One-pot two-step synthesis of alkyl levulinates directly from furfural by combining Ni_3Sn_2 alloy nanoparticles and montmorillonite K10

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Table S1 Effect of alcohol solvent on the alcoholysis of furfuryl alcohol by montmorillonite K10 in long-chain alcohol solvents[a]

Entry	Alcohol solvent	Conv. / %	Yield[b] / %
1	1-Pentanol	>99	47
2	1-Hexanol	>99	38

[a] Reaction conditions: montmorillonite K10, 50 mg; furfuryl alcohol, 0.30 mmol; naphthalene, 0.30 mmol; solvent, 3.0 mL; N_2 pressure, 1.0 MPa; reaction temperature, 393 K; reaction time, 12 h. [b] Corresponding alkyl levulinate yield was identified and quantified using ^{1}H NMR.

Table S2 Comparison of the catalytic results obtained for the alcoholysis of furfuryl alcohol to ethyl levulinate by montmorillonite K10 and other Brønsted acid catalysts.

Entry	Catalyst	Reaction temperature / K	Reaction time / h	Yield / %	References
1	Montmorillonite K10	393	8	73	This work
2	Al-TUD-1	413	2	48	[1]
3	$H_3PW_{12}O_{40}$	393	2	63	[2]
4	GCC	423	1	67	[3]
5	Purolite CT151	353	5	71	[4]

Table S3 The catalytic activity of Ni_3Sn_2 alloy nanoparticles for the chemoselective hydrogenation of furfural to furfuryl alcohol compared with various alcohol parameters

Alcohol solvent	Time / h	ε^a	π^{*b}	α^c	β^d
Methanol	20	32.7	0.60	0.93	0.66
Ethanol	4	24.6	0.54	0.83	0.75
1-Propanol	28	20.1	0.52	0.78	0.84
1-Butanol	30	17.8	0.47	0.79	0.88
2-Propanol	26	19.9	0.48	0.76	0.95

[a] Dielectric constant [5,6]. [b] Dipolarity/polarizability [7]. [c] Hydrogen-bond donor capability [7]. [d] Hydrogen-bond acceptor capability [5,7].

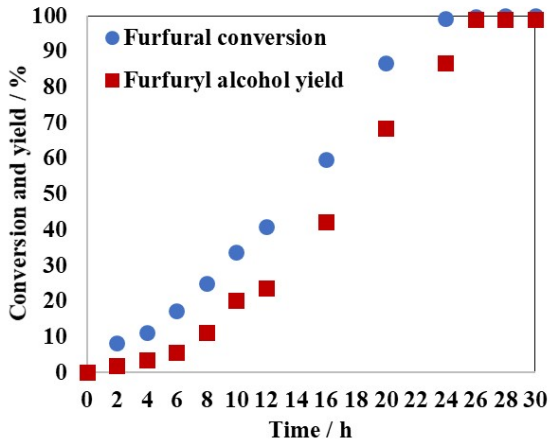

Fig. S1 Furfural hydrogenation by Ni_3Sn_2 alloy nanoparticles in 2-propanol solvent. Reaction conditions: Ni_3Sn_2 alloy nanoparticles, 2.75 mg; furfural, 0.30 mmol (furfural/Ni molar ratio = 15); *n*-dodecane, 0.30 mmol; 2-propanol, 3.0 mL; H_2 pressure, 1.0 MPa; reaction temperature, 453 K.

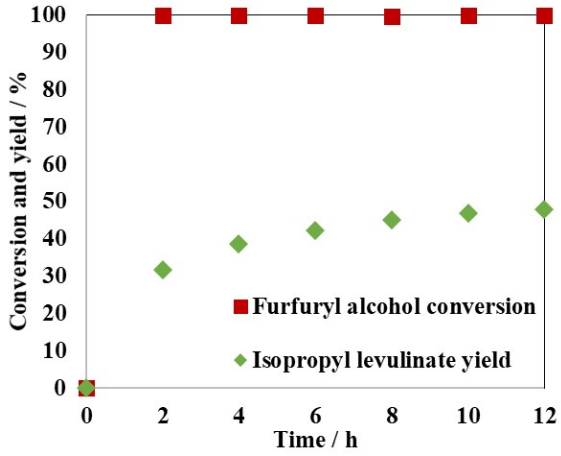

Fig. S2 Alcoholysis of the in situ formed furfuryl alcohol by montmorillonite K10 in 2-propanol solvent. Reaction conditions: Ni_3Sn_2 alloy nanoparticles, 2.75 mg; montmorillonite K10, 50 mg; furfural, 0.30 mmol; *n*-dodecane, 0.30 mmol; N_2 pressure, 1.0 MPa; reaction temperature, 393 K; reaction time, 12 h.

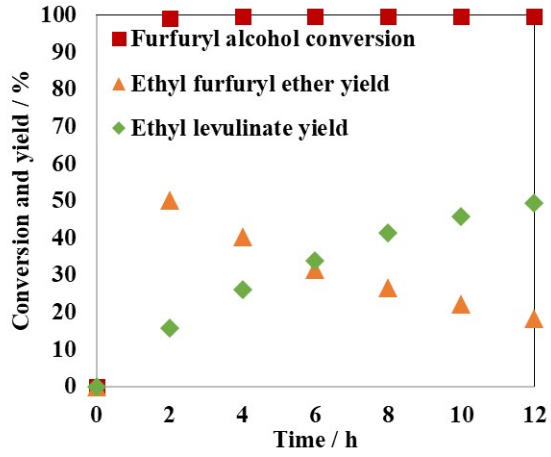

Fig. S3 Time profile for the alcoholysis of furfuryl alcohol by montmorillonite K10 in ethanol solvent (6.0 mL). Reaction conditions: montmorillonite K10, 50 mg; furfuryl alcohol, 0.30 mmol; *n*-dodecane, 0.30 mmol; ethanol,

6.0 mL; N_2 pressure, 1.0 MPa; reaction temperature, 393 K.

References

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