

CATALYTIC ACTIVITY OF Ni_xSn_y INTERMETALLICS

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ABSTRACT

Ni_xSn_y intermetallics were prepared via mechanical alloying to obtain Ni₃Sn, Ni₃Sn₂, and Ni₃Sn₄ by using various ratios of Ni/Sn. The intermetallics were characterized by XRD and FE-SEM-EDX elemental maps to determine crystallography information and composition uniformity, respectively. Catalytic activity of these intermetallic catalysts was studied on selective hydrogenation of α , β -unsaturated aldehyde (cinnamaldehyde) using formic acid as proton and hydride donor to obtain cinnamyl alcohol which is widely used in perfume and personal care product industries. The optimal conditions, including solvent, time, temperature, and type of Ni_xSn_y intermetallic catalysts, were investigated. It was found that Ni₃Sn₄ intermetallic showed the best activity and selectivity to cinnamyl alcohol under atmospheric pressure at 60 °C for 3h in tetrahydrofuran solvent. All products were detected by GC-FID.

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INTRODUCTION

Cinnamyl alcohol is used in perfume, cosmetics, pharmaceutical, and chemical industry. The precursor of cinnamyl alcohol is cinnamaldehyde which is a type of α , β -unsaturated aldehyde. Cinnamaldehyde can be hydrogenated to hydrocinnamaldehyde or cinnamyl alcohol, depending on the hydrogenated position as illustrated in Figure 1.

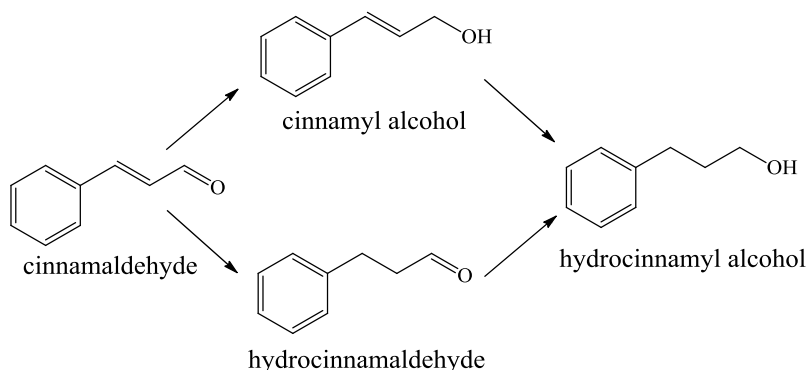


Figure 1 Cinnamaldehyde hydrogenation pathways

Typically, monometallic catalysts, such as platinum and palladium, are widely applied in hydrogenation reactions, but because of its high value, nickel, which is also a Pt-group

metal, is, thus, a good candidate due to its similar catalytic behavior to platinum (Gallezot *et al.*, 1998). In general, C=C bond is more active than C=O bond and thermodynamics favors hydrogenation of C=C over C=O bond (Bailón-García *et al.*, 2013). Therefore, to overcome these general behavior and obtain unsaturated alcohol, cinnamyl alcohol, the C=O bond should be the adsorbed position. The second metal adding to form bimetallic such as Ni-Au (Prakash *et al.*, 2016), Pt-Sn (Taniya *et al.*, 2012), Ni-In (Li *et al.*, 2013), and Pd-Sn (Hammoudeh *et al.*, 2003) was applied to improve selectivity to either C=C hydrogenation or C=O hydrogenation depending on type of second metal that was added. This phenomena caused by charge transfer of properly electropositive and electronegative metal combination that created $\delta^+\delta^-$ sites which favor to interact with C=O bond (Bailón-García *et al.*, 2013). Both activity and selectivity not only directly affected by type of catalyst but also the reaction conditions. The optimal solvent was numerously studied by many researchers earlier (Mäki-Arvela *et al.*, 2005, Pham-Huu *et al.*, 2001, Shirai *et al.*, 2001). By using non-steric alcohols such as methanol and ethanol, even the activity was good but acetal and hemiacetal were found as byproducts (Shirai *et al.*, 2001). In addition, polar solvents, for example, tetrahydrofuran and isopropyl alcohol, led to greater selectivity to cinnamyl alcohol comparing with non-polar solvents, for example, hexane and toluene, which resulting in greater selectivity to hydrocinnamaldehyde (Liu *et al.*, 2015). To avoid acetal and hemiacetal byproducts, aprotic solvents including tetrahydrofuran and 1, 4-dioxane, which has high and low dipole moment, respectively, were used as solvents in this research. In this work, formic acid was used as hydrogen source due to its high hydrogen content nontoxicity, and being liquid at room temperature. Generally, there are 2 pathways of formic acid decomposition, dehydrogenation and dehydration as shown in Figure 2. The previous studies of other researchers revealed that formic acid decomposed to hydrogen and carbon dioxide on metal surface via formate route as illustrated in Figure 3 (Singh *et al.*, 2016). Thus, we could obtained hydrogen from formic acid. In this research, the Ni_xSn_y intermetallics were synthesized by mechanical alloying with various Ni/Sn ratios to produce various phase of Ni_xSn_y intermetallics and the optimal conditions of C=O hydrogenation, including solvent, time, temperature, and type of Ni_xSn_y intermetallic catalysts, were investigated.

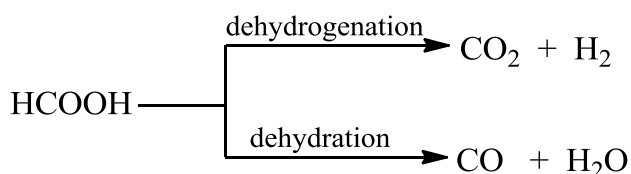


Figure 2 Decomposition pathways of formic acid

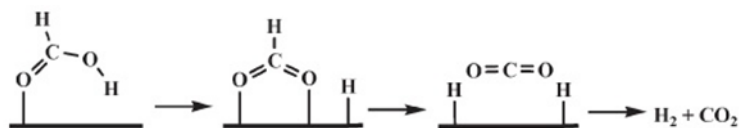


Figure 3 Dehydrogenation of formic acid via formate route (Singh *et al.*, 2016).

EXPERIMENTAL

A. Catalyst Synthesis

Ni_xSn_y intermetallics were prepared via mechanical alloying method, as mentioned elsewhere (Pithakratanayothin *et al.*, to be submitted). Ni and Sn powders ($32 \leq \mu m$) with various Ni/Sn ratios were mixed and milled using the following conditions: 5:1 ball-to-powder ratio, 300 rpm speed, and 30 h milling time. Then the mixture was heated in a vacuum chamber and further characterized by XRD (Rigaku X-ray diffractometer with $CuK\alpha$ radiation, $\lambda = 0.154 \text{ \AA}$) using a scanning speed of $1 \text{ }^\circ C/min$ in a range of $20\text{--}80^\circ 2\theta$.

B. Catalytic Activity Study

Ni_xSn_y intermetallic catalysts (300 mg) and cinnamaldehyde (630 μL , 5 mmol) were placed in a round bottom flask using various solvents (10ml). The mixture was refluxed and stirred while adding formic acid intermittently. The solution was taken for GC-FID analysis using a capillary ZB-5MS column (30 m x 250 μm x 0.5 μm , Agilent Technologies, USA) with 1 μL injection volume, a 1.0 mL/min flow rate, $110 \text{ }^\circ C$ column temperature, and 9 min run time.

RESULTS AND DISCUSSION

A. Catalysis Activity Study

From Table 1, time and temperature were the first and second conditions that were investigated. At first, Ni_3Sn was fixed to study both optimal time and temperature. The results revealed that the reaction rapidly underwent along 5 h from the beginning and obviously retarded later. In term of temperature, conversion of cinnamaldehyde was significantly lower when the reaction was carried out at $50 \text{ }^\circ C$ due to its lack of kinetic energy in the system. On the other hand, at too high temperature, 80° and $70 \text{ }^\circ C$, the reaction was too turbulent which led to fluctuation of conversion, whereas $60 \text{ }^\circ C$ reaction temperature showed the best conversion. Therefore, $60 \text{ }^\circ C$ for 5 h was stipulated to be temperature and time for further study of solvent effect.

Table 1 Overall conversion of cinnamaldehyde using 300 mg of Ni_3Sn , 5 mmol cinnamaldehyde, 25 μl of formic acid per 5 min, 10 ml of THF at; (a) 60° , (b) 50° , (c) 70° , and (d) $80 \text{ }^\circ C$

Time [h]	% Conversion	Time [h]	% Conversion
1	11.5	10	56.4
2	18.5	11	59.2
3	29.7	12	62.6
4	40.1	13	64.0
5 ^a	44.2	14	64.7

6	45.2	15	65.7
7	51.2	5 ^b	25.3
8	51.9	5 ^c	39.8
9	53.8	5 ^d	10.6

From Table 2, THF and 1,4-Dioxane having different dipole moment did not show much variation in term of the activity, whereas the selectivity to cinnamyl alcohol was obviously higher by using THF (Liu *et al.*, 2015) due to the higher dipole moment and polarity of THF that preferred to react with C=O bond. For that reason, THF was chosen to be the solvent to study type of Ni_xSn_y intermetallics effect.

Table 2 Overall conversion of cinnamaldehyde and yield of cinnamyl alcohol using 300 mg of Ni₃Sn, 5 mmol cinnamaldehyde, 25 μ l of formic acid per 5 min, 10 ml of solvent at 60 °C

Time [h]	THF		1, 4-Dioxane	
	% Conv.	% Yield of COL	% Conv.	% Yield of COL
1	11.5	0.2	16.2	0.1
2	18.5	0.3	23.3	0.1
3	29.7	0.7	32.0	0.1
4	40.1	0.9	42.8	0.1
5	44.2	1.4	45.5	0.1

By using various intermetallics, Ni₃Sn₄ showed the greatest TON, see Figure 4 and Table 3, due to its low coordination sites, relating to lattice parameter changing (Chen *et al.*, 2012) that was created by adding Sn. In general, Sn was inactive for hydrogenation (Rodiansono *et al.*, 2012), however showed some activity in this case because of formic acid which acted as co-catalyst. Generally, hydrogenation of α , β -unsaturated aldehyde under mild conditions was attractive and challenging, the focused products in this study underwent via hydrogenation. The selectivities of the hydrogenation pathway were 4.0, 3.4, and 7.8% for Ni₃Sn (hexagonal), Ni₃Sn₂ (hexagonal), and Ni₃Sn₄ (monoclinic), respectively, meaning that the crystal system had an influence on the reaction pathway and the monoclinic structure of Ni₃Sn₄ showed a better performance in hydrogenation over the hexagonal structure of Ni₃Sn and Ni₃Sn₂. The number of acid sites determined by NH₃-TPD showed an increase in the number of active sites with increasing the Sn content as following; Ni₃Sn₄ (0.4773 mmol/g) > Ni₃Sn₂ (0.0835 mmol/g) > Ni₃Sn (0.0307 mmol/g) > Ni (0.0129 mmol/g). This evidence was related to cinnamyl alcohol product, the hydrogenation at C=O bond, due to the interaction of lone pair electrons and the acid sites on metal surface. Hydrocinnamaldehyde was also obtained because Ni which was electronegative

composition might create repulsive force with oxygen atom at C=O bond, leading to C=C bond adsorption instead. In addition, further hydrogenation resulted in hydrocinnamyl alcohol product. In this condition, benzaldehyde and cinnamic acid were found as products at high yield (Marteau *et al.*, 2013, Yadav *et al.*, 2013). Moreover, the COL yields at 3, 4, and 5 h reaction times were 1.83, 1.87, and 2.03 % by using Ni₃Sn₄ intermetallics at 60 °C, respectively. Therefore, 3 h reaction time was the optimal reaction time for cinnamyl alcohol production.

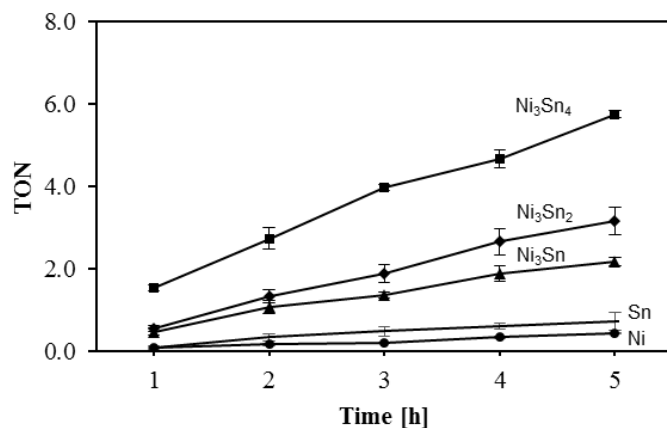


Figure 4 Turnover numbers (TON) of Ni, Ni₃Sn, Ni₃Sn₂, Ni₃Sn₄, and Sn; 300 mg of catalyst, 5 mmol cinnamaldehyde, 25 µl of formic acid per 5 min, 60 °C, 10 ml of THF

Table 3 Selectivity Percentage of all products using various catalysts, 5 mmol cinnamaldehyde, 25 µl of formic acid per 5 min, 60 °C, 5 h, 10 ml of THF

Catalyst	Desired series			Other products	
	COL	HCALD	HCOL	Benzaldehyde	Cinnamic acid
Ni	4.5	0.0	0.6	53.2	41.6
Ni ₃ Sn	2.9	1.1	0.0	58.6	37.3
Ni ₃ Sn ₂	1.9	1.4	0.1	69.6	26.9
Ni ₃ Sn ₄	3.7	2.0	2.1	56.5	35.8
Sn	2.3	0.0	0.0	58.1	39.6

CONCLUSIONS

Ni₃Sn, Ni₃Sn₂, and Ni₃Sn₄ intermetallics were synthesized via mechanical alloying by using 43, 58, and 75% tin contents with nickel, respectively. The catalytic activity study revealed that Ni₃Sn₄ showed the highest activity and selectivity to hydrogenation pathway over other type of Ni_xSn_y intermetallics. Formic acid, hydrogen donor and co-catalyst, caused the

hydrogenation reaction, leading to hydrocinnamaldehyde, cinnamyl alcohol, and hydrocinnamyl alcohol formation under mild conditions. Benzaldehyde and cinnamic acid were synthesized as by-products via oxidation and retro-aldol condensation, respectively.

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REFERENCES

- Bailón-García, E., Maldonado-Hódar, F., Pérez-Cadenas, A. and Carrasco-Marín, F.** (2013). *Catalysts* **3**(4), 853.
- Chen, X., Li, M., Guan, J., Wang, X., Williams, C. T. and Liang, C.** (2012). *Industrial & Engineering Chemistry Research* **51**(9), 3604-3611.
- Gallezot, P. and Richard, D.** (1998). *Catalysis Reviews* **40**(1-2), 81-126.
- Hammoudeh, A. and Mahmoud, S.** (2003). *Journal of Molecular Catalysis A: Chemical* **203**(1-2), 231-239.
- Li, C., Chen, Y., Zhang, S., Xu, S., Zhou, J., Wang, F., Wei, M., Evans, D. G. and Duan, X.** (2013). *Chemistry of Materials* **25**(19), 3888-3896.
- Liu, H., Li, Z. and Li, Y.** (2015). *Industrial & Engineering Chemistry Research* **54**(5), 1487-1497.
- Mäki-Arvela, P., Hájek, J., Salmi, T. and Murzin, D. Y.** (2005). *Applied Catalysis A: General* **292**, 1-49.
- Marteau, C., Ruyffelaere, F., Aubry, J. M., Penverne, C., Favier, D. and Nardello-Rataj, V.** (2013). *Tetrahedron* **69**(10), 2268-2275.
- Pham-Huu, C., Keller, N., Ehret, G., Charbonniere, L. c. J., Ziessel, R. and Ledoux, M. J.** (2001). *Journal of Molecular Catalysis A: Chemical* **170**(1-2), 155-163.
- Pithakratanayothin, S., Ruangdaj, T., Wongkasemjit, S. and Chaisuwan, T.** (To be submitted) *Catalysis Science & Technology*.
- Prakash, M. G., Mahalakshmy, R., Krishnamurthy, K. R. and Viswanathan, B.** (2016). *Catalysis Today* **263**, 105-111.
- Rodiansono, Khairi, S., Hara, T., Ichikuni, N. and Shimazu, S.** (2012). *Catalysis Science & Technology* **2**(10), 2139-2145.
- Shirai, M., Tanaka, T. and Arai, M.** (2001). *Journal of Molecular Catalysis A: Chemical* **168**(1-2), 99-103.
- Singh, A. K., Singh, S. and Kumar, A.** (2016). *Catalysis Science & Technology* **6**(1), 12-40.
- Taniya, K., Jinno, H., Kishida, M., Ichihashi, Y. and Nishiyama, S.** (2012). *Journal of Catalysis* **288**, 84-91.
- Yadav, G. D. and Fernandes, G. P.** (2013). *Catalysis Today* **207**, 162-169.