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A Novel Preparation Method of Ni–Sn Alloy Catalysts Supported on Aluminium Hydroxide: Application to Chemoselective Hydrogenation of Unsaturated Carbonyl Compounds

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A novel method was applied for the preparation of Ni–Sn alloy catalysts that were utilized for chemoselective hydrogenation of unsaturated carbonyl compounds, producing unsaturated alcohols almost exclusively. The formation of the Ni–Sn alloy may have played a key role in the enhancement of the chemoselectivity.

The chemoselective hydrogenation of the C=O bond in α,β-unsaturated ketones and aldehydes has been extensively studied because the unsaturated alcohols that it forms are important in the production of a variety of fine chemicals.[1] It is well known that the group 9 and 10 metals, such as Rh, Ir, Ni, Pd, and Pt, generally hydrogenate the C=C bond more easily than the C=O bond of α,β-unsaturated aldehydes.[2] After a large number of attempts have been made,[3–5] only Ir-, Os-, and Pt-based catalysts produced unsaturated alcohols so far.[6] To improve the chemoselective hydrogenation of the C=O group, the modification of the above-mentioned metals is necessary, i.e., the addition of more electropositive metals[7] or the use of oxide supports that strongly interact with the active metals.[8] While these modified catalyst systems have been effective, catalyst preparation critically depends on the precise control of the amounts of the second metal.[9] Recently, the tin alloying of the platinum group has been extensively studied and widely applied in various chemical transformations.[10] Pt–Sn/SiO_2 showed a higher selectivity toward furfuryl alcohol (FFalc) rather than Pt/SiO_2 in the hydrogenation of furfural (FFald).[11] Delbecq et al. suggested that an increase of the charge density of Pt metal by the addition of hyperelectronic metals or by the formation of a metal alloy could enhance the affinity toward C=O rather than the C=C bond to form unsaturated alcohols in the hydrogenation of α,β-unsaturated aldehydes.[12] However, precious metals, such as Pt, were utilized in these catalyst systems. Therefore, alternative economical and eco-friendly heterogeneous catalysts that would ensure the preferred hydrogenation of the C=O group over C=C are highly desired.

In the present work, we prepared Ni–Sn alloy catalysts with different Ni/Sn ratios and applied them in the selective hydrogenation of FFald to FFalc. The chemoselectivity of Ni–Sn catalysts in C=O hydrogenation could be controlled by changing the additive amount of Sn. The selective hydrogenations of various unsaturated carbonyl compounds by Ni–Sn catalysts were also studied. Ni–Sn alloy catalysts supported on aluminium hydroxide (denoted as Ni–Sn(x)/AlOH, x = Ni/Sn molar ratio) were synthesized by the hydrothermal treatment of a mixture of Raney Ni supported on aluminium hydroxide (R-Ni/AlOH) and $SnCl_2 \cdot H_2O$ in EtOH/H_2O. R-Ni/AlOH was prepared by following Petro's protocol.[13] The details of catalyst preparation and product analyses are provided in the Supporting Information (SI).[14]

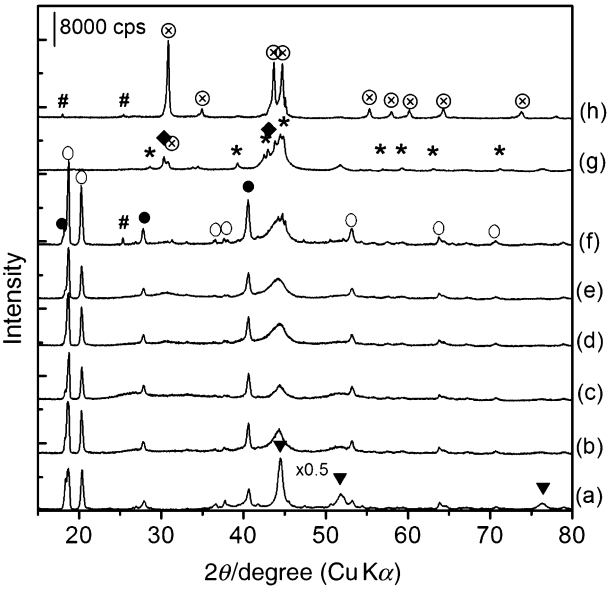


Figure 1. XRD patterns of (a) R-Ni/AlOH and Ni–Sn(x)/AlOH before H_2 treatment with Ni/Sn molar ratios of (b) 7.9, (c) 3.7, (d) 3.0, (e) 1.4, and (f) 1.0, and Ni–Sn(x)/AlOH after H_2 treatment at 773 K for 1 h with Ni/Sn molar ratios of (g) 3.0 and (h) 1.4. (●) Bayerite; (○) gibbsite; (#) β-Sn; (▼) Ni(0), (★) Ni_3Sn, (⊗) Ni_3Sn_2, and (◆) Ni_3Sn_4.

The XRD patterns of R-Ni/AlOH showed sharp diffraction peaks at $2\theta = 44.3$, 51.6, and 76.3° which correspond to the Ni(111), Ni(200), and Ni(220) species, respectively (Figure 1a). The sharp diffraction peaks were also observed at $2\theta = 18.26$, 27.8, and 40.54° that were recognized as bayerite and at $2\theta = 18.7$, 20.36, 36.66, 37.76, 53.18, 63.88, and 70.72° which were assigned to gibbsite (Figures 1a–1f).[13,15] In contrast, the XRD patterns of Ni–Sn/AlOH exhibited broadened peaks at $2\theta = 44.44°$ due to the formation of Ni–Sn alloys, i.e., Ni_3Sn and Ni_3Sn_2 (Figures 1b–1f).[15,16] In fact, the XRD patterns of Ni–Sn/AlOH after H_2 treatment at 773 K for 1 h showed that Ni_3Sn, Ni_3Sn_2, and Ni_3Sn_4 alloy phases were formed for Ni–Sn(3.0)/AlOH (Figure 1g). On the other hand, Ni_3Sn_2 alloy and β-Sn were formed for Ni–Sn(1.4)/AlOH (Figure 1h).[15] The H_2 treatment also caused the transformation of bayerite and gibbsite to amorphous alumina which have no detectable peaks in XRD analysis (Figures 1g and 1h).[17]

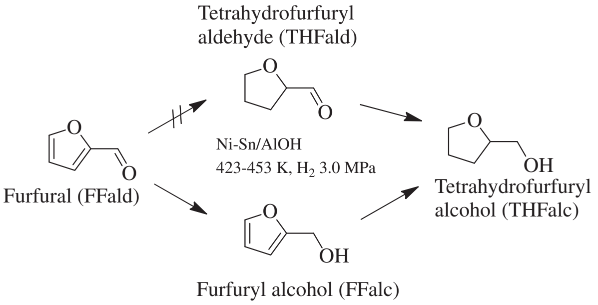
The results of the chemoselective hydrogenation of FFald by various catalysts are summarized in Table 1, and the reaction pathways are shown in Scheme 1.

It can be observed that by using Ni–Sn(7.9)/AlOH and Ni–Sn(3.7)/AlOH catalysts, FFalc yields were 78% and 80%,

Table 1. Hydrogenation of FFald by Ni–Sn/AlOH catalysts

Entry	Catalyst[a]	Sn[b] /mmol g^{-1}	Temp /K	Convn[c] /%	Yield[d] /%
1	Ni–Sn(7.9)/AlOH	0.45	453	>99	78(22)
2	Ni–Sn(3.7)/AlOH	0.75	453	99	80(19)
3	Ni–Sn(3.0)/AlOH	1.04	423	72	71(1)
4	Ni–Sn(3.0)/AlOH	1.04	453	98	94(4)
5[e]	Ni–Sn(3.0)/AlOH	1.04	453	99	96(3)
6[f]	Ni–Sn(3.0)/AlOH	1.04	453	97	93(4)
7[g]	Ni–Sn(3.0)/AlOH	1.04	453	66	59(7)
8	Ni–Sn(3.0)/AlOH[h]	1.04	453	>99	70(30)
9	Ni–Sn(1.4)/AlOH	2.14	453	>99	92(8)
10	Ni–Sn(1.4)/AlOH[h]	2.14	453	>99	100(0)
11	Ni–Sn(1.0)/AlOH	3.96	453	97	91(6)
12[f]	Ni–Sn(1.0)/AlOH	3.96	453	97	91(6)
13	R-Ni/AlOH	0	453	>99	0(100)
14	SnO	—	453	4	0(0)
15	SnO_2	—	453	28	6(3)
16	$SnCl_2\cdot 2H_2O$	—	453	72	3(1)

[a] The value in the parenthesis is Ni/Sn molar ratio. *Reaction conditions*: catalyst (0.05 g), FFald (1.1 mmol), *i*-PrOH (3 mL), H_2 (3.0 MPa), 1 h. [b] Loading amount of Sn, determined by ICP-AES. [c] Conversion, determined by GC using an internal standard. [d] Yield of FFalc. The value in the parenthesis is yield of tetrahydrofurfuryl alcohol (THFalc), determined by GC using an internal standard technique. [e] 3 h. [f] Reuse experiment after the second run. [g] Initial H_2 pressure was 2.0 MPa. [h] After H_2 treatment at 773 K for 1 h.



Scheme 1. Reaction pathways of FFald hydrogenation by Ni–Sn/AlOH catalysts.

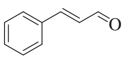
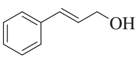
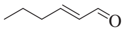
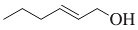
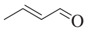
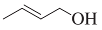
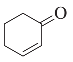
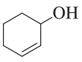
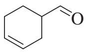
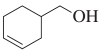
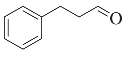
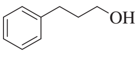
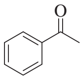
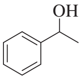
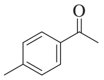
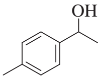
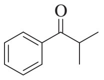
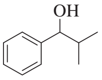
respectively (Entries 1 and 2). By increasing the loading amount of Sn (up to 1.04 mmol g^{-1}), a remarkable increase of FFalc yield was achieved (Entry 4, 94%). In the case of Ni–Sn(3.0)/AlOH, an increase of the reaction temperature from 423 to 453 K gave a notable increase in FFalc yield from 71% to 94%, (Entries 3 and 4). After 3 h, the FFalc yield slightly increased to 96% and, in contrast, that of tetrahydrofurfuryl alcohol (THFalc) decreased to 3% (Entry 5). This result suggests that further hydrogenation of the C=C furan ring in FFald did not proceed in the presence of the Ni–Sn(3.0)/AlOH catalyst. Additionally, FFalc yield decreased significantly when an initial H_2 pressure of 2.0 MPa was applied (Entry 7, 59%). On the other hand, R-Ni/AlOH converted FFald to give >99% THFalc (Entry 13), indicating that R-Ni/AlOH hydrogenated both C=C and C=O of FFald. Moreover, SnO, SnO_2, and $SnCl_2\cdot 2H_2O$ did not produce the hydrogenated products under the same conditions (Entries 14–16). The used Ni–Sn(3.0)/AlOH and Ni–Sn(1.0)/AlOH catalysts were easily separated by either simple centrifugation or filtration in air, and then they were utilized repeatedly without any special treatments. The catalysts were found to be reusable without any significant loss of activity or chemoselectivity (Entries 4 and 6, 11 and 12).[18] Furthermore, the hydrogenation of FFalc using the Ni–Sn(3.0)/AlOH catalyst resulted in only an 8.7% THFalc yield at 453 K and 3 MPa of H_2, even after 6 h. These results suggest that the addition of tin to nickel retards the C=C hydrogenation activity of nickel. Swift et al. reported that the formation of a Ni–Sn alloy by the addition of tin to a Ni/SiO_2 catalyst remarkably changed the reactivity of Ni/SiO_2 due to the change in the electron density of nickel metal.[19a] Delbecq et al. indicated that the C=O hydrogenation selectivity in the hydrogenation of α,β-unsaturated aldehydes could be enhanced by the formation of a Pt–Sn alloy due to the higher affinity toward C=O rather than the C=C bond, as noted previously.[12] Resasco et al. reported that the selective hydrogenation of C=O versus C=C in α,β-unsaturated aldehydes by a Pd–Cu alloy supported on silica was caused by the preferable η^2-coordination of C=O to Pd.[19b] After H_2 treatment at 773 K for 1 h, Ni–Sn(3.0)/AlOH catalyst gave 70% and 30% yields of FFalc and THFalc, respectively (Entry 8). In contrast, Ni–Sn(1.4)/AlOH catalyst gave 100% FFalc without the formation of THFalc (Entry 10). Therefore, we conclude that the formation of a Ni–Sn alloy may facilitate in the adsorption mode of the FFald molecule through the C=O group, giving rise to much higher yields and selectivity of FFalc rather than THFalc. These results are consistent with the fact that no tetrahydrofurfuryl aldehyde (THFald) was observed in all the catalytic results. Therefore, we speculate that FFald hydrogenation by Ni–Sn/AlOH catalysts does not proceed via THFald due to the formation of the Ni–Sn alloy (Scheme 1).

The scope of the present Ni–Sn/AlOH catalyst in the hydrogenation of various aldehydes and ketones was examined, as summarized in Table 2. Hydrogenation of the α,β-unsaturated aldehyde, cinnamaldehyde, over Ni–Sn(3.0)/AlOH yielded 92% cinnamyl alcohol at 433 K for 15 h (Entry 1). *trans*-2-Hexenaldehyde yielded 85% 2-hexene-1-ol at 403 K for 2 h (Entry 2) while crotonaldehyde yielded 45% crotyl alcohol under the same conditions (Entry 3). In the case of the hydrogenation of the α,β-unsaturated ketone, 2-cyclohexene-1-one, a 91% yield of 2-cyclohexen-1-ol was obtained at 383 K for 1 h (Entry 4). In addition, the hydrogenation of 3-cyclohexenecarbaldehyde yielded 87% 3-cyclohexenemethanol at 403 K after 6 h (Entry 5).

Hydrogenation of the aromatic aldehyde, 3-phenylpropanal, showed a high yield of aromatic alcohol (Entry 6, 96%). Furthermore, hydrogenation of aromatic ketones, such as acetophenone and *p*-methylacetophenone, gave high yields of 1-phenylethanol (95%) and 1-*p*-tolylethanol (96%), respectively, at 433 K after 3 h (Entries 7 and 8). Isobutyrophenone yielded 86% 2-methyl-1-phenyl-1-propanol under the same conditions (Entry 9).

In conclusion, chemoselective hydrogenation of unsaturated carbonyl compounds was achieved by Ni–Sn alloy catalysts, providing remarkable chemoselectivity for their corresponding unsaturated alcohols. The formation of the Ni–Sn alloy possibly

Table 2. Hydrogenation of various ketones and aldehydes catalysed by Ni–Sn(3.0)/AlOH catalyst[a]

Entry	Substrate	Product	Temp /K	Time /h	Convn /%[b]	Yield /%[c]
1			433	15	94	92
2			403	2	>99	85
3			423	6	60	45
4			383	1	96	91
5			403	6	>99	87
6			433	6	>99	96
7			433	3	>99	95
8			433	3	98	96
9			433	3	88	86

[a]*Reaction conditions*: catalyst (0.05 g), substrate (1.1 mmol), *i*-PrOH (3 mL), H_2 (3 MPa). [b]Conversion. [c]Yield, determined by GC using an internal standard technique.

plays a key role in the enhancement of the chemoselectivity. Further investigations of the alloy structure formed–reactivity relationship are now in progress.

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