Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Mechanistic Effects of Solvent Systems on the Ni-Sn Catalyzed Lignin derivative to None-oxygenates

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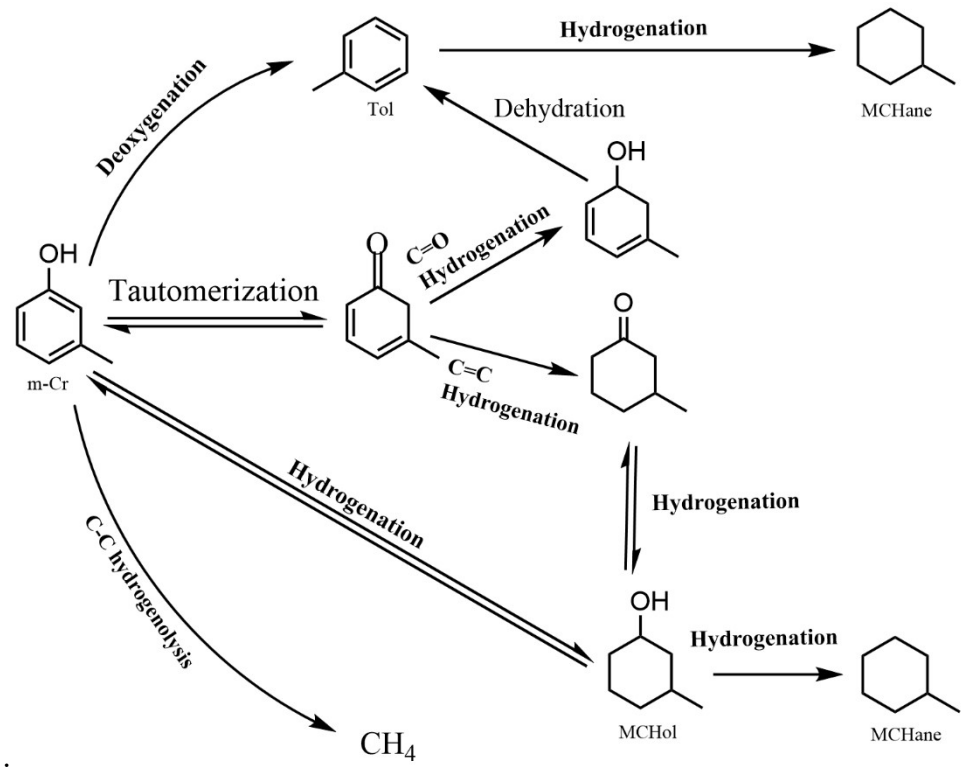


Scheme S1. The HDO pathway of m-cresol

$C_6H_5OH + * \longleftrightarrow C_6H_5\text{-}OH*$ (i)

$4H_2 + 8* \longleftrightarrow 8H^*$ (ii)

$C_6H_5OH* + H* \longleftrightarrow C_6H_6{-}OH*$ (iii)

$C_6H_6OH* + 5H* \longleftrightarrow C_6H_{11}{-}OH*$ (iv)

$C_6H_{11}OH* + H* \longleftrightarrow C_6H_{11}* + H_2O*$ (v)

$C_6H_{11}* + H_2O* + H* \longleftrightarrow C_6H_{12}* + H_2O*$ (vi)

$C_6H_{12}* + H_2O* \longleftrightarrow C_6H_{12} + H_2O + 2*$ (vii)

Scheme S2. Elementary steps involved in HDO reaction pathway (eqn (iv) shows five individual elementary hydrogenation steps)

Table S1. Atomic ratio of Ni and Sn species in catalysts obtained from XPS spectra

	Ni distribution/%		Atomic ratio	Sn distribution/%		Atomic ratio
	Ni^0	Ni^{2+}	Ni^0/Ni^{2+}	Sn^0	Sn^{2+}	Sn^0/Sn^{2+}
Fresh catalyst	29.2	70.7	0.41	54.3	45.7	1.19
Used catalyst with 12 water added	24.5	75.5	0.32	60.2	39.8	1.51
Used catalyst with 24 water added	21.6	78.4	0.28	53.6	46.4	1.16
Used catalyst with 52 water added	23.8	72.2	0.33	35.4	64.6	0.55

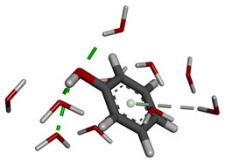
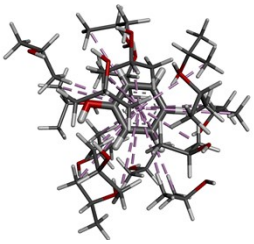
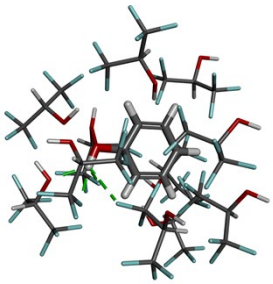
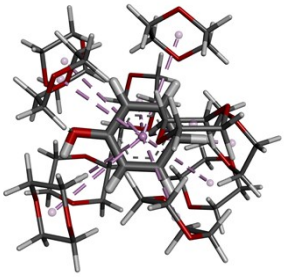
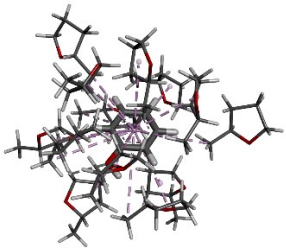
Table S2. Amount of acid sites calculated using py-FTIR spectra of $5NiSn/SiO_2$.

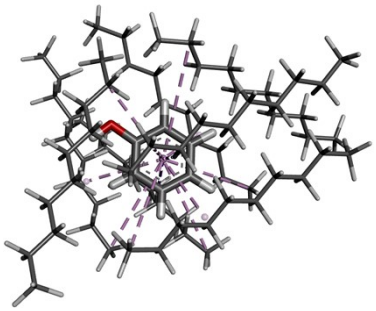
Desorption	Total amount of acid (mmol/g-catalyst)		
Temperature (°C)	Fresh catalyst	Used catalyst with 12 water added	Used catalyst with 52 water added
150	7.053	4.775	1.918
250	2.161	1.375	0.072

Table S3. Products of the HDO of m-cresol conducted in different solvents.

Solvent	m-Cresol conversion/%	Selectivity MCHane/%	Selectivity MCHone/%	Selectivity MCHol/%	Selectivity others/%
Isopropanol	96.4	43.1	7.9	41.8	7.2
HFIP	94.1	79.2	9.0	11.6	0.2
Ethyl acetate	88.0	48.2	9.8	41.0	1.0
2-Me-THF	95.8	54.0	8.5	9.2	28.3
1,4-Dioxane	96.2	79.9	7.2	8.4	4.5
n-Hexane	95.5	70.4	7.2	21.9	0.5
n-Heptane	93.6	73.6	7.6	18.2	0.6
n-Otcane	94.8	81.4	5.4	9.2	4.0
n-Decane	96.3	92.2	1.2	1.4	5.2
n-Hexadecane	95.9	57.2	7.7	23.4	11.7

Table S4. Representative solvent models and interaction forces.

Solvent	Model	Hydrophobic interaction	H-Bond
water		0	3
Isopropanol		14	1
HFIP		11	4
1,4-Dioxane		10	0
2-Methyltetrahydrofuran		21	1

n-Decane		12	0

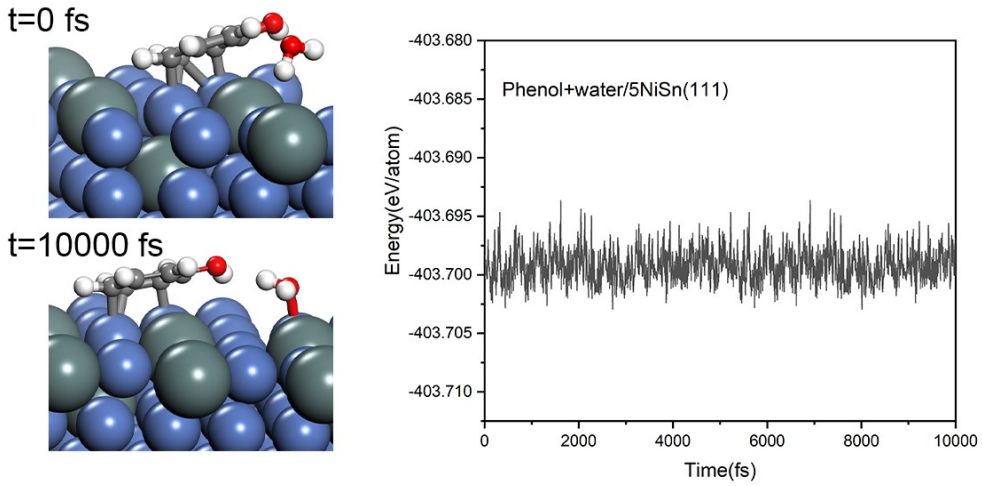


Figure S1. Initial and final structures for the phenol+water/5NiSn(111) AIMD simulation (left) and the total energy fluctuations for the phenol+water/5NiSn(111) AIMD simulations (right).

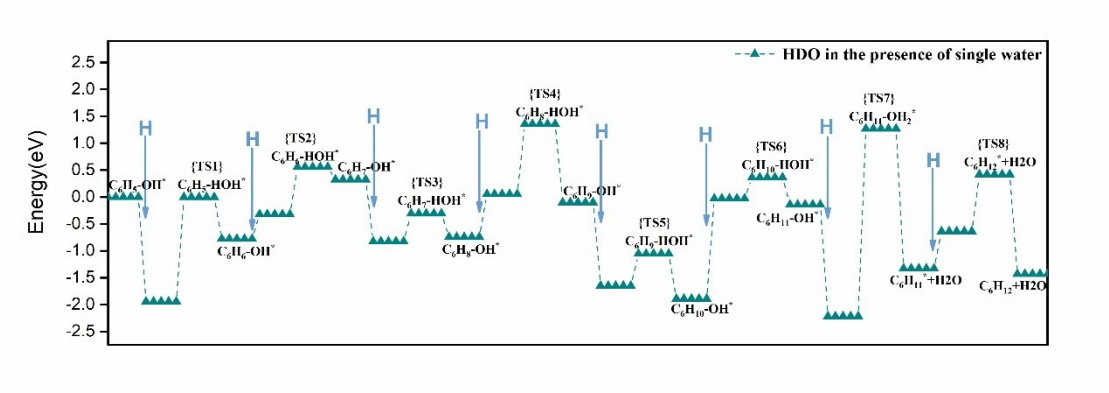


Figure S2. Reaction energetics on the 5NiSn (111) catalyst during HDO reaction in the presence of single water.

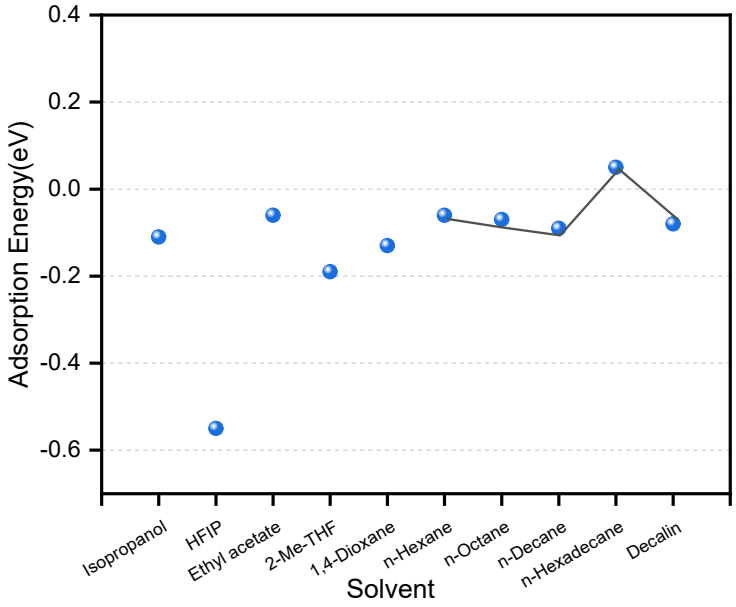


Figure S3. Adsorption energy of solvent on catalyst 5NiSn (111)

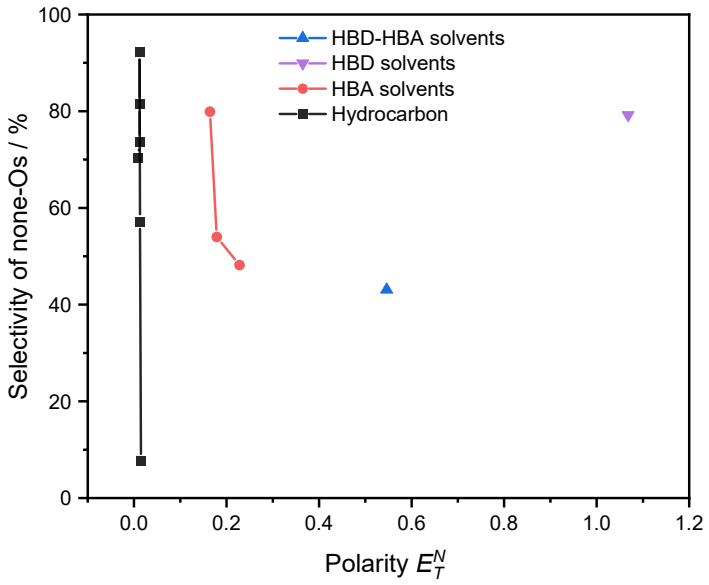


Figure S4. Hydrogenation selectivity of none-Os versus solvent polarity E_T^N.