followed by ultrasonication. Several droplets of dispersion were placed on carbon-coated copper grids.

S2. FIGURES



Fig. S1. N₂ adsorption/desorption isotherms of fresh amorphous alloy catalysts prepared by different reducing agents. Solid line: Adsorption; Dash line: Desorption.



Fig. S2. BJH pore size distribution of fresh amorphous alloy catalysts prepared by different reducing agents

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Fig. S3. HRTEM images of fresh amorphous alloy catalysts prepared by different reduction agents. The insert is the corresponding particle size distribution (PSD) and SAED image.

The amorphous character of the as-prepared alloy catalysts was verified by selected-area electron-diffraction (SAED) image, which shows a halo diffraction pattern rather than distinct dots (He *et al.* 2002) (Fig. S3, insert).



Fig. S4. XRD patterns of fresh amorphous alloy catalysts prepared by different reducing agents

All catalysts exhibited two broad peaks around $2\theta = 25^{\circ}$ and 45° , respectively. The former is attributed to the amorphous boron oxides (Li *et al.* 2001) and the latter indicates the presence of a typical amorphous alloy structure (Yoshida *et al.* 1982). The former peak intensity gradually increased while the latter peak intensity decreased with the decrease of Ni/Co ratio from 3/1 to 1/3. In addition, NiB-K showed extra broad peaks that locating on $2\theta = 35^{\circ}$ and 60° , which are also ascribed to oxidized boron species in the forms of Na₂B₄O₇ and BO₂⁻ (Li *et al.* 2006), indicating that the BH₄⁻ hydrolysis was strongly occurring during the preparation process of NiB-K.

S3. REFERENCES

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