LETTER

A non-noble amorphous Co–Fe–B catalyst highly selective in liquid phase hydrogenation of crotonaldehyde to crotyl alcohol

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A nanosized amorphous Co–Fe–B catalyst exhibited higher selectivity and yield to crotyl alcohol than noble Pt-based catalysts in the hydrogenation of crotonaldehyde and could be prepared by a facile chemical reduction method.

The selective hydrogenation of α,β-unsaturated aldehydes to their corresponding unsaturated alcohols is among one of the most important reactions in the preparation of various fine chemicals such as fragrances, agrochemicals and pharmaceuticals.[1,2] However, the manipulation of selectivity in the hydrogenation of α,β-unsaturated aldehydes is a considerable challenge, since the production of saturated aldehyde or saturated alcohol is thermodynamically more favorable than that of unsaturated alcohol. Therefore, great efforts have been devoted to enhancing the catalytic activity towards the C=O group, while simultaneously suppressing the activity towards the C=C double bonds of α,β-unsaturated aldehydes.

In principle, the selectivity for a desired unsaturated alcohol is determined by the relative accessibility and the binding strength of the C=C and the C=O bonds to the catalyst.[2,3] In this sense, a properly designed catalyst with more suitable surface sites, which invoke the polarization of the C=O bond or inhibit the adsorption of α,β-unsaturated aldehydes in the C=C bonding configuration, can lead to high selectivity in the hydrogenation of α,β-unsaturated aldehydes. In a generalized context of feasible ways to modify the active sites of a catalyst, the addition of a second, more electropositive metal[4–7] or the use of oxide supports,[8–11] is efficient in promoting the catalytic performance. The presence of electronic effects has been proposed to be responsible for the improved selectivity.

In this paper, an attempt has been made to develop the nanosized amorphous Co–Fe–B catalyst based on a facile chemical reduction method, as amorphous Co–B catalysts have been found moderately selective in the hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols.[12–14] We identified that over a Co–Fe–B catalyst with a specific formulation, the high selectivity for crotyl alcohol is retained even at high crotonaldehyde conversion, thus leading to a crotyl alcohol yield of 63.5 mol%, which is much higher than those reported for Pt-based catalysts, within our knowledge.

The bulk composition of the as-prepared Co–Fe–B catalyst was determined to be $Co_{30.8}Fe_{37.1}B_{32.1}$, in atomic ratios, by chemical analysis (ICP-AES, IRIS Intrepid), with the Co : Fe ratio somewhat higher than the nominal ratio used in the preparation. It was found that the introduction of iron drastically increased the specific surface area, the surface area of the Co–Fe–B catalyst being 35 $m^2\ g^{-1}$, about twofold that of Co–B catalyst. Accordingly, the transmission electron micrographs

(TEM, JEOL JEM2011) in Fig. 1 reveal the average particle size of 16 and 9 nm for Co–B and Co–Fe–B catalysts, respectively, with the latter bearing a much narrower particle size distribution than the former. The selected-area electron diffraction patterns (SAED, insets in Fig. 1) present only diffractive halos rather than distinct dots, consistent with the long-range disordering but short-range ordering structure characteristic of amorphous alloys.[15]

Fig. 2 compares the X-ray photoelectron spectra (XPS, Perkin Elmer PHI5000C) of Co 2p, B 1s and Fe 2p core levels for the Co–B and Co–Fe–B catalysts. It can be concluded on a qualitative basis that the incorporation of iron increased the amount of oxidized Co (Co^{2+})[16] and B (B^{3+})[17] species on the surface in a way which is unclear for the time being. For the Co–Fe–B catalyst, iron exists in both the metallic and oxidized states, with the Fe $2p_{3/2}$ binding energies (BEs) at ∼707.1 and 709.8 eV, respectively.[17] It is worth noting that the B 1s BE of elemental B in these amorphous catalysts is ∼188.2 eV, about 1.2 eV higher than that of pure boron powder. For metal-rich borides such as NiB, Ni_2B, CoB, Co_2B and FeB, based on magnetic susceptibility, ^{59}Co NMR and high resolution bremsstrahlung isochromat measurements, it is suggested that B donates electrons to the metal.[18] The BE shift of B in the present case can be interpreted in a similar manner.

The liquid phase hydrogenation of crotonaldehyde (CRAL) over nanosized amorphous Co–B and Co–Fe–B catalysts results in crotyl alcohol (CROL), butanal (BUAL), butanol (BUOL), and diacetal (1,1-diethoxybutane, DA) from the side reaction between BUAL and ethanol used as solvent (Scheme 1). Table 1 summarizes the initial selectivity for CROL and product distribution corresponding to the maximum yield of CROL with Co–B and Co–Fe–B catalysts. It turns out that iron has a remarkable positive effect on the selectivity in CRAL hydrogenation. With the Co–B catalyst, BUAL is the preferred product, while the initial selectivity for CROL is only about 23.4%, with the maximum yield of CROL being 18.0 mol%. In contrast, over the Co–Fe–B catalyst, the initial selectivity for CROL amounts to 71.0%, and the maximum yield of CROL reaches as high as 63.5 mol%. It is worth emphasizing here that, although some elaborately designed Pt-based catalysts can give rise to a higher selectivity for CROL (>70%),[7,9,11] the value is only achievable at low conversion and a yield comparable to the present case has never been reported to the best of our knowledge. More recently, on a highly loaded Co–SiO₂ catalyst prepared by Djerboua et al.,[19] the extrapolated CROL selectivity at zero CRAL conversion exceeds 90%. However, the selectivity decreases linearly to 77% at CRAL conversion of 55%, still resulting in a CROL yield inferior to the present case.
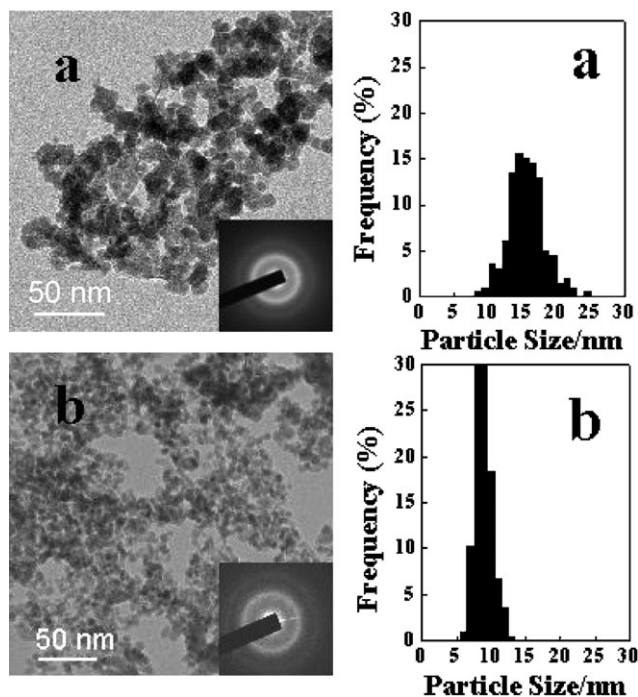
Fig. 1 The TEM images and particle size distributions of (a) Co–B and (b) Co–Fe–B catalysts. Insets are the corresponding SAED patterns.
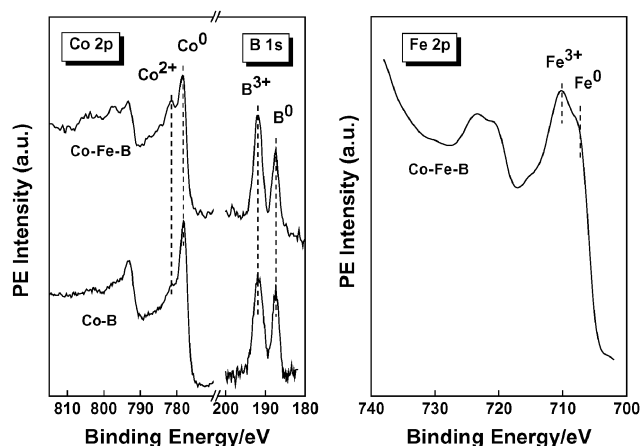

Fig. 2 The XPS spectra of Co 2p, B 1s and Fe 2p levels of the nanosized amorphous Co–B and Co–Fe–B catalysts.

In a control experiment, no hydrogenation products were detectable using a similarly prepared amorphous Fe–B catalyst, implying that iron itself is not active and selective at all in the title reaction. Further analysis of the initial formation rates of CROL ($r_{C=O}$) and BUAL ($r_{C=C}$) over Co–B and Co–Fe–B catalysts revealed that the improved selectivity for CROL after iron addition is not caused by enhancing the reactivity of the C=O group; rather, iron suppresses more the reactivity of the C=C group than that of the C=O group, thus reversing the $r_{C=O} : r_{C=C}$ ratio from $0.33 : 1$ to $2.5 : 1$.
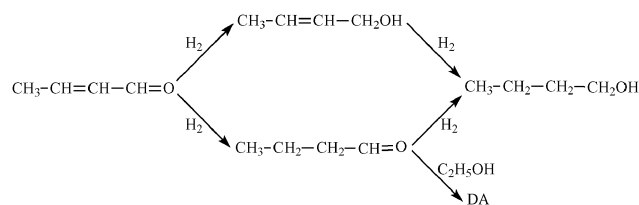
Scheme 1 Crotonaldehyde hydrogenation network.

Based on a systematic theoretical calculation, Delbecq and Sautet suggested that the main attractive action in adsorbing aldehyde on surfaces *via* the C=O bond is the back-donation from the metal orbitals into the π^*_{CO} orbital. Either the shift-down of the π^*_{CO} orbital or the shift-up of the metal orbitals facilitates a better interaction and stronger adsorption, which is crucial for an improved selectivity for the unsaturated alcohol.[20] In the present case, XPS revealed that there are substantial amounts of oxides of iron, cobalt and boron on the Co–Fe–B catalyst. Although the presence of surface oxides is adverse to the activity of the catalyst by blocking the active sites, they can function as Lewis acid sites and lower the π^*_{CO} orbital by complexation with the C=O group. On the other hand, donation of electrons from elemental B is anticipated to shift the orbitals of metallic Co up. Meanwhile, the increased electron density on metallic Co in the Co–Fe–B catalyst relative to elemental Co without any electronic interaction with B, can weaken the binding of the C=C group on the active sites.[20] The synergic effect between the surface oxides and the electron-rich metallic Co can account for the smaller decrease in the hydrogenation activity of the C=O group relative to the C=C group. It is worth mentioning here that the present method is also applicable in the selective hydrogenation of cinnamylaldehyde to cinnamyl alcohol. Over another amorphous Co–Fe–B catalyst with a formulation somewhat different from the present one, a cinnamyl alcohol yield of >95% was obtained.

In summary, over the nanosized amorphous Co–Fe–B catalyst, higher selectivity and yield of crotyl alcohol can be achieved in the hydrogenation of crotonaldehyde. The unique electronic structure of the amorphous metal boride catalyst and the existence of more surface oxides evoked by iron incorporation, facilitate the activation of the C=O bond relative to the C=C bond, thus rendering an excellent selectivity towards crotyl alcohol over the non-noble Co–Fe–B catalyst.

Experimental

The nanosized amorphous Co–Fe–B catalyst was prepared as follows. 12.7 ml of an aqueous solution of KBH_4 (2.0 M) was added, in a flow rate of 1.5 ml min^{-1}, to 17.0 ml of an aqueous solution containing 3.4 mmol $CoCl_2$ and 5.1 mmol $FeCl_3$ at 293 K. Gentle stirring was maintained throughout the reduction. When no hydrogen bubbles were released, the resulting black precipitate was centrifuged and washed with distilled water to neutrality, then with ethanol three times to replace water. The catalyst was stored in ethanol for activity tests and

Table 1 Results of crotonaldehyde hydrogenation over Co–B and Co–Fe–B catalysts

| Catalyst | Conversion[a] (%) | Selectivity[a] (mol%) | | | | Y_{CROL}[a] (mol%) | S[b] (mol%) | $r_{C=O}$[b] (mmol min^{-1} g$_{cat}^{-1}$) | $r_{C=C}$[b] (mmol min^{-1} g$_{cat}^{-1}$) |
		CROL	BUAL	BUOL	DA				
Co–B	89.3	20.2	41.7	38.1	0	18.0	23.4	0.29	0.89
Co–Fe–B	94.7	67.1	26.3	4.3	2.3	63.5	71.0	0.069	0.028

[a] Values corresponding to the maximum yield of crotyl alcohol. [b] Initial selectivity to crotyl alcohol (*S*), and the initial formation rates of crotyl alcohol ($r_{C=O}$) and butanal ($r_{C=C}$).

characterization. For comparison, Co–B and Fe–B catalysts were prepared in a way similar to that of the Co–Fe–B catalyst.

Crotonaldehyde (97%) was further purified by distillation before activity tests. 0.50 g of catalyst, 45 ml of ethanol and 5.0 ml of crotonaldehyde were transferred into a 220 ml stainless steel autoclave. The hydrogenation was performed at 373 K, 1.0 MPa of H_2, and a stirring rate of 1000 rpm to exclude diffusion effects. The reaction products were analyzed by a GC122 gas chromatograph equipped with a flame ionization detector (FID) and a 30 m PEG-20M capillary column.

Acknowledgements

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