Furfural Hydrogenation to Furfuryl Alcohol over a Novel Ni–Co–B Amorphous Alloy Catalyst

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The ultrafine Ni–Co–B amorphous catalysts were employed in liquid-phase furfural hydrogenation, which showed higher activity and better selectivity to furfuryl alcohol than either Ni–B, or Co–B, or the mixture of Ni–B and Co–B catalysts. The promoting effect of Co-dopant was briefly discussed.

Furfuryl alcohol (FFA) is an important intermediate in the manufacturing of lysine, vitamin C, plastics, and many furan-type resins. It can also be used as a solvent, lubricant, dispersing agent, and plastifier. There are two ways of producing FFA through hydrogenation of furfural (FFR), gas phase and liquid phase.[1–3] Most companies adopt gas phase hydrogenation, while in some countries, e.g. in China, liquid phase hydrogenation is frequently employed and the Cu–Cr catalyst and its modified forms are usually employed.[3] Raney metal, such as Raney Ni, Raney Co and Raney Cu, have also been reported as active catalysts in FFR hydrogenation.[4] The disadvantages of these catalysts are the poor activity or/and the poor selectivity to FFA. Perhaps, the greatest drawback is their high toxicity, which causes severe environmental pollution. In this paper, we reported a novel ultrafine Ni–Co–B amorphous alloy, which is proved to be a clean and effective catalyst for FFR hydrogenation to FFA.

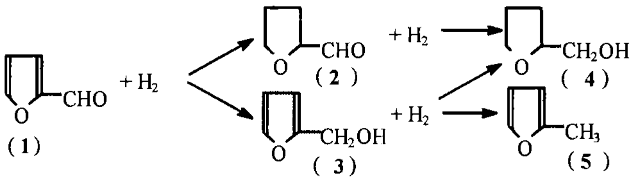
The Ni–Co–B sample was prepared in the procedure described as follows: 34 mL 2.0 M KBH_4 aqueous solution containing 0.20 M NaOH was added dropwise over 1.5 h period into 20 mL aqueous solution containing desired amount of $NiCl_2$ and $CoCl_2$ at 273 K and vigorous stirring. The molar ratio between KBH_4 and the total metal was 4 : 1 , which could ensure the complete reduction of both Ni^{2+} and Co^{2+} in the solution. The reaction was kept for another 1.0 h until no significant bubbles were observed. The black solid was washed free from Cl^- and K^+ ions with distilled H_2O (until pH 7 was obtained). Then, it was further washed with absolute alcohol (EtOH) and finally, kept in EtOH until the time of use. The crystallized Ni–Co–B alloy was obtained by treating the fresh sample at 773 K for 2 h in N_2 flow. The Ni–B and Co–B samples were prepared in the similar way to that of Ni–Co–B by using the solution containing $NiCl_2$ or $CoCl_2$ alone. The ultrafine Ni powder was prepared by using hydrazine hydrate ($NH_2NH_2{\cdot}H_2O$) instead of KBH_4 at 361 K.

The XRD patterns revealed that the fresh Ni–Co–B sample was present in an amorphous structure regardless the molar ratio (X_{Co}), since only one broad peak around $2\theta = 45°$ was observed.[5] After being treated at 773 K for 2 h in N_2 flow, various diffractional peaks appeared, showing the occurrence of crystallization at high temperature since the amorphous structure is thermodynamically metastable. The XRD patterns also demonstrated that most of Ni–Co–B alloy decomposed into metallic Ni and Co after being crystallized. According to the TEM pictures, the fresh Ni–Co–B sample was present in spherical particles with the average size around 200–300 nm. While, big lumps appeared after being crystallized, showing the gathering of the Ni–Co–B alloy particles at high temperature.

The XPS spectra of the Ni–Co–B sample revealed that the nickel and cobalt were mainly present in the metallic state with the binding energy (BE) of 853.1 eV ($Ni2_{p_{3/2}}$) and 777.8 eV ($Co2_{p_{3/2}}$), respectively. In comparison with the standard BE values of pure metallic Ni and Co, very little or no BE shift was observed. The boron species were present in two states. In B_{1s} level, the peak around 188.2 eV was attributed to the alloying B with Ni. While the peak around 192.5 eV was attributed to the boron oxides. In contrast to Co and Ni, the BE value of the alloying B was 1.1 eV higher than that of pure B, showing that partial electron was donated, which was most likely accepted by the alloying Ni and Co. The failure in observing the BE shift of either Ni or Co was mainly attributed to the much bigger size of their atoms in comparison with the B atom.[6]

Liquid phase hydrogenation of FFR was performed at 373 K and 1.0 MPa in a stainless steel autoclave, in which 1.0 g catalyst, 10 mL FFR, and 30 mL EtOH were mixed. During the hydrogenation, the reaction mixture was stirred vigorously at 1200 rpm to eliminate the diffusion effects. The hydrogenation activity was determined by monitoring the drop of H_2 pressure with the reaction time within initial 1.0 h period, from which, the initial specific activity (R^m /mmol·h^{-1}·g^{-1}), the H_2 uptake rate per gram of catalyst was calculated according to the ideal gas equation. The areal activity (R^s /mmol·h^{-1}·m^{-2}), the H_2 uptake rate per m^2 of catalyst's surface area (determined by BET method) was also calculated in order to exclude the effect of metal dispersion. The reaction products were analyzed by a gas chromatograph (GC 102) equipped with a 10% TEG-GDX 102 column and an FID, in which the oven temperature was 461 K.

Usually, the reaction was very complex. Besides the main product FFA (**3**), various side products could be formed. A possible reaction scheme was described as follows.



Under the present conditions, the as-prepared Ni–Co–B catalyst was found to be highly selective in FFR hydrogenation with almost the exclusive formation of FFA (selectivity > 99%). The activities of different catalysts were summarized in Table 1.

As shown in Table 1, the activity of Ni–Co–B amorphous catalyst was much higher than that of Ni–B amorphous catalyst. Since the activity of Co–B amorphous catalyst was much lower than that of Ni–B, one can consider that Ni served as the active sites while Co acted as the promoters in the Ni–Co–B amorphous catalyst. As no significant increase in the activity was observed when Co–B was mixed mechanically with Ni–B, one can conclude that the promoting effect of Co-dopant was mainly attributed to its chemical effect.

Table 1. Some properties of the as-prepared catalysts[a]

Sample	Composition /atom%	S_{BET} /$m^2 \cdot g^{-1}$	R^m /$mmol \cdot h^{-1} \cdot g^{-1}$	R^S /$mmol \cdot h^{-1} \cdot m^{-2}$
Ni–B(fresh)	$Ni_{75.0}B_{25.0}$	17.8	168.3	9.46
Co–B(fresh)	$Co_{76.0}B_{24.0}$	25.3	75.7	2.99
Ni–Co–B(fresh)[b]	$Ni_{35.6}Co_{34.7}B_{29.7}$	23.4	254.4	10.87
Ni–Co–B(cry)[c]	$Ni_{35.6}Co_{34.7}B_{29.7}$	7.8	56.8	7.28
Ni–B + Co–B[d]	/	22.3	91.7	4.11
Ni powder	Ni	13.8	99.4	7.20

[a]Reaction conditions: 1.0 g catalyst, 10 mL FFR, 30 mL EtOH, 1.0 MPa, 373 K. [b]X_{Co} = 0.50. [c]Obtained by treating the fresh sample at 773 K in N_2 flow for 2.0 h. [d]Mixture of Ni–B and Co–B amorphous alloys (X_{Co} = 0.50).

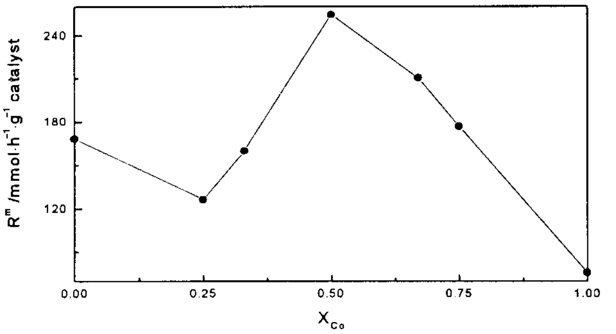


Figure 1. Dependence of the activity (R^m) of Ni–Co–B amorphous catalyst on the Co content (X_{Co}). Other reaction conditions are given in Table 1.

To understand the promoting effect of Co-dopant, the dependence of the hydrogenation activity of Ni–Co–B amorphous alloy catalyst on the Co content (X_{Co}) was measured. As shown in Figure 1, the activity first increased and then decreased with the increase of X_{Co}. The optimum X_{Co} was located at 0.50. The kinetic studies revealed that the hydrogenation of FFR under the present conditions was first order with respect to hydrogen pressure and zero order with respect to FFR concentration. This implied that the adsorption of FFR on the catalyst's surface was nearly saturated, while the adsorption of hydrogen was quite unsaturated. As the hydrogen and carbonyl group shared the same active sites, the more the carbonyl group adsorbed, the less the hydrogen adsorbed and in turn the lower the hydrogenation activity obtained. This could explain why the Co–B amorphous catalyst exhibited much lower activity than the corresponding Ni–B one since the CO thermal-programmed desorption (TPD) curves demonstrated that the Co active sites had much strong adsorbing ability for the carbonyl group than the Ni actives. In addition, the higher activity of Ni–B amorphous alloy than that of pure Ni powder could also be understood by considering the electron-enrichment of Ni active sites in the Ni–B sample owing to the presence of alloying B, which could repel the adsorption of carbonyl group (as confirmed by CO TPD which showed that the CO desorption peak shifted negatively 50 K in the presence of alloying B), leaving more Ni active sites for the hydrogen adsorption.

Based on the above assumption, the promoting effect of Co-dopant on the activity of Ni–Co–B amorphous catalyst could be explained by considering the following factors: (1) The addition of the Co-dopant leads to an increase in the surface area (see Table 1); (2) Comparing the composition of Ni–Co–B sample with that of Ni–B sample, one can see that the addition of the Co-dopant caused a considerable increase in the B content, which made Ni active sites more electron-rich owing to the electron-donation of the alloying B; (3) In Ni–Co–B amorphous catalyst, the Co sites favored the adsorption of carbonyl group in FFR, which could save more Ni active sites for hydrogen chemisorption.

Except for the above promoting effects of the Co-dopant, it should also be noted that the Ni content in the Ni–Co–B alloy decreased with the increase of Co content since the same amount of catalysts (1.0 g) was used in all the experiments. At low Co content (X_{Co} < 0.50), the promoting effect of Co-dopant was dominant. So, the activity increased with the increase of Co content; At high Co content (X_{Co} > 0.50), the decrease of Ni content was dominant. Under that case, the activity decreased with the increase of Co content.

Another important result drawn from Table 1 is the abrupt decrease in the activity of Ni–Co–B amorphous catalyst after being crystallized. On one hand, this could be attributed to the decrease in the surface area due to the gathering of Ni–Co–B particles at high temperature. On the other hand, since considerable decrease in R^s value of the Ni–Co–B catalyst was also observed after crystallization, the change in the nature of the active sites, both the structural and electronic effects, should also be considered to explain the crystallization deactivation. The structural effect was mainly attributed to the unique amorphous characteristics which has been claimed to favor most of hydrogenating reactions.[7,8] In addition, our calculation from the EXAFS data also demonstrated that the Ni active sites in Ni–Co–B amorphous alloy were more highly unsaturated and their distribution was more homogeneous than in the corresponding crystallized Ni–Co–B catalyst. It was also found that the interaction between neighboring active sites in the Ni–Co–B amorphous alloy was much stronger than that in the crystallized Ni–Co–B catalyst. These structural properties were favorable for the hydrogen adsorption and in turn the hydrogenating reactions.[9] The electronic effect was mainly attributed to electron-rich active sites in the Ni–Co–B amorphous alloy owing to the electron-donation of the alloying B. As discussed above, such active sites could decrease the adsorption of FFR via carbonyl group and in turn, increase the hydrogen adsorption. After being crystallized, the XRD patterns demonstrated that most of Ni–Co–B alloy decomposed into metallic Ni and Co. Thus, the electronic effect disappeared, which could also account for the lower activity of the crystallized Ni–Co–B catalyst.

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