Liquid phase hydrogenation of crotonaldehyde over Sn-promoted amorphous Co–B catalysts

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Abstract

The promoting effect of tin (Sn) on the liquid phase hydrogenation of crotonaldehyde over amorphous Co–B catalyst has been investigated. $SnCl_2$ or $SnCl_4$ was introduced to the reactant before hydrogenation or incorporated to the Co–B catalyst during the reduction of $CoCl_2$ by potassium borohydride. The overall activity of the Co–B catalyst was suppressed upon the addition of the tin salts in the reactant. However, an appropriate amount of either tin salt remarkably improved the reactivity towards the C=O bond, thus leading to a higher selectivity and yield of crotyl alcohol. On the other hand, incorporation of tin to the catalyst by co-reduction was mainly against the formation of crotyl alcohol. $SnCl_2$ caused a sharp drop of the reactivity towards the C=O bond rather than the C=C bond. Although $SnCl_4$ increased both the reactivities of the C=O and C=C bonds, the former increased to a less extent than the latter. Their different catalytic behavior was tentatively interpreted on the basis of XPS measurements.
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1. Introduction

Unsaturated alcohols derived from selective hydrogenation of their corresponding α,β-unsaturated aldehydes are important intermediates in the production of perfumes, flavorings, and pharmaceuticals [1]. However, the manipulation of the selectivity in the hydrogenation of α,β-unsaturated aldehydes is of considerable challenge, as production of saturated aldehyde or saturated alcohol is thermodynamically more favorable than that of the unsaturated alcohol [2–4]. The only feasible way to enhance the selectivity to unsaturated alcohol is to kinetically activate the C=O bond rather than the C=C bond over delicately designed catalysts. For example, monometallic Pt catalysts usually produce the saturated aldehyde, and it is necessary to modify them either through a support effect (SMSI) [4] or by addition of a second metal [5] to improve the selectivity towards the hydrogenation of the C=O bond.

Since the 1980s, ultrafine amorphous metal boride (M-B) catalysts prepared by the reduction of metal salts with borohydride, which have advantages of amorphous and ultrafine powders, have attracted much attention in catalysis [6–11]. It has been claimed that amorphous Co–B catalyst can be a promising candidate for selective hydrogenation of α,β-unsaturated aldehydes. In a recent work, Chen et al. [12] reported a selectivity of nearly 100% for furfural hydrogenation over Mo-doped amorphous Co–B catalysts. For cinnamaldehyde hydrogenation, the optimal yield of cinnamyl alcohol was 87.6% over amorphous Co–B catalyst, much higher than the yield over Raney Ni, Raney Co, or crystallized Co–B catalysts [13]. For crotonaldehyde which has no bulky substituent on β-carbon to be a steric hindrance to C=C adsorption [14], the selectivity to crotyl alcohol over P-2WCo–B was only 29.2% at a conversion of 30.1% [15]. Co–B catalyst modified by a small quantity of metal salts including $CuCl_2$, $FeCl_2$, $CrCl_3$, $Cd(OAc)_2$, $Zn(OAc)_2$, $RuCl_3$, and $Co(OAc)_2$, was relatively more selective; the selectivity to crotyl alcohol was 44% at a conversion of 52% [16].

It has been well documented that tin is an efficient modifier in promoting the catalytic performance of the noble metal catalysts in selective hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols [17–23]. Surprisingly, there is no work on the promoting effect of tin on Co–B or other Co-based catalysts in crotonaldehyde hydrogenation. In the present paper, we disclose the results of a detailed study on the hydrogenation of crotonaldehyde over amorphous Co–B catalysts modified by adding tin salts prior to crotonaldehyde hydrogenation or prior to the reduction of the Co–B catalyst. Moreover, the effect of the tin salts with different valences on the activity and selectivity has been investigated and rationalized.

2. Experimental

2.1. Catalyst preparation

The unpromoted Co–B catalyst was prepared as follows. KBH_4 aqueous solution (12.7 ml of 2.0 M) containing 0.20 M NaOH was added to 17.0 ml of 0.59 M $CoCl_2$ aqueous solution at 293 K. The flow rate was 1.5 ml min^{-1}. A gentle stirring was kept throughout the reaction using a magnetic stirrer. When no bubbles were released, the black precipitate was centrifuged and washed with distilled water six times, followed by ethanol three times. The catalyst was stored in ethanol for activity test and characterization.

The tin-containing catalysts were prepared by the procedure identical to that of the Co–B catalyst, except that a certain amount of $SnCl_2$ or $SnCl_4$ was mixed with the $CoCl_2$ solution followed by reduction with KBH_4. These catalysts were designated as X% $CoSn_{II}B$ or X% $CoSn_{IV}B$, where X% represented the nominal molar percentage of tin salt added relative to Co in the solution, while the subscript II or IV stood for the valence of tin in the salts.

2.2. Characterization

The bulk compositions of the samples were analyzed by inductively coupled plasma (ICP, IRIS Intrepid). Powder X-ray diffraction (XRD) pattern of the samples were acquired on a Bruker AXS D8 Advance X-ray Diffractometer using Ni-filtered Cu Kα radiation (λ = 0.15418 nm). The tube voltage and current were 40 kV and 40 mA, respectively. The sample with solvent was put in the in situ cell, with argon flow (99.9995%) purging the sample during the detection to avoid oxidation. X-ray photoelectron spectra (XPS, Perkin Elmer PHI5000C) were recorded with Al Kα radiation as the excitation source ($h\nu$ = 1486.6 eV). The sample pressed into a self-supported disc was mounted on the sample plate. Then it was degassed in the pretreatment chamber at 383 K for 2 h in vacuo before being transferred into the analyzing chamber where the background pressure was lower than 2×10^{-9} Torr. All the binding energy (BE) values were obtained after removing the surface oxides by Ar ion sputtering and referenced to the C 1s peak of contaminant carbon at 284.6 eV with an uncertainty of ±0.2 eV.

2.3. Activity test

Crotonaldehyde was purified by distillation before the activity test. Liquid phase hydrogenation of crotonaldehyde over the Co–B catalyst was carried out in a 220 ml stainless steel autoclave in which 0.50 g of the as-prepared catalyst, 45 ml of ethanol, 5.0 ml of crotonaldehyde, and a certain amount of $SnCl_2$ or $SnCl_4$ were charged. For the sake of simplicity, the tin salt modified Co–B catalyst prior to the hydrogenation will be referred to hereafter as X% $SnCl_2$ Co–B or X% $SnCl_4$ Co–B, where X% represented the molar percentage of tin salt added to the reactant with respect to Co in the Co–B catalyst. The reactor was purged with hydrogen. After the desired temperature, 373 K, was reached, the H_2 pressure was maintained at 1.0 MPa and the stirring (1000 rpm) was commenced, which was taken as the beginning of the reaction. The process of the reaction was monitored by analyzing the samples withdrawn from the autoclave at intervals on a gas chromatograph equipped with a 50 m PEG-20M capillary column and a flame ionization detector (FID).

The same catalytic tests were performed on $CoSn_{II}B$ and $CoSn_{IV}B$ catalysts, except that neither $SnCl_2$ nor $SnCl_4$ was added to the reactant. In this way, the effect of the two different modification strategies on the catalytic behavior of Co–B catalyst can be readily compared and elucidated.

3. Results and discussion

3.1. Catalyst characterization

Table 1 lists the bulk compositions and BET surface areas of the as-prepared Co–B and CoSnB catalysts prepared by co-reduction. From the bulk composition, it can be concluded that only a portion of tin is incorporated in the catalyst during the co-reduction process. The content of tin in the catalysts increases from 0.7 to 3.1 mol% and from 0.6 to 2.6 mol% with the increase of $SnCl_2$ and $SnCl_4$, respectively, in the solution from 1 to 5% relative to the amount

Table 1
Some physical characters of the Co–B and CoSnB catalysts

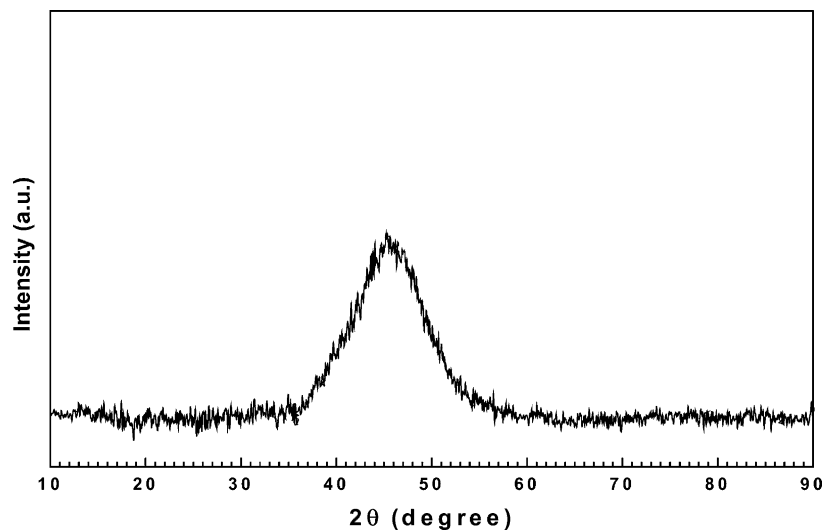| Catalyst	Nominal Sn/Co (mol%)	Bulk composition (atomic ratio)	S_{BET} ($m^2 g^{-1}$)
Co–B	0	$Co_{65.6}B_{34.4}$	17.8
$CoSn_{II}B$	1	$Co_{62.8}Sn_{0.7}B_{37.5}$	21.2
	2	$Co_{62.6}Sn_{1.2}B_{36.2}$	32.8
	5	$Co_{61.7}Sn_{3.1}B_{35.2}$	66.3
$CoSn_{IV}B$	1	$Co_{63.0}Sn_{0.6}B_{36.4}$	37.6
	2	$Co_{62.1}Sn_{1.3}B_{36.6}$	54.4
	5	$Co_{62.6}Sn_{2.6}B_{34.8}$	76.8

Fig. 1. A typical XRD pattern of the as-prepared samples.

of $CoCl_2$. As compared to Co–B, CoSnB has larger specific surface areas. The surface area is found to increase with the increase of tin content in both the $CoSn_{II}B$ and $CoSn_{IV}B$ catalysts, consistent with the results of Mo-doped Co–B catalysts [12].

The XRD profile (Fig. 1) confirms that all the as-prepared catalysts are of amorphous character, as there is only a broad feature at around $2\theta = 45°$ [11]. It is further supported by the appearance of the diffractive halo rather than distinct dots in the SAED patterns of the samples (not shown here).

3.2. Catalytic behavior in crotonaldehyde hydrogenation

The products in the liquid phase hydrogenation of crotonaldehyde (CRAL) over the as-prepared amorphous catalysts are found to be saturated aldehyde (BUAL, butyraldehyde), unsaturated alcohol (CROL, crotyl alcohol) and saturated alcohol (BUOL, butanol). Besides, the diacetal (DA, 1,1-diethoxybutane), determined by GC-MS, is also produced by the side reaction between butyraldehyde and ethanol used as a solvent, as depicted in Scheme 1. Acetal of crotonaldehyde is not formed under the present reaction conditions, in agreement with the results of cinnamaldehyde hydrogenation over Pt–Sn/nylon [17] and crotonaldehyde hydrogenation over Pt–Sn/polyamide [23].

The formation of DA is remarkable when the modification is through introduction of the tin salts to the reactant, which is attributable to the acidic character of the salts.

The typical time course of crotonaldehyde hydrogenation over the 1% $SnCl_4$ Co–B catalyst is illustrated in Fig. 2. Similar profiles are also observed during performing the hydrogenations over other CoSnB catalysts with different tin contents and Co–B catalyst with different amount of $SnCl_2$ or $SnCl_4$ introduced into the reactant. In general, the yield of crotyl alcohol increases and reaches a maximum at the crotonaldehyde conversion between 75 and 95%. At higher conversions, the complete saturation of crotonaldehyde leads to the formation of butanol at the expense of crotyl alcohol. The simultaneous appearance of crotyl alcohol and butyraldehyde in the initial stage may indicate that hydrogenation of the C=C bond and C=O group occurs through parallel reactions.

The effect of the tin salts added to the reactant is shown in Table 2, in which the product distribution corresponding to the maximum yield of crotyl alcohol is summarized. It is found that over the Co–B catalyst without modification, the maximum yield of crotyl alcohol is 18.0 mol% at the selectivity of 20.2 mol% and the conversion of 89.3%. However, the yield of crotyl alcohol over the 1% $SnCl_2$ Co–B catalyst is nearly doubled and passes through a maximum at 37.6%
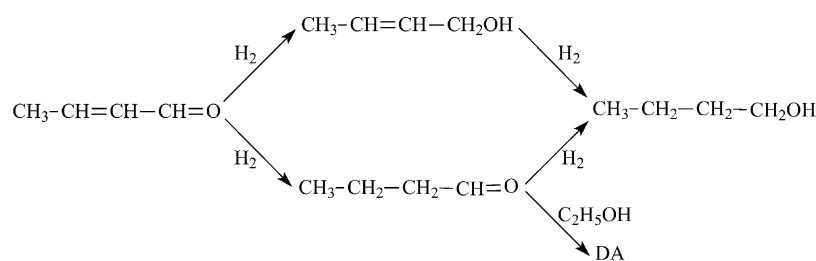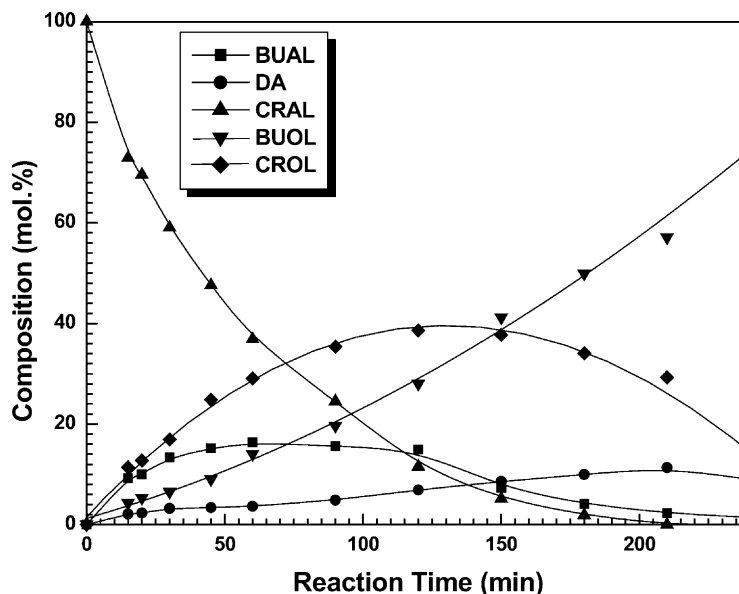

Scheme 1.

Fig. 2. Time dependence of crotonaldehyde hydrogenation over 1% SnCl$_4$ Co–B catalyst. Reaction conditions: $T = 373$ K, $p_{H_2} = 1.0$ MPa, crotonaldehyde/ethanol/W_{Co} = 5 ml/45 ml/0.50 g.

over the 2% SnCl$_2$ Co–B catalyst. At higher SnCl$_2$/Co ratios, the yield of crotyl alcohol drops. Moreover, the reaction rate is greatly retarded.

The effect of SnCl$_4$ added to the reactant on the selectivity of unsaturated alcohol is almost the same as that of SnCl$_2$, although for achieving the maximum yield of crotyl alcohol, the optimal amount of SnCl$_4$ is somewhat lower than that of SnCl$_2$. It should be noted that over the 1% SnCl$_4$ Co–B catalyst the yield of crotyl alcohol is 38.6 mol%, which is one of the best results reported in the open literatures dealing with crotonaldehyde hydrogenation over Co-based catalysts [15,16,24–27].

The following part of Table 2 lists the results of crotonaldehyde selective hydrogenation over the CoSn$_{II}$B and CoSn$_{IV}$B catalysts prepared by the co-reduction method. It is found that this preparation approach has a marginal or adverse effect on the formation of crotyl alcohol. Thus it can be concluded that Co–B catalyst modified by a small amount of tin salts in the reactant is more effective in selective hydrogenation of crotonaldehyde than co-reduced CoSnB catalysts.

These modification approaches also exert different influences on the initial hydrogenation rate of crotonaldehyde (r_{CRAL}), which is obtained by fitting and differentiating the concentration–time curves. As shown in the last column of Table 2, tin salts in the reactant always suppress r_{CRAL}, although the observed decrease due to SnCl$_4$ is less than that due to SnCl$_2$ at identical Sn/Co ratio. On the other hand,

Table 2
Promoting effects of tin on amorphous Co–B catalyst for crotonaldehyde hydrogenation

Catalyst	Reaction time[a] (min)	Conversion[a] (%)	Selectivity[a] (mol.%)				Yield of CROL[a] (mol%)	r_{CRAL}[b] (mmol min^{-1} g$_{Co}$$^{-1}$)
			CROL	BUAL	BUOL	DA		
Co–B	120	89.3	20.2	38.1	41.7	0	18.0	1.25
1% SnCl$_2$ Co–B	180	92.9	38.2	11.5	42.2	8.1	35.5	0.70
2% SnCl$_2$ Co–B	150	85.9	43.7	16.7	32.7	6.9	37.6	0.66
5% SnCl$_2$ Co–B	180	86.8	39.9	15.7	28.3	16.1	34.6	0.50
10% SnCl$_2$ Co–B	720	75.4	16.8	13.7	5.61	63.9	12.7	0.15
0.5% SnCl$_4$ Co–B	120	90.9	37.1	18.9	38.6	5.5	33.7	1.00
1% SnCl$_4$ Co–B	120	88.5	43.7	16.9	31.7	7.8	38.6	0.90
2% SnCl$_4$ Co–B	120	79.9	45.6	18.6	25.5	10.3	36.5	0.84
5% SnCl$_4$ Co–B	270	94.9	34.1	15.5	22.0	28.4	32.4	0.63
1% CoSn$_{II}$B	150	93.7	20.1	24.8	53.6	1.5	18.9	0.86
2% CoSn$_{II}$B	120	80.3	22.1	33.4	42.2	2.3	17.7	0.86
5% CoSn$_{II}$B	180	93.9	17.4	35.0	45.7	2.0	16.4	0.70
1% CoSn$_{IV}$B	60	86.5	17.2	46.3	35.5	1.0	14.9	1.78
2% CoSn$_{IV}$B	60	86.3	16.8	57.4	24.8	1.0	14.5	1.85
5% CoSn$_{IV}$B	90	84.8	13.6	65.5	19.1	1.8	11.5	1.20

[a] Values corresponding to the maximum yield of crotyl alcohol.
[b] Initial hydrogenation rate of crotonaldehyde.

tin in $CoSn_{II}B$ catalysts affects r_{CRAL} similarly to $SnCl_2$ or $SnCl_4$ added to the reactant, while over $CoSn_{IV}B$ catalysts r_{CRAL} pronouncedly increases and then drops at higher tin loadings. The increase in r_{CRAL} over $CoSn_{IV}B$ catalysts may be caused by the higher active surface area as a result of their higher surface area.

3.3. Modification mechanism

To gain a deep insight into the mechanism of these modification approaches on the selectivity to crotyl alcohol, the initial formation rates of butyraldehyde ($r_{C=C}$) and crotyl alcohol ($r_{C=O}$) over these catalysts are plotted in Fig. 3. For the Co–B catalyst, $r_{C=C}$ and $r_{C=O}$ are 0.67 and 0.21 mmol min^{-1} g$_{Co}$$^{-1}$, respectively, which directly explains the low selectivity and the low yield of crotyl alcohol. When a small amount of $SnCl_2$ or $SnCl_4$ is added to the reactant, the reactivity of the C=C bond drastically dropped by ~50% and keeps on decreasing at higher dosages. Hotta and Kubomatsu [28] found that small amount of Co-, Mn-, or $NiCl_2$, added to Raney Co catalyst just prior to the start of the hydrogenation of 2-methyl-2-pentenal, strongly suppressed the activity towards the C=C bond. They further demonstrated that the rate constants for the formation of saturated alcohol and saturated aldehyde decreased with an increase in the amount of salts added, which led to higher selectivity to unsaturated alcohol.

In the present case, the higher selectivity to crotyl alcohol cannot be simply attributed to the lower reactivity of C=C bond over the $SnCl_2$ or $SnCl_4$-modified Co–B

catalysts. Fig. 3 proves that $r_{C=O}$ increases to 0.27 and 0.34 mmol min^{-1} g$_{Co}$$^{-1}$ for 2% $SnCl_2$ Co–B and 1% $SnCl_4$ Co–B, respectively. So the positive effect of tin salts in the reactant resulted from both decelerating the hydrogenation of the C=C bond and accelerating the hydrogenation of the C=O bond, while the former contributes more to the improvement of the selectivity to crotyl alcohol.

Following the same approach, the slight increase in the yield of crotyl alcohol over 1% $CoSn_{II}B$ catalyst is attributed to the less decrement of $r_{C=O}$ than $r_{C=C}$. On the other hand, over all $CoSn_{IV}B$ catalysts, although $r_{C=O}$ is higher than or comparable to that over Co–B, $r_{C=C}$ increases much faster than $r_{C=O}$, thus resulting in the lower selectivity to crotyl alcohol.

In the case of catalytic hydrogenation, it is generally assumed that the reactive bond is the one involved in chemisorption on the surface. The relative accessibility and the binding strength of the C=C and C=O bonds to the catalyst in crotonaldehyde are decisive for the selectivity [5,14]. Presumably, the tin salts in the reactant exert their influence on the selectivity by adsorption on the surface of the Co–B catalyst. The tin ions preferentially occupy the active sites relating to C=C bond adsorption, leading to monotonous decrease of $r_{C=C}$ with increased Sn/Co ratios as shown in Fig. 3. On the other hand, the adsorbed tin ions function as Lewis acid sites, the crotonaldehyde molecule being adsorbed via the donation of a lone electron pair from the oxygen of the carbonyl group. This bonding induces the polarization of the C=O bond which is favorable for nucleophilic attack on the carbon atom by hydrogen dissociatively
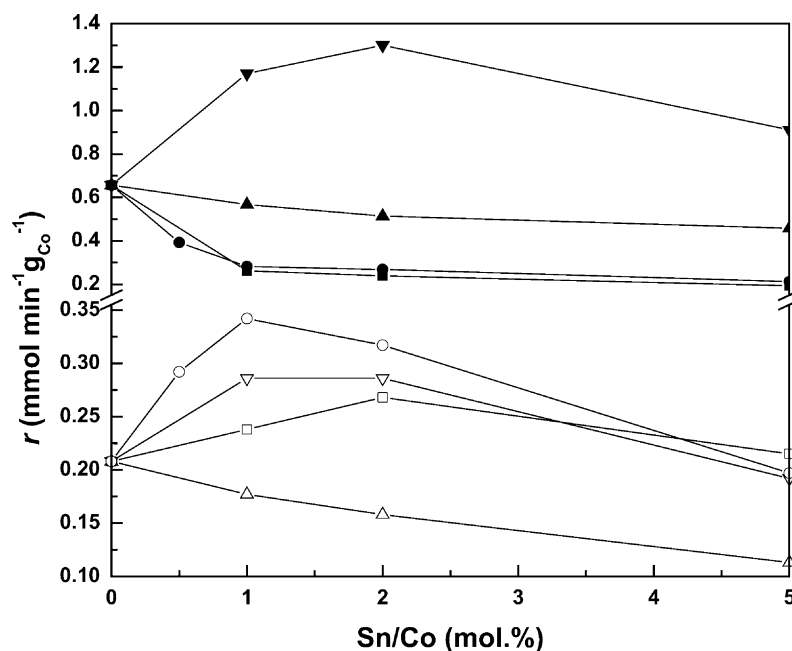

Fig. 3. Influence of the nominal Sn/Co atomic ratio on the initial formation rates of butyraldehyde ($r_{C=C}$, full symbols) and crotyl alcohol ($r_{C=O}$, open symbols). (■, □) $SnCl_2$ introduced into the reactant; (●, ○) $SnCl_4$ introduced into the reactant; (▲, △) $SnCl_2$ introduced during the preparation of the catalyst; (▼, ▽) $SnCl_4$ introduced during the preparation of the catalyst.

adsorbed on neighboring active sites and, thus, enhances the hydrogenation of this functional group. Similar model was successfully applied to illustrate the enhanced selectivity to unsaturated alcohols in liquid phase hydrogenation of cinnamaldehyde and citral over carbon-supported Ru–Sn catalysts by Galvagno et al. [18,19]. The decrease of $r_{C=O}$ at higher $SnCl_2$ or $SnCl_4$ dosages can be ascribed to the excessive adsorption of the tin ions on the active sites, which impedes the formation of unsaturated alcohol.

It is interesting that for Pt–Sn binary catalysts an appropriate amount of tin can afford improved selectivity to crotyl alcohol and overall activity as compared to monometallic Pt catalysts, while in CoSnB catalysts tin mainly plays a negative role. The positive effect of tin in the Pt–Sn catalysts depends on the Sn/Pt atomic ratio, the preparation method, and mainly, the interaction between Pt and metallic and oxidized tin species [20,22,29,30]. So the information on the surface characteristics of the CoSnB catalysts may throw some light on our understanding of the activation mechanism of the catalysts.

In Fig. 4, it is found that for 1% $CoSn_{II}B$ catalyst, tin is predominantly in its metallic state, with the $Sn3d_{5/2}$ level at 485.1 eV, while tin in 1% $CoSn_{IV}B$ catalyst is mainly in the oxidized state with the BE of $Sn3d_{5/2}$ at 486.4 eV [31]. It should be noted that XPS unfortunately cannot discriminate between Sn(II) and Sn(IV). Such a difference may account for the higher $r_{C=O}$ over $CoSn_{IV}B$ than that over $CoSn_{II}B$ or Co–B following a similar interpretation to that for Pt–Sn catalysts. On the other hand, metallic tin supposedly hinders the hydrogenation of crotonaldehyde by physically covering the active sites, whereas the formation of a less active Co–Sn–B alloy can be an alternative explanation. Moreover, according to Fig. 3, it seems that $r_{C=O}$ is affected more adversely than $r_{C=C}$ by metallic tin, implying that metallic tin preferentially blocks the active sites for C=O bond saturation.

It must be stressed that our interpretation above based on the surface states of tin is somewhat simplified. The incorporation of tin in the catalysts arouses comprehensive changes in the surface states of cobalt and boron, as shown in Fig. 4. It is found that for Co–B and 1% $CoSn_{II}B$ catalysts, cobalt is in the metallic state with the BE of $Co2p_{3/2}$ at 778.0 eV [31]. For 1% $CoSn_{IV}B$ catalyst, there is a shoulder peak at higher BE, indicating the existence of oxidized Co species. For boron in Co–B and 1% $CoSn_{II}B$ catalysts, besides its elemental state with B1s level at 187.5 eV, B_2O_3 is identified [32], which originates from the hydrolysis of BH_4^- during the reduction process [33]. It is noteworthy that the BE of elemental boron has positively shifted by 0.4 eV relative to pure boron due to the alloying effect between metallic Co and elemental B [12,13,34,35]. However, the alloying effect is weakened in the presence of oxidized tin and cobalt species, as manifested by the +0.1 eV shift of the B1s level of elemental boron for the 1% $CoSn_{IV}B$ catalyst. The differences in the surface species of cobalt and the electronic state of boron shall also affect the catalytic behavior
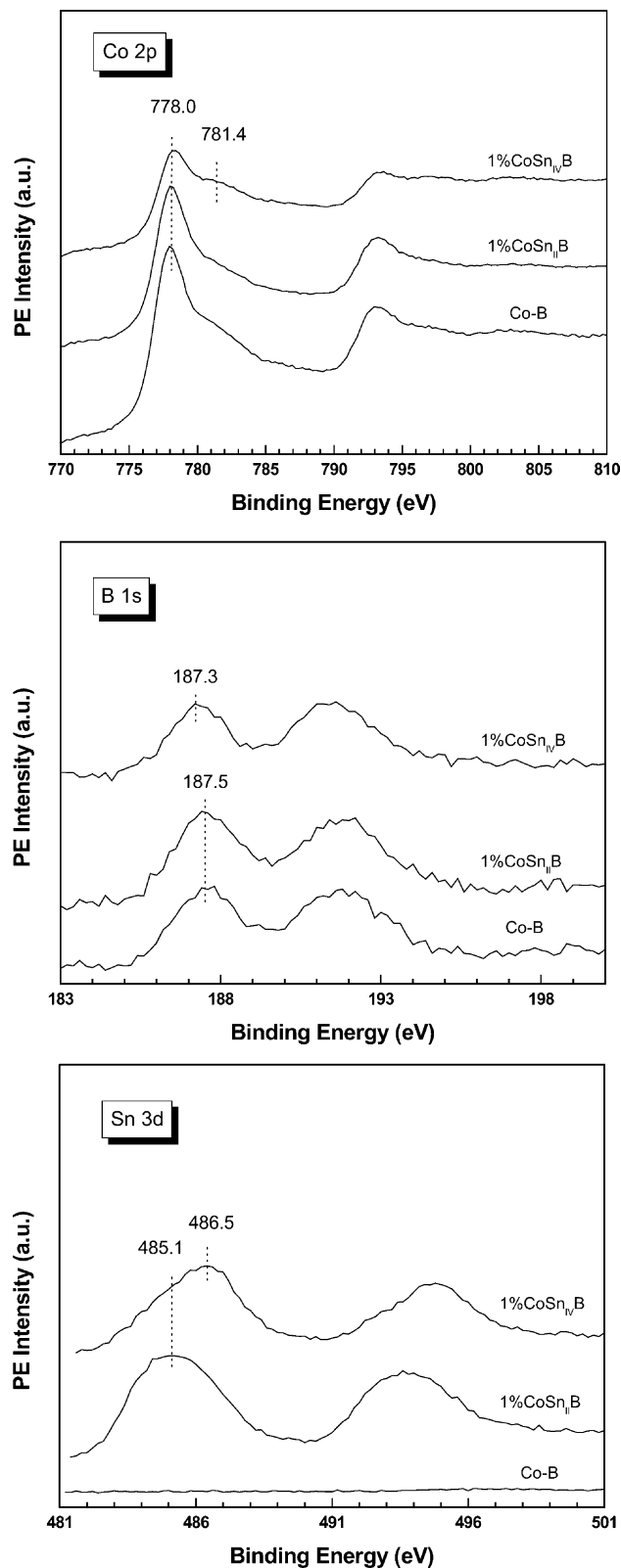

Fig. 4. The XPS spectra of Co2p, Sn3d, and B1s of Co–B, 1%$CoSn_{II}B$ and 1% $CoSn_{IV}B$ samples.

of the CoSnB catalysts, albeit in a way unclear at the time being.

4. Conclusions

Two modification approaches of tin on the amorphous Co–B catalyst in liquid phase hydrogenation of crotonalde-hyde were investigated and compared. A small amount of $SnCl_2$ or $SnCl_4$ added to the reactant prior to the hydrogena-tion process remarkably improved the selectivity to crotyl alcohol, while incorporation of tin to the Co–B catalyst by co-reduction mainly lowered the selectivity to the target product. It is found that the catalytic behavior is closely re-lated to the chemical states of the surface tin species. Ad-sorbed tin ions suppressed the hydrogenation rate of the C=C bond, but accelerated the hydrogenation rate of the C=O bond. Metallic tin decreased the hydrogenation rate of the C=O bond more than that of the C=C bond, while tin oxide increased the hydrogenation rate of the C=C bond more than that of the C=O bond, both resulting in a loss of selectivity towards unsaturated alcohol.

Acknowledgements

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