Type of chemical reaction from cinnamaldehyde using nickel-tin intermetallics under mild conditions

A. Noomnual[*,**], S. Pithakratanayothin[*], S. Wongkasemjit[*,**], T. Chaisuwan[*,**]

[*]The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand,
dsujitra@chula.ac.th
[**]The Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok 10330, Thailand

ABSTRACT

Ni_3Sn, Ni_3Sn_2, and Ni_3Sn_4 intermetallics were synthesized via mechanical alloying with different contents of nickel and tin, 43, 58, 73% of tin contents, respectively. These intermetallics were characterized by XRD and SEM-EDX. As catalysts, the activity of Ni_xSn_y intermatallics was studied in term of chemical reactions using cinnamaldehyde. Moreover, formic acid was considered to be used as a hydride donor and also as a co-catalyst in order to obtain cinnamyl alcohol. In this work, the optimal time, temperature, amount and type of Ni_xSn_y intermetallics, and also amount of formic acid were investigated. Ni_3Sn_4 had the highest turnover number. The final products of cinnamyl alcohol, hydrocinnamaldehyde, cinnamic acid, and benzaldehyde detected by GC-FID were obtained.

Keywords: Ni_xSn_y intermetallics, chemical reaction studied, cinnamaldehyde, formic acid, mild conditions

1 INTRODUCTION

Selective hydrogenation of α, β-unsaturated aldehyde (e.g. cinnamaldehyde) to unsaturated alcohol (cinnamyl alcohol) is considerably interesting in the chemical industry due to its fragrance and flavor applications, as shown in Figure 1 [1].
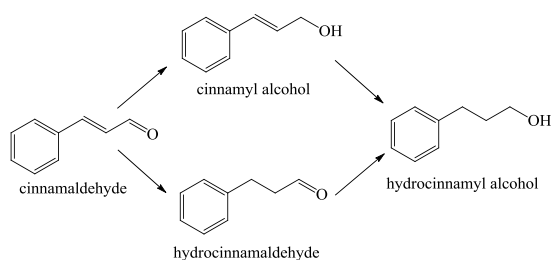

Figure 1: hydrogenation of cinnamaldehyde

Since hydrogenation of C=C bond is generally more favorable than C=O bond, the selective hydrogenation of C=O bond is thus challenging. Two basic ways to obtain unsaturated alcohol are to hinder the C=C bond adsorption by increasing the repulsive four-electron interactions with a metal while favoring the interaction of the C=O bond by adding Lewis acid site on that metal [2]. Bimetallic catalysts, such as Pt-Sn [3], Ni-Ag [4], and Ni-In [5], were investigated to increase selectivity of unsaturated alcohols. On the other hand, Ni-Si [6], and Ni-Ir [7] revealed the selectivity for saturated aldehyde. Combining these two approaches, bimetallics containing both electropositive and electronegative properties thus plays an important role for the selective hydrogenation of α, β-unsaturated aldehyde. Moreover, it was also illustrated that solvent, having polarity and steric hindrance, had influence on the hydrogenation reaction, polar solvents activated the hydrogenation of the C=O bond in cinnamaldehyde at 50 °C and 1bar H_2 whereas non-polar solvents favored hydrogenation of C=C bond [8]. Acetal or hemiacetal by-products were obtained by using alcohol, polar aprotic solvent. However, these by-products formation could be retarded by using bulky alcohol or aprotic solvent [8-14].

In this work, formic acid was chosen as a hydrogen source [15-16] and co-catalyst due to its non-toxicity, high hydrogen content, and being liquid at room temperature. Formic acid can be decomposed via 2 pathways, as depicted in Figure 2.
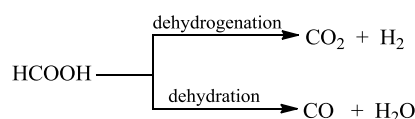

Figure 2: Formic acid decomposition pathways

The decomposition of formic acid on metals and bimetallics were studied [17-20]. It was found that formate route plays the dominant role and the rate-determining step is to dissociate formate into CO_2 and H_2. The most stable adsorption configuration of formic acid is an O-bidentate bridging structure, as illustrated in Figure 3 [21].
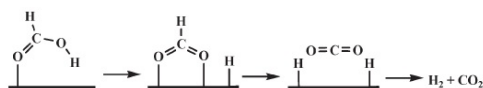
Figure 3: General mechanism of formic acid decomposition over various surfaces through formate route [21].

In this work, we prepared Ni_xSn_y intermetallics via mechanical alloying technique and studied their catalytic activity on chemical reaction of cinnamaldehyde using formic acid as a hydrogen donor and co-catalyst. The optimal time, temperature, amount and type of Ni_xSn_y intermetallics, and also amount of formic acid were investigated.

2 EXPERIMENTAL

2.1 Catalyst synthesis

Ni_xSn_y intermetallics were prepared by mechanical alloying, as mentioned elsewhere [22]. 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 diffactometer with CuKα radiation, $\lambda= 0.154$ Å) using a scanning speed of 1 °C/min in a range of 20–80° 2θ.

2.2 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 °C column temperature, and 9 min run time.

3 RESULTS AND DISCUSSION

Synthesis of intermetallics was found that using different contents of nickel and tin (43, 58, 73%), Ni_3Sn, Ni_3Sn_2, and Ni_3Sn_4, respectively, were successfully prepared. In the activity study, only Ni_3Sn catalyst was chosen to observe what type of chemical reaction took place, using various conditions, as summarized in Table 1.

From Table 1, the conversion increased by time at 60 °C. This phenomenon could be due to the fact that the system achieved enough kinetic energy, leading to ~45% conversion in both THF and 1, 4-dioxane solvents at the same temperature for 5 h reaction time. However, too high temperature (above boiling point of THF, 70° and 80 °C) resulted in a lower conversion. Because the conversion

increased from 44.2 to 56.4% after 5 h reaction time and almost became steady. The optimal reaction time was then set at 5 h.

Table 1: Percentage of conversion obtained from using Ni_3Sn, 5 mmol cinnamaldehyde, 25 μL of formic acid per 5 min with various reaction conditions

Solvent	Temperature (°C)	Reaction time (h)	Conversion (%)
THF	50	5	25.3
	60	3	27.7
	60	5	44.2
	60	10	56.4
	70	5	39.9
	80	5	10.6
1, 4-Dioxane	60	5	45.5

By using Ni_3Sn, hydrocinnamaldehyde (HCALD) and cinnamyl alcohol (COL) were produced via hydrogenation. In addition, the oxidation of cinnamaldehyde to cinnamic acid [23] and the retro-aldol condensation to benzaldehyde and acetaldehyde [24] were found with more than 15% yield and the reaction scheme was illustrated in Fig. 4.
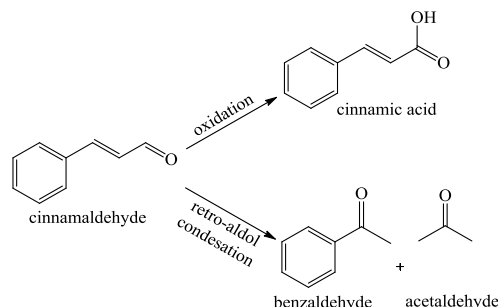

Figure 4: Scheme of oxidation and retro-aldol condensation of cinnamaldehyde

The more polar solvent, THF, led to the higher yield, 1.4% COL, as compared to 0.7% when using 1. 4-dioxane, because THF activated C=O bond, leading to a better COL formation, see Fig. 5 [15]. These optimal conditions; THF as solvent at 60 °C for 5 h reaction time, were fixed to investigate how tin content in the Ni_xSn_y intermetallics affected to the reaction.

To study the effect of the Sn content, type of catalyst was varied while fixing the other parameters. Evidently, the higher Sn content resulted in the higher turnover number (TON), as can be seen in Fig. 6, showing the TON order as following; Ni_3Sn (2.2) < Ni_3Sn_2 (3.2) < Ni_3Sn_4 (5.8).
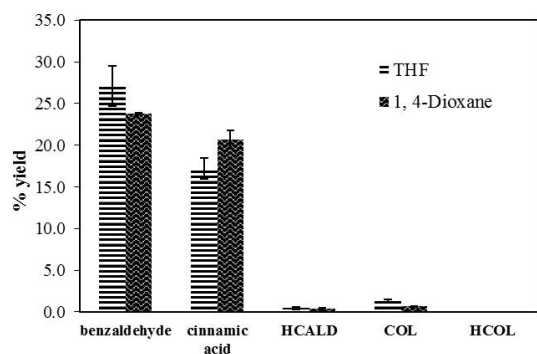
Figure 5: Plots of all products using Ni_3Sn, 5 mmol cinnamaldehyde, 25 μL of formic acid per 5 min with two different solvents at 60 °C for 5 h.

These results indicated that interstitial Sn expanded the lattice and changed the crystal system with high-index facets which related to the greater activity [6,25]. Generally, only Sn itself is inactive for hydrogenation [26], but the activity of the Sn in this system was achieved due to a help of formic acid, protonating the starting cinnamaldehyde and forcing the reaction to move forward.
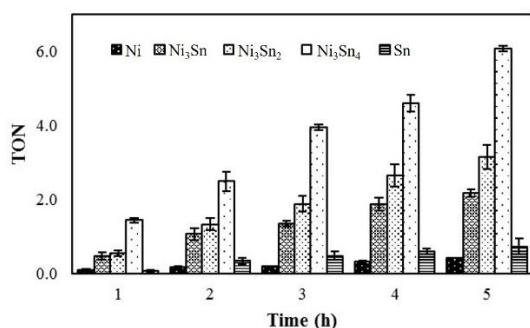

Figure 6: Plots of turnover number (TON) versus time of various Ni_xSn_y intermetallics, Ni, and Sn powders using 5 mmol cinnamaldehyde, 25 μL of formic acid per 5 min with THF at 60 °C.

All catalysts gave benzaldehyde and cinnamic acid as major products although small amounts of hydrogenated products, HCALD, COL, and HCOL, were also detected. Ni_3Sn_4 showed the maximum yield of all products, comparing to the others, as shown in Table 2.

Table 2: Yield Percentage of all products using various catalysts, 5 mmol cinnamaldehyde, 25 μL of formic acid per 5 min with THF at 60 °C for 5 h

Catalyst	Benzal-dehyde	Cinnamic acid	HCALD	COL	HCOL
Ni	23.4	18.3	0.0	1.9	0.3
Ni_3Sn	27.1	17.2	0.5	1.4	0.0
Ni_3Sn_2	31.8	12.3	0.7	0.9	0.1
Ni_3Sn_4	31.7	20.0	1.1	2.0	1.2
Sn	20.8	14.2	0.0	0.8	0.0

Since hydrogenation of α, β-unsaturated aldehyde was remarkably challenging, hydrogenation pathway was mainly concerned. From Fig. 7, most reactions underwent via hydrogenation at 2 h reaction time. Amount of catalyst was the next parameter that needed to be studied because the number of active sites had an impact on the amount of the reactant that interacted on the catalyst surface. By loading 150 and 900 mg of Ni_3Sn_4, conversions obtained were lower than that obtained using 300 mg of Ni_3Sn_4 (25.2%). The reason for these results is due to too small (150 mg) and too high (900 mg) amounts of catalyst, causing too low and too much active sites, respectively. Too much catalyst provided too much number of active sites and led to not only rapid decomposition of formic acid but also a decrease in the active site by formic acid, resulting in a smaller amount of cinnamaldehyde to interact with the catalyst [21]. Finally, the increase of formic acid directly affected to the increase of activity and changed the selectivity of benzaldehyde formation.
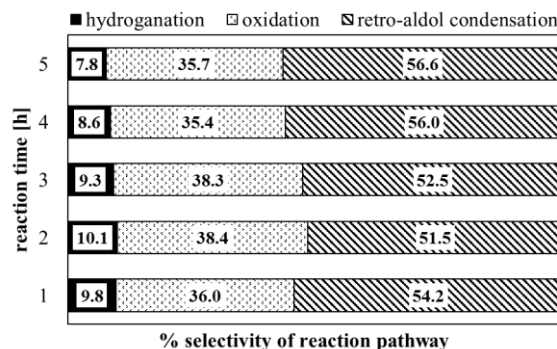

Figure 7: % selectivity of reaction pathways using Ni_3Sn_4, 5 mmol cinnamaldehyde, 25 μL of formic acid per 5 min with THF at 60 °C.

4 CONCLUSIONS

Ni_3Sn, Ni_3Sn_2, and Ni_3Sn_4 intermetallics were synthesized via mechanical alloying by using 43, 58, and 75% tin contents with nickel, respectively. The catalytic activity study revealed that benzaldehyde and cinnamic acid were synthesized via oxidation and retro-aldol condensation, respectively. Formic acid, hydrogen donor and co-catalyst, caused the hydrogenation reaction, leading to hydrocinnamaldehyde, cinnamyl alcohol, and hydrocinamyl alcohol formation under mild conditions.

ACKNOWLEDGEMENTS

REFERENCES

[1] C. S. Letizia, J. Cocchiara, J. Lalko, A. Lapczynski and A. M. Api, Food and Chemical Toxicology, 43, 837-866. 2005.

[2] E. Bailón-García, F. Maldonado-Hódar, A. Pérez-Cadenas and F. Carrasco-Marín, Catalysts, 3, 853. 2013.

[3] K. Taniya, H. Jinno, M. Kishida, Y. Ichihashi and S. Nishiyama, Journal of Catalysis, 288, 84-91. 2012.

[4] M. G. Prakash, R. Mahalakshmy, K. R. Krishnamurthy and B. Viswanathan, Catalysis Today, 263, 105-111. 2016.

[5] C. Li, Y. Chen, S. Zhang, S. Xu, J. Zhou, F. Wang, M. Wei, D. G. Evans and X. Duan, Chemistry of Materials, 25, 3888-3896. 2013.

[6] X. Chen, M. Li, J. Guan, X. Wang, C. T. Williams and C. Liang, Industrial & Engineering Chemistry Research, 51, 3604-3611. 2012.

[7] W. Lin, H. Cheng, L. He, Y. Yu and F. Zhao, Journal of Catalysis, 303, 110-116. 2013.

[8] H. Yamada and S. Goto, Journal of Chemical Engineering of Japan, 36, 586-589. 2003.

[9] P. Mäki-Arvela, J. Hájek, T. Salmi and D. Y. Murzin, Applied Catalysis A: General, 292, 1-49. 2005.

[10] J. Hájek, N. Kumar, P. Mäki-Arvela, T. Salmi, D. Y. Murzin, I. Paseka, T. Heikkilä, E. Laine, P. Laukkanen and J. Väyrynen, Applied Catalysis A: General, 251, 385-396. 2003.

[11] M. Shirai, T. Tanaka and M. Arai, Journal of Molecular Catalysis A: Chemical, 168, 99-103. 2001.

[12] H. Liu, Z. Li and Y. Li, Industrial & Engineering Chemistry Research, 54, 1487-1497. 2015.

[13] L. Zhang, J. M. Winterbottom, A. P. Boyes and S. Raymahasay, Journal of Chemical Technology & Biotechnology, 72, 264-272. 1998.

[14] C. Pham-Huu, N. Keller, G. Ehret, L. c. J. Charbonniere, R. Ziessel and M. J. Ledoux, Journal of Molecular Catalysis A: Chemical, 170, 155-163. 2001.

[15] G. Wienhöfer, F. A. Westerhaus, K. Junge and M. Beller, Journal of Organometallic Chemistry, 744, 156-159. 2013.

[16] A. Yepez, J. M. Hidalgo, A. Pineda, R. Cerny, P. Jisa, A. Garcia, A. A. Romero and R. Luque, Green Chemistry, 17, 565-572. 2015.

[17] Q. Luo, M. Beller and H. Jiao, Journal of Theoretical and Computational Chemistry, 12, 1330001. 2013.

[18] Q. Luo, T. Wang, M. Beller and H. Jiao, Journal of Molecular Catalysis A: Chemical, 379, 169-177. 2013.

[19] L. Jia, D. A. Bulushev, S. Beloshapkin and J. R. H. Ross, Applied Catalysis B: Environmental, 160–161, 35-43. 2014.

[20] Z. Wei, J. Sun, Y. Li, A. K. Datye and Y. Wang, Chemical Society Reviews, 41, 7994-8008. 2012.

[21] A. K. Singh, S. Singh and A. Kumar, Catalysis Science & Technology, 6, 12-40. 2016.

[22] S. Pithakratanayothin, T. Ruangdaj, S. Wongkasemjit, and T. Chaisuwan, Catalysis Science and Technology. [To be submitted]

[23] C. Marteau, F. Ruyffelaere, J. M. Aubry, C. Penverne, D. Favier and V. Nardello-Rataj, Tetrahedron, 69, 2268-2275. 2013.

[24] G. D. Yadav and G. P. Fernandes, Catalysis Today, 207, 162-169. 2013.

[25] D. Wang, H. Jiang, X. Zong, Q. Xu, Y. Ma, G. Li and C. Li, Chemistry – A European Journal, 17, 1275-1282. 2011.

[26] Rodiansono, S. Khairi, T. Hara, N. Ichikuni and S. Shimazu, Catalysis Science & Technology, 2, 2139-2145. 2012.