Synthesis of Pt₃Sn Catalyst Using Solvothermal Method Assisted by Deep Eutectic Solvents for Selective Hydrogenation of Furfural to Furfuryl Alcohol

Ruonan Wang^a, Xuran Ma^a, Dairui Ding^a, Bowen Huang^{*b}, Zhiguo Zhu^a, Ting Su^a, Weiping Liao^a, Hongying Lü^{*a}, Kaixuan Yang^{*a}

^aCollege of Chemistry and Chemical Engineering, Yantai University, Yantai 264005,

P. R. China

^bCollege of Materials Science and Engineering, Hunan University, Changsha 410082,

P.R. China

*To whom correspondence should be addressed: Email: yangkaixuanyt@ytu.edu.cn;

hylv@ytu.edu.cn

Table of contents

 Table S1. Physicochemical properties of Pt-Sn catalysts with different synthesis

 temperature

Table S2. Physicochemical properties of Pt-Sn catalysts with different Pt/Sn ratio

Table S3. The calculated charge transfers between Pd and Sn in Pt₃Sn unit cell.

Table S4. FAL hydrogenation to FOL over different Pt-Sn catalysts.

Table S5. Calculated *k* of FAL hydrogenation over Pt/CNTs and PtSn_{0.5}/CNTs-100 under different temperature.

Scheme S1. Proposed adsorption mechanism of FAL and H₂ on different catalysts.

Fig. S1. (a) N₂ adsorption and desorption isotherm of Pt-Sn catalysts with (a) different synthesis temperature and (b) Pt/Sn ratio.

Fig. S2. SEM image and the corresponding elemental EDX mapping of $PtSn_{0.2}/CNTs$ -100

Fig. S3. SEM image and the corresponding elemental EDX mapping of PtSn_{0.33}/CNTs-100

Fig. S4. SEM image and the corresponding elemental EDX mapping of $PtSn_{0.5}/CNTs$ -100

Fig. S5. SEM image and the corresponding elemental EDX mapping of PtSn_{1.0}/CNTs-100

Fig. S6. SEM image and the corresponding elemental EDX mapping of PtSn_{2.0}/CNTs-100

Fig. S7. (a) STEM image and (b) TEM image of Pt/CNTs. The inset images correspond

to the particle size distribution of catalyst and lattice fringe of Pt, respectively.

Fig. S8. (a) STEM image and (b) the particle size distribution of Pt/CNTs-IM.

Fig. S9. Variation of conversion and selectivity with reaction time for the hydrogenation of FAL over (a) $PtSn_{0.5}/CNTs-60$, (b) $PtSn_{0.5}/CNTs-80$, (c) $PtSn_{0.5}/CNTs-100$, (d) $PtSn_{0.5}/CNTs-140$, (e) $PtSn_{0.5}/CNTs-180$. Reaction condition: 140 °C, 2 MPa, 1 h, THF as solvent, and 50 mg catalyst.

Fig. S10. Variation of conversion and selectivity with reaction time for the hydrogenation of FAL over (a) Pt/CNTs, (b) $PtSn_{0.2}/CNTs-100$, (c) $PtSn_{0.33}/CNTs-100$,

(d) $PtSn_{0.5}/CNTs-100$, (e) $PtSn_{1.0}/CNTs-100$, (f) $PtSn_{2.0}/CNTs-100$. Reaction condition: 140 °C, 2 MPa, 1 h, THF as solvent, and 50 mg catalyst.

Fig. S11. STEM images of $PtSn_{0.5}/CNTs-60$, $PtSn_{0.5}/CNTs-140$, and $PtSn_{0.5}/CNTs-180$. The inset images correspond to the particle size distribution.

Fig. S12. Fitting of the pseudo-first-order kinetic model to the hydrogenation of FAL experimental datas collected over (a) $PtSn_{0.5}/CNTs-100$ and (b) Pt/CNTs.

Fig. S13. Stability test over $PtSn_{0.5}/CNTs-100$ with low FAL conversion. Reaction conditions: 0.05 g catalyst, 80 °C, 2 MPa, H₂O as solvent, and 50 min.

Fig. S14. SEM image and the corresponding elemental EDX mapping of spent PtSn_{2.0}/CNTs-100

Samples	$S_{BET}(m^2/g)$
PtSn _{0.5} /CNTs-60	146.6
PtSn _{0.5} /CNTs-80	148.5
PtSn _{0.5} /CNTs-100	142.1
PtSn _{0.5} /CNTs-140	135.4
PtSn _{0.5} /CNTs-180	143.1

Table S1. Physicochemical properties of Pt-Sn catalysts with different synthesis

temperature

Samples	$S_{_{BET}}(m^{2}/g)$
CNT	144.5
Pt/CNTs	147.3
PtSn _{0.2} /CNTs-100	142.4
PtSn _{0.5} /CNTs-100	142.1
PtSn _{1.0} /CNTs-100	138.4
PtSn _{2.0} /CNTs-100	120.9

Table S2. Physicochemical properties of Pt-Sn catalysts with different Pt/Sn ratio

Atom	Pt(1)	Pt(2)	Pt(3)	Sn(1)
Charge transfer (e) ^a	0.413	0.326	0.470	-1.209

Table S3. The calculated charge transfers between Pd and Sn in Pt_3Sn unit cell.

a. "-" means getting electrons

Entry	Catalyst	T (°C)	Time (h)	Pressure (MPa)	Con. (%)	Sel. (%)	Ref.
1	Pt-Sn/SiO ₂	100	5	20	47	100	[1]
2	Pt-Sn@mSiO ₂	160	_a	1	99	97	[2]
3	PtSn _{0.2} /SiO ₂	100	8	10	100	96	[3]
4	PtSn _{0.8} /SiO ₂	100	8	10	71	98	[3]
5	Pt ₁ Sn _{0.3} /HMSNs	100	5	10	99	98	[4]
6	Pt-Sn/SiO ₂	100	5	20	63	99	[5]
7	PtSn _{0.10} @UiO- 66-NH ₂	160	10	-	60	98	[6]
8	PtSn _{0.5} /CNTs- 100	80	6	20	>99	>99	This work

 Table S4. FAL hydrogenation to FOL over different Pt-Sn catalysts.

^a performed in a fixed-bed reactor.

Catalyst	T/K	k(min ⁻¹)	R ²
Pt/CNTs-100	313.15	0.00072	0.99
	323.15	0.00119	0.99
	333.15	0.00172	0.99
	353.15	0.00313	0.99
PtSn _{0.5} /CNTs-100	313.15	0.000904	0.99
	323.15	0.001418	0.99
	333.15	0.001812	0.99
	353.15	0.002997	0.98

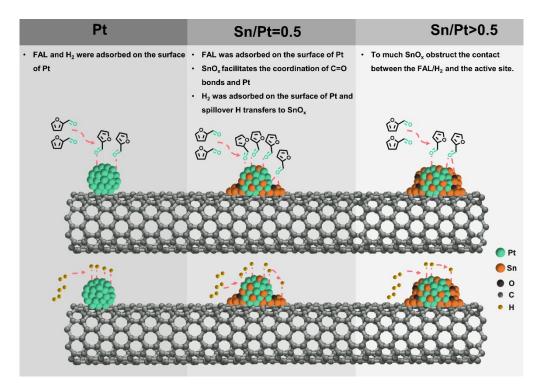
Table S5. Calculated k of FAL hydrogenation over Pt/CNTs-100 and PtSn_{0.5}/CNTs-

100 under different temperature.

					5		
Entry	Con.% ^a		Sel.% ^a				
		FOL	THFOL	2-MF	2-MTHF	Unknown chemicals ^b	
1	96.9	99.4	0	0	0	0.6	
2	95.9	97.9	1.2	0	0	0.9	
3	95.9	96.1	2.7	0	0	1.2	
4	95.5	95.7	2.9	0.6	0	0.8	
5	96.9	94.3	3.8	1.2	0	0.7	
6	94.9	91.2	4.7	2.2	0	1.9	
7	96.0	91.7	5.5	1.4	0	1.4	
8	94.0	90.4	6.3	2.3	0	1.0	
9	92.9	90.6	6.4	1.2	0	1.8	
10	91.7	86.9	9.6	1.5	0	2.0	

 Table S6. Hydrogenation of FAL over different catalysts.

^aReaction conditions: 80 °C, 2 MPa, 4 h, 50 mg catalyst, and H₂O as solvent. ^bCalculated by carbon balance.



Scheme S1. Proposed adsorption mechanism of FAL and H₂ over different catalysts.

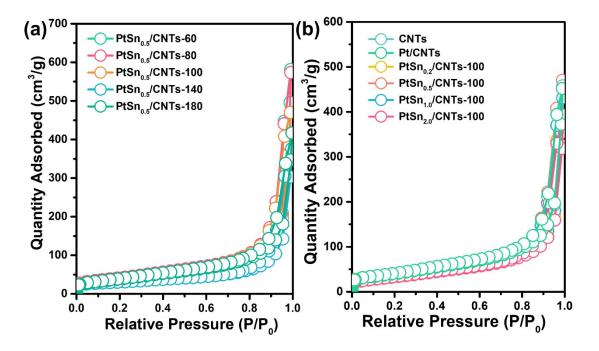


Fig. S1 (a) N_2 adsorption and desorption isotherm of Pt-Sn catalysts with (a) different

synthesis temperature and (b) Pt/Sn ratio.

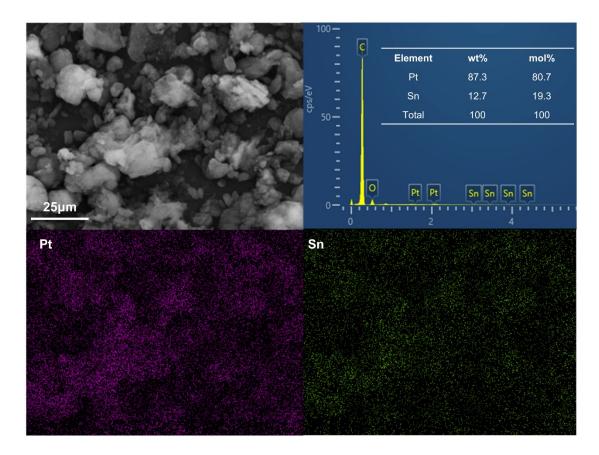


Fig. S2 SEM image and the corresponding elemental EDX mapping of $PtSn_{0.2}/CNTs$ -

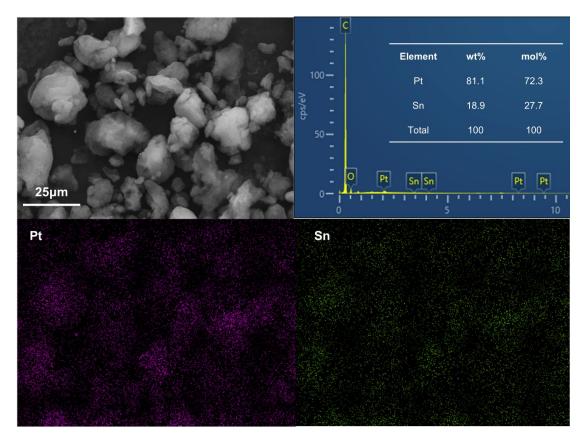


Fig. S3 SEM image and the corresponding elemental EDX mapping of $PtSn_{0.33}/CNTs$ -

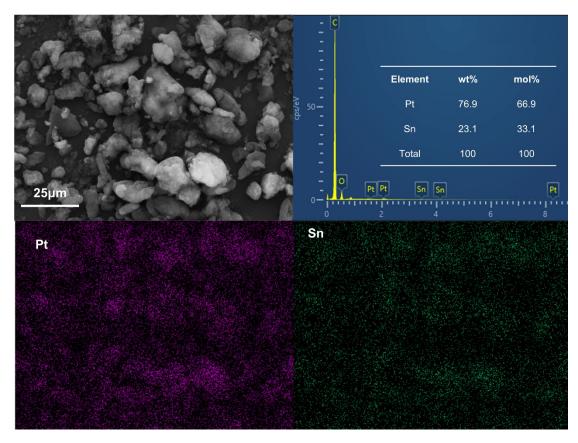


Fig. S4 SEM image and the corresponding elemental EDX mapping of $PtSn_{0.5}/CNTs$ -

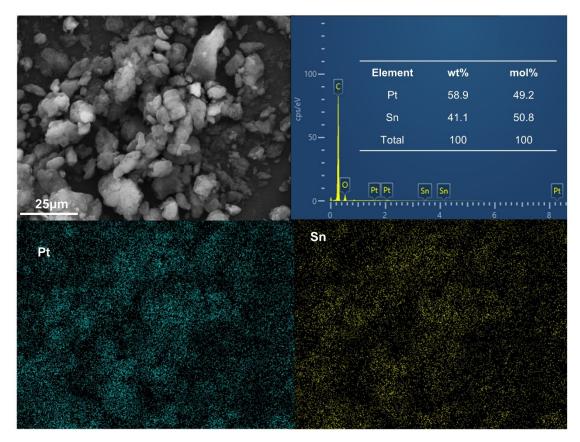


Fig. S5 SEM image and the corresponding elemental EDX mapping of $PtSn_{1.0}/CNTs$ -

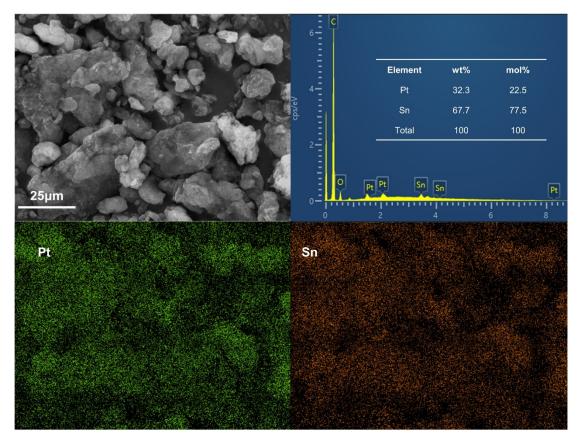


Fig. S6 SEM image and the corresponding elemental EDX mapping of $PtSn_{2.0}/CNTs$ -

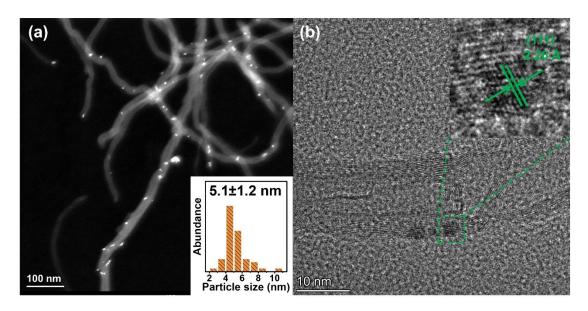


Fig. S7 (a) STEM image and (b) TEM image of Pt/CNTs. The inset images correspond to the particle size distribution of catalyst and lattice fringe of Pt, respectively.

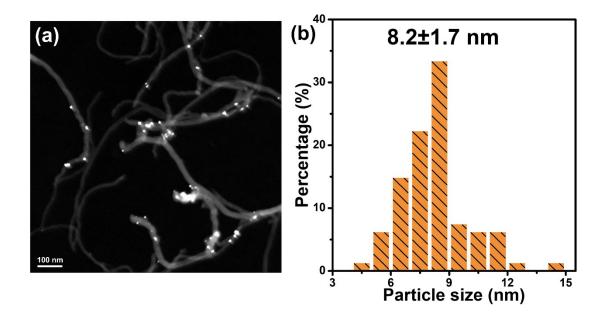


Fig. S8 (a) STEM image and (b) the particle size distribution of $PtSn_{0.5}/CNTs$ -IM.

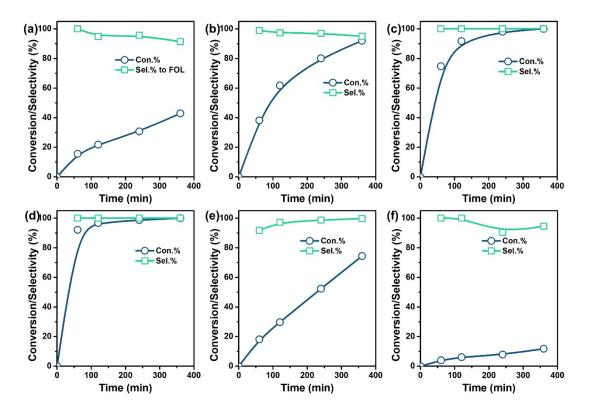


Fig. S9 Variation of conversion and selectivity with reaction time for the hydrogenation of FAL over (a) Pt/CNTs, (b) $PtSn_{0.2}/CNTs-100$, (c) $PtSn_{0.33}/CNTs-100$, (d) $PtSn_{0.5}/CNTs-100$, (e) $PtSn_{1.0}/CNTs-100$, (f) $PtSn_{2.0}/CNTs-100$. Reaction condition: 140 °C, 2 MPa, 1 h, THF as solvent, and 50 mg catalyst.

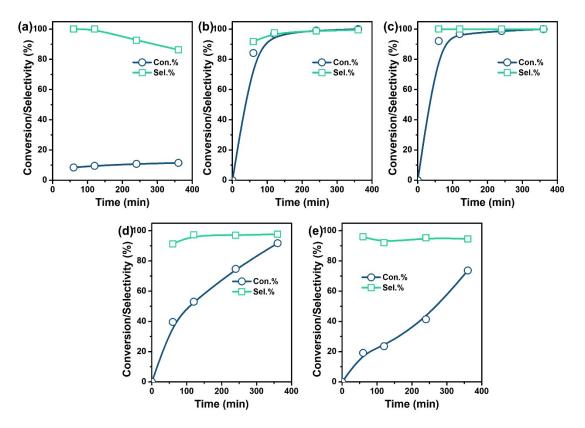


Fig. S10 Variation of conversion and selectivity with reaction time for the hydrogenation of FAL over (a) $PtSn_{0.5}/CNTs-60$, (b) $PtSn_{0.5}/CNTs-80$, (c) $PtSn_{0.5}/CNTs-100$, (d) $PtSn_{0.5}/CNTs-140$, (e) $PtSn_{0.5}/CNTs-180$. Reaction condition: 140 °C, 2 MPa, 1 h, THF as solvent, and 50 mg catalyst.

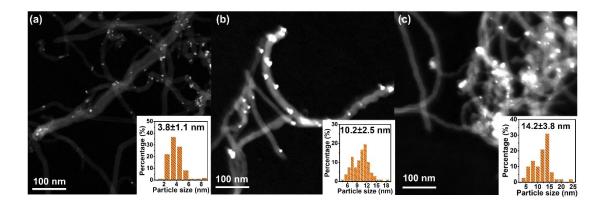


Fig. S11 STEM images of $PtSn_{0.5}/CNTs-60$, $PtSn_{0.5}/CNTs-140$, and $PtSn_{0.5}/CNTs-180$.

The inset images correspond to the particle size distribution.

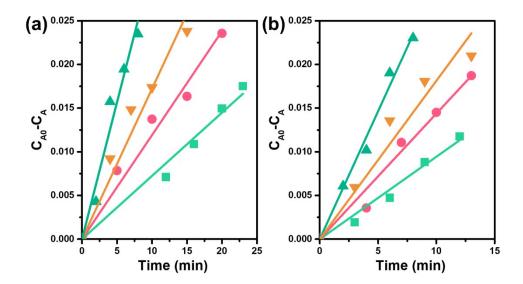


Fig. S12 Fitting of the pseudo-zero-order kinetic model to the hydrogenation of FAL experimental data collected over (a) $PtSn_{0.5}/CNTs-100$ and (b) Pt/CNTs-100.

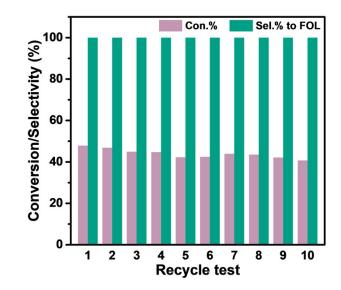


Fig. S13 Stability test over $PtSn_{0.5}/CNTs-100$ with low FAL conversion. Reaction conditions: 0.05 g catalyst, 80 °C, 2 MPa, H₂O as solvent, and 50 min.

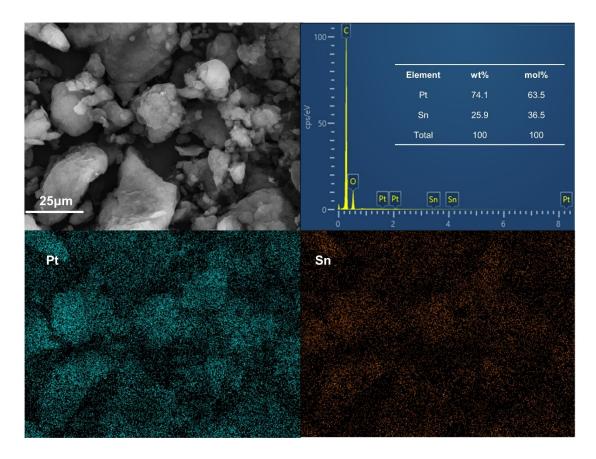


Fig. S14 SEM image and the corresponding elemental EDX mapping of spent $PtSn_{2.0}/CNTs-100$

Reference

- Á. O'driscoll, J. Leahy and T. Curtin, The influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol, *Catal. Today*, 2017, 279, 194-201.
- R. V. Maligal-Ganesh, C. Xiao, T. W. Goh, L.-L. Wang, J. Gustafson, Y. Pei, Z. Qi, D. D. Johnson, S. Zhang, F. Tao and W. Huang, A ship-in-a-bottle strategy to synthesize encapsulated intermetallic nanoparticle catalysts: exemplified for furfural hydrogenation. *ACS Catal.*, 2016, 6, 1754-1763.
- V. Vetere, A. B. Merlo, J. F. Ruggera and M. L. Casella, Transition metal-based bimetallic catalysts for the chemoselective hydrogenation of furfuraldehyde, *J. Braz. Chem. Soc.*, 2010, 21, 914-920.
- T. Xiao, P. Yan, K. Li, C. Yang, H. Yu, J. Wang, H. Yin and S. Zhou, Hollow Mesoporous Nanoreactors with Encaged PtSn Alloy Nanoparticles for Selective Hydrogenation of Furfural to Furfuryl Alcohol, *Ind. Eng. Chem. Res.*, 2021, 60, 6078-6088.
- A. i. O'Driscoll, T. Curtin, W. Y. Hernández, P. Van Der Voort and J. J. Leahy, Hydrogenation of furfural with a Pt–Sn catalyst: The suitability to sustainable industrial application, *Org. Process Res. Dev.*, 2016, 20, 1917-1929.
- B. Zhang, Y. Pei, R. V. Maligal-Ganesh, X. Li, A. Cruz, R. J. Spurling, M. Chen, J. Yu, X. Wu and W. Huang, Influence of Sn on stability and selectivity of Pt–Sn@ UiO-66-NH₂ in furfural hydrogenation, *Ind. Eng. Chem. Res.*, 2020, 59, 17495-17501.