Supporting information for

Understanding the Role of Atomic Ordering in the Crystal Structures of Ni_xSn_y towards efficient Vapor Phase Furfural Hydrogenation

Vijaykumar S. Marakatti,¹ Nidhi Arora,¹ Sandhya Rai,² Saurav Ch. Sarma,¹ Sebastian C. Peter¹*

¹New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore-560064, India.

² Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore-560064, India.

*Corresponding author: sebastiancp@jncasr.ac.in. Phone: 080-22082998, Fax: 080-22082627

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Ni/Sn ^a	Ni/Al ^a	Ni/Sn ^b	Ni/Al ^b	Phase	Conversion of Furfural	Selectivity for furfural
					(%)	alcohol (%)
3.5	2.5	3.32	2.45	Ni ₃ Sn	78.2	20.7
3	2.5	3.10	2.28	Ni ₃ Sn+NiSn	76.0	25.1
2.5	2.5	2.40	2.38	Ni ₃ Sn+NiSn	69.8	30.2
2	2.5	1.92	2.56	Ni_3Sn_2	66.2	68.2
1.5	2.5	1.43	2.63	Ni ₃ Sn ₂	67.8	61.2
1.0	2.5	0.90	2.48	Ni ₃ Sn ₄	2.3	72.0
0.75	2.5	0.75	2.32	$Ni_3Sn_4 + NiSn$	1.9	80.5

Table S1. The Physico-chemical properties of Ni_xSn_y-Al₂O₃ catalyst with catalytic activity in furfural hydrogenation.

A-Synthetic composition; b-Composition of synthesized material as determined by ICP-OES (standard deviation = ± 0.1)

Table S2. The selectivity of side products in furfural hydrogenation over various Ni_xSn_y -Al₂O₃IMCs.

Ni _x Sn _y -Al ₂ O ₃ IMCs		Selectivity (%)							
	FA	Furan	THF	2-	butanol	2-MF	2-THFA	Others*	Carbon balance
				MTHF					(%)
Ni ₃ Sn ₄	74.1	2.5	0.9				16.1	6.4	98.9
Ni ₃ Sn ₄	72.0	2.1	1.3				20.8	3.8	99.0
Ni ₃ Sn ₄	76.2	0.6	0.5				19.7	3.0	99.2
Ni ₃ Sn ₄	71.4	1.0	0.4				18.1	9.1	
Ni ₃ Sn ₂	57.1	19.9	4.4	3.3	0.6	2.3	1.5	11.1	94.7
Ni ₃ Sn ₂	61.2	15.2	3.9	2.1	0.7	3.0	1.2	12.7	94.3
Ni _{1.5} Sn	73.5	14.7	2.0	1.5	0.2	1.1	1.7	5.3	95.4
Ni _{1.5} Sn	72.5	16.8	2.5	0.8	0.75	0.1	2.6	3.95	98.6
Ni ₃ Sn	24.0	17.2	8.3	4.2	10.2	20.8	2.2	13.1	
Ni ₃ Sn	20.7	21.6	9.3	3.7	8.6	21.1	1.82	13.2	93.7
Ni ₃ Sn	26.5	23.9	8.3	3.5	10.1	15.4	1.03	11.2	91.6
Ni ₃ Sn	71.7	0.8	0.1	-	-	-	24.6	2.8	91.2
Ni	8.11	52.8	3.5	0.2	3.4	5.0	17.3	11.7	78.5

*mainly include 1,5 and 1,2- pentanediol,2-petnanol other hydrocarbons

Intermetallic compound	Bulk	Surface
(Ni/Al=2.5)	Ni/(Ni+Sn) ^a	Ni/(Ni+Sn) ^b
Ni ₃ Sn	0.75	0.57
Ni_3Sn_2	0.60	0.50
Ni ₃ Sn ₄	0.42	0.28

Table S3. Surface and bulk composition of Ni_xSn_y IMCs.

^a calculated form the Ni/Sn ratio from the stochiometric formula, ^b calculated from XPS

Table S4. Results of the fitting analysis in terms of coordination number (CN) interatomic distance(R) for references.

Ni-Sn	Ni ₃ Sn ₄	Ni ₃ Sn ₂	Ni _{1.5} Sn	Ni ₃ Sn
IMCs				
CN _{Ni-Ni}	1.36 (2)	1.0(1)	1.479(1)	1.5 (4)
CN _{Ni-Sn}	0.552(4)	1.148(1)	0.897(1)	1.1 (2)
$\Delta E0$	2.89	3.30	2.75	3.34
R _{Ni-Ni}	2.54 (2.64)	2.60 (2.57)	2.60 (2.59)	2.61 (2.61)
R _{Ni-Sn}	2.62 (2.66)	2.60 (2.64)	2.60 (2.68)	2.61 (2.61)
σ^2 _{Ni-Ni}	0.01243	0.01562	0.01554	0.01606
σ^2 Ni-Sn	0.00427	0.00919	0.01369	0.01320
R factor	0.02	0.009	0.011	0.003

The values in the parentheses are theoretical bond lengths and coordination Numbers.

Table S5. Surface energy of the exposed plane of Ni_3Sn_4 and Ni_3Sn compounds determined by the DFT study.

IMCs	Plane	E _{ads} (J/m ²)	
	S		
Ni ₃ Sn	(100)	-0.0324	
	(101)	0.0162	
	(201)	1.8612	
Ni ₃ Sn ₄	(111)	7.0814	
	(310)	-8.7324	
	(40-1)	-14.057	
	(31-2)	-8.5583`	
Ni_3Sn_2	(112)	-2.7661	
	(122)	0.9119	
	(210)	0.0301	
Ni _{1.5} Sn	(101)	-4.7079	
	(102)	7.4965	
	(110)	2.0656	
Ni	(111)	-1.1878	

Determination of exposed plane: We have initially chosen several planes based on the high intensity peak in the XRD and HR-TEM analysis for surface energy calculations as given in below Table. Based on the calculations, we observed that in some case the maximum intensity peak of XRD is the exposed plane and in some case not. The high-resolution TEM images of exposed planes of each compound were also determined on different particles to check reproducibility of the exposed plane in them. In all the case, we observed the consistency on the observed exposed plane. Moreover, theoretically determined exposed planes having lower surface energy were well matched with the observed HR-TEM analysis. Therefore, the reaction mechanistic pat ways were made over the following planes. For example: In case of Ni₃Sn₂, (112) was the exposed plane as supported by XRD (100 % intense peak), HR TEM (d spacing) and DFT calculations {lower surface energy of (112) compared to (122) and (210)}. We have chosen (122) and (210) plane to compare with (112) in DFT surface energy calculation studies because they have high intensity peaks in XRD next to (112) plane. Since all other experiment conditions support the (112) we have taken this as the exposed plane.

In case of Ni₃Sn₄ the (111) was the exposed plane as supported by XRD (100 % intense peak) whereas (40-1) was the exposed plane as determined by HR TEM (d spacing) and DFT calculations {lower surface energy of (40-1) compared to (111) (310) and (31-2)}. We have chosen (40-1), (31-2) and (310) plane to compare with (40-1) in DFT surface energy calculation studies because they have high intensity peaks in XRD next to (111) plane. Since TEM and DFT studies support the (40-1) we have taken this as the exposed plane.

Similarly, in case of Ni₃Sn the exposed plane was (100) and (101) as determined by the HRTEM and surface energy calculation compared to (201) plane with 100% intense peak. In case of Ni_{1.5}Sn, the exposed plane was (101) as determined by the HR-TEM, XRD and Surface energy calculations.

Table S6. Elemental composition at different regions of each Ni_xSn_y-Al₂O₃ IMCs.

Nominal	Nominal Amount		tomic % con			
		determined by EDAX				
Ni/Sn	Ni /Al	Ni	Sn	Al	Ni/Sn	Ni/Al
1.0	1.5	38.05	41.42	22.51	0.91	1.69
		41.04	37.39	24.55	1.1	1.67
1.0	2.5	39.73	46.20	14.06	0.86	2.82
		40.55	44.31	15.12	0.91	2.68
1.0	3.5	44.84	41.01	14.14	1.09	3.17
		44.99	42.70	12.29	1.05	3.66
1.5	1.5	41.93	30.47	27.59	1.37	1.52
		41.76	29.60	28.62	1.41	1.45
1.5	2.5	51.85	39.34	21.10	1.43	2.45
		52.31	38.25	20.87	1.36	2.50
1.5	3.5	50.15	36.89	12.95	1.86	3.87
		51.35	35.74	12.90	1.43	3.98
3.5	1.5	50.35	15.64	34.0	3.21	1.48
		50.38	15.22	34.39	3.31	1.46
3.5	2.5	60.89	20.02	19.08	3.04	3.2
		61.1	17.65	21.19	3.46	2.88
3.5	3.5	65.22	17.48	17.29	3.70	3.77
		64.43	16.50	19.05	3.90	3.38

Table S7. Comparison of Catalytic Activity of the Ni _x Sn _y -IMCs with Other Reported Sol	id
Catalysts	

Catalyst	Furfural Conversion (%)	Furfural alcohol selectivity (%)	Yield (%)
CuCr/TiO ₂	90	79	71.1
Cu/SiO ₂	98	73	71.5
Cu-Ca-SiO ₂	100	99	99
Co-Cu/SiO ₂	65	64	41.6
PtSn@mSiO ₂	100	98	98
PdCu/Zeolite –Y	58	58	33.6
Cu-Ni-Mg-Al-oxide	80	64	51.2
Ni ₃ -Sn ₂ -Al ₂ O ₃	67.8	61.2	41.5



Figure S1. The XRD pattern comparison of synthesized Ni_xSn_y-Al-LDH (Ni/Sn = 0.75, 1.5, 2.5 and, 3.5) with Mg-Al LDH phase.



Figure S2. The TEM images of synthesized Ni_xSn_y-Al- LDH having Ni/Sn = 0.75 (a&b), Ni/Sn 3.5 (c&d))



Figure S3. The XRD pattern of Ni₃Sn Al-LDH annealed at different temperature of 700 and 800 °C



Figure S4. The XRD Pattern of Ni_{1.5}Sn Al-LDH annealed at different temperature of 700 and 800 °C.



Figure S5. Comparison of XRD pattern of synthesized Ni_xSn_y having different Ni/Sn ratio (Ni/Al= 1.5) with simulated XRD pattern.

^{*} Indicates the presence of the NiSn phase.



Figure S6. The XRD pattern of Ni-Al-LDH annealed at 800 $^\circ\mathrm{C}$



Figure S7. The TEM image of Ni/Al₂O₃ annealed at 800 °C (a&b)



Figure S8. XRD pattern of Al₂O₃ synthesized by precipitation method and annealed at 800 °C



Figure S9. DRIFT, STEM, and elemental color mapping of Ni₃Sn₄ separated by Al₂O₃. The spherical particles show the homogeneous distribution of Ni and Sn indicating the formation of IMCs. The well separated Al₂O₃ matrix from the particles can also be observed.



Figure S10. EDAX spectra of Ni₃Sn₄ with different Ni/Al ration (a&b) Ni/Al = 1.5, (c&d) Ni/Al = 2.5, (e and f) Ni/Al = 3.5.



Figure S11. XRD pattern of Ni₃Sn₂, Ni_{1.5}Sn compounds with different Ni/Al ratios.



Figure S12. (a) TEM images and (b) High resolution image of Ni₃Sn₂ showing well separated nanoparticles.



Figure S13. EDAX spectra of Ni_{1.5}Sn with different Ni/Al ration (a&b) Ni/Al= 1.5, (c&d) Ni/Al = 2.5, (e and f) Ni/Al = 3.5.



Figure S14. EDAX spectra of Ni₃Sn with different Ni/Al ration (a&b) Ni/Al= 1.5, (c&d) Ni/Al =2.5, (e and f) Ni/Al =3.5.



Figure S15. DRIFT, STEM, and elemental color mapping of Ni₃Sn separated by Al_2O_3 . The spherical particles show the homogeneous distribution of Ni and Sn indicating the formation of IMCs. The well separated Al_2O_3 matrix from the particles can also be observed.



Figure S16. Normalized XANES spectra for Ni-K-edge of Ni_xSn_y nanoparticles.



Figure S17. Effect of a) WHSV and b) H_2 /Fufural for the Ni₃Sn₂-Al₂O₃ (Ni/Al = 2.5) IM catalyst for the furfural hydrogenation reaction.



Figure S18.Deactivtion study for the Ni_3Sn_2 - Al_2O_3 (Ni/Al = 1.5) IM catalyst for the furfural hydrogenation reaction.