

Hydrogenation of Cinnamaldehyde to Cinnamyl Alcohol over An Ultrafine Co-B Amorphous Catalyst

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Abstract: A novel Co-B amorphous alloy catalyst in the form of ultrafine particles was prepared by chemical reduction of CoCl_2 with aqueous NaBH_4 , which exhibited excellent activity and selectivity during the hydrogenation of cinnamaldehyde to cinnamyl alcohol in liquid phase. The optimum yield of cinnamyl alcohol was 87.6%, much better than the yield of using Raney Ni, Raney Co and other Co-based catalysts.

Keyword: Co-B amorphous catalyst, hydrogenation, cinnamaldehyde, cinnamyl alcohol.

The selective hydrogenation of α , β -unsaturated carbonyl compounds to unsaturated alcohols caused wide attention because of its practical importance and fundamental interest¹. A typical example is the hydrogenation of cinnamaldehyde (CMA) to cinnamyl alcohol (CMO), one of the important starting materials for production of perfumes, flavorings, pharmaceuticals, and other fine chemicals. However, it is a challenging task to accomplish selective hydrogenation of the C=O bond since the C=C bond is more easily hydrogenated. Only a few catalysts suitable for that purpose have been reported hitherto, most of them are Pt- and Co-based catalysts²⁻⁶. So this hydrogenation reaction is still in the forefront of recent catalysis research including the preparation of new catalysts or their modification by adding metal salts. As well known, the amorphous alloys represent a new class of materials with short-range ordering structure and special physical and chemical properties which may provide a pathway to novel, more active and selective catalysts. Various Ni-based amorphous catalysts have been used for decades, but reports on Co-based amorphous catalysts are limited⁷⁻¹⁰. In this communication, we reported an ultrafine Co-B amorphous catalyst prepared by chemical reduction, which exhibited higher activity and/or better selectivity to CMO than other catalysts including Raney Co, Raney Ni, and crystallized Co-B catalyst for CMA hydrogenation in liquid-phase.

Experimental

The Co-B amorphous catalyst was prepared by reducing CoCl_2 with 2.0 mol/L KBH_4 (molar ratio = 1:4) in aqueous solution at room temperature. The resulting black solid was washed with distilled H_2O until pH reached 7, then washed with alcohol (EtOH) for

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three times and finally stored in EtOH. The crystallized Co-B was obtained by treating the fresh Co-B at 773 K in H₂ flow for 2.0 h. Raney Co and Raney Ni were prepared by alkali leaching commercially available Co-Al and Ni-Al alloy (50/50, w/w), respectively.

The composition of the Co-B catalyst was determined by means of inductively coupled plasma (ICP, Jarrell-As Scan 2000). Its particle size was evaluated by the transmission electron micrograph (TEM, Hitachi H 600). The active surface area (S_{act}) was measured by H₂ chemisorption as described previously⁸. The structure of the Co-B catalyst was investigated by X-ray powder diffraction (XRD, Bruker AXS D8-Advance with Cu K α radiation) and its surface electronic state was analyzed by X-ray photoelectron spectroscopy (XPS) with C_{1s} = 284.6 eV as the reference¹¹.

Liquid phase hydrogenation of CMA was carried out at 383 K and 1.0 MPa in a 500 mL stainless steel autoclave containing 5.0 g catalyst, 15 mL CMA, and 105 mL EtOH with vigorous stirring to eliminate the diffusion effects. The initial specific activity (the H₂ uptake rate per gram of cobalt, R^{m} = mol/h-g Co) was obtained according to the drop of P_{H_2} within the first 0.5 h. In order to compare the intrinsic activities, the areal activity (the H₂ uptake rate per m² of the active surface area, R^{s} = mol/h-m² Co) was also calculated according to R^{m} and S_{act} . During the reaction, the samples were withdrawn every 30 min to determine the actual conversion and selectivity. The reaction products were analyzed by gas chromatography (GC 102) with FID.

Results and Discussion

The amorphous structure of the as-prepared Co-B sample was determined by XRD patterns. One broad peak around $2\theta = 45^\circ$ appeared for the fresh Co-B sample. After the Co-B sample treating at 773 K for 2 h, a lot of sharp peaks appeared in XRD, corresponding to metallic Co, crystalline Co₂B alloy and crystalline Co₃B alloy. These results demonstrated that the fresh Co-B sample was present in a typical amorphous structure and the heating treatment caused the crystallization¹⁰ together with the partial decomposition of Co-B alloy. TEM morphology revealed that the fresh Co-B sample was present in the form of ultrafine particles with the average size around 100 nm. Treatment at high temperature caused the gathering of these Co-B alloy particles.

The XPS spectra of the Co-B amorphous catalyst demonstrated that all cobalt species were present in the metallic state corresponding to the binding energy (BE) of 778.3 eV. While, boron species were present in both the alloying and oxidizing states corresponding to BE of 188.2 eV and 192.5 eV, respectively. The BE value of alloying B was 1.0 eV higher than that of the pure boron powder (187.2 eV), indicating that partial electrons transferred from B to the vacant d-orbital of Co, making the Co electron-rich, but the BE shift of the metallic Co was not observed due to the atomic weight of Co is greater than that of B¹¹.

The composition and the active surface area (S_{act}) of various catalysts were listed in **Table 1**, from which one can see that the crystallization had no appreciable influence on the composition but it caused an abrupt decrease in S_{act} , owing to the gathering of Co-B alloy particles at high temperature.

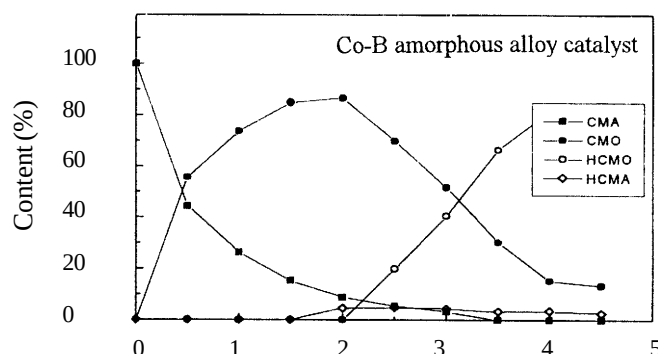
Table 1 Structural properties and catalytic behaviors of the as-prepared catalysts^a

Catalyst	Bulk Comp.	S_{act} (m ² /g)	R^{m} (mol/h·g)	R^{s} (mol/h·m ²)	Conv. (%)	Selectivity (%)			Yield (%)
						CMO	HCMA	HCMO	
Fresh Co-B	Co _{75.4} B _{24.6}	15.8	0.018	0.0011	55.6	100	0.00	0.00	55.6
Cryst. Co-B ^b	Co _{75.4} B _{24.6}	7.8	0.0062	0.00079	22.4	100	0.00	0.00	22.4
Raney Co	/	30.9	0.012	0.00039	37.1	43.0	48.6	8.40	16.0
Raney Ni	/	43.0	0.082	0.0019	100	0.00	0.00	100	0.00

^aReaction conditions: 5.0 g catalyst, 15 mL CMA, 105 mL EtOH, 383 K, 1.0 MPa, 1000 rpm, reaction for 0.5 h. ^bObtained by treating the fresh Co-B sample at 773 K under H₂ flow for 2 h.

Over Co-B amorphous catalyst, the dependence of the contents of CMA and various products on the reaction time is shown in **Figure 1**. One can see that the as-prepared Co-B catalyst exhibited very high selectivity to CMO. Before CMA conversion reached to 92.1%, no 3-phenylpropanol (HCMO) but only trace of dihydrocinnamaldehyde (HCMA) was detected. After reaction for 2 h, the optimum CMO yield (87.6%) was obtained at CMA conversion of 92.1% and CMO selectivity of 95.1%.

Figure 1 Reaction profile of CMA hydrogenation over the Co-B amorphous catalyst



From **Table 1**, the following results were obtained. 1. Although Raney Ni exhibited very high activity during the CMA hydrogenation, it was not suitable for the title reaction since the C=C bond will be hydrogenated to form HCMO in this conditions. 2. Catalysis by Raney Co, the hydrogenation reaction was also less selective to give HCMO. The Co-B amorphous catalyst exhibited much higher activity and selectivity to CMO. In addition, the Co-B catalyst could be used repetitively for more than 5 times without significant deactivation. 3. The selectivity of the crystallized Co-B to CMO was high but the CMO yield was only 22.4% due to the poor activity.

The higher activity of the Co-B amorphous catalyst than that of its corresponding crystallized form could be attributed to the decrease of S_{act} during the crystallization. The higher R^{s} value of the Co-B amorphous alloy implied that some intrinsic effects should also be considered. One important promoting effect was the unique short-range ordering but long-range disordering structure⁹. Another important promoting effect was the electronic interaction between the metallic Co and alloying B, making Co electron-

rich. According to the kinetic studies, the CMA hydrogenation reaction was first-order with respect to P_{H_2} while zero-order with respect to [CMA]. This means that the increase in the hydrogen adsorption could enhance the hydrogenation activity while the change of CMA adsorption had no effect on the hydrogenation activity. The active sites of the electron-rich Co may favor the competitive adsorption of H_2 against that of CMA¹² and thus enhance the hydrogenation activity since more hydrogen could be adsorbed by the catalyst.

The higher activity of Co-B amorphous alloy catalyst, especially the higher R^S , than that of Raney Co could also be interpreted in terms of both the structural and electronic effects as discussed above. While, the better selectivity to CMO over the Co-B amorphous catalyst than that over Raney Co could be understood by considering the adsorption model of CMA on the Co active sites. According to the IR spectra, Blyholder and Shibabi pointed out that the metal-oxygen bond rather than the metal-carbon bond was responsible for the bonding between the C=O and Co metal¹³. In the absence of promoters, this bonding strength is similar to that of the C=C and Co, so the reactivity of the carbonyl group is comparable to that of the C=C group. That is the reason that hydrogenation with Raney Co catalyst gives equal selectivities to HCMA and CMO. For the Co-B amorphous catalyst, the presence of the electron-deficient B could enhance the adsorption strength of the carbonyl group *via* a side-bond interaction⁴. Besides the electronic effects, the structural promoting effects, such as the homogeneous distribution and the highly unsaturated coordination of Co active sites *etc.* should also be considered. These works are being underway.

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