

SUPPORTING INFORMATION for

Propanol Amination over Supported Nickel Catalysts: Reaction Mechanism and Role of the Support

Christopher R. Ho^{1,2}, Vincent Defalque¹, Steven Zheng¹, Alexis T. Bell^{1,2*}

Department of Chemical and Biomolecular Engineering
University of California
Berkeley, CA 94720-1462

and

Chemical Sciences Division
Lawrence Berkeley National Laboratory
Berkeley, CA 94720

***To whom correspondences should be addressed: bell@cchem.berkeley.edu**

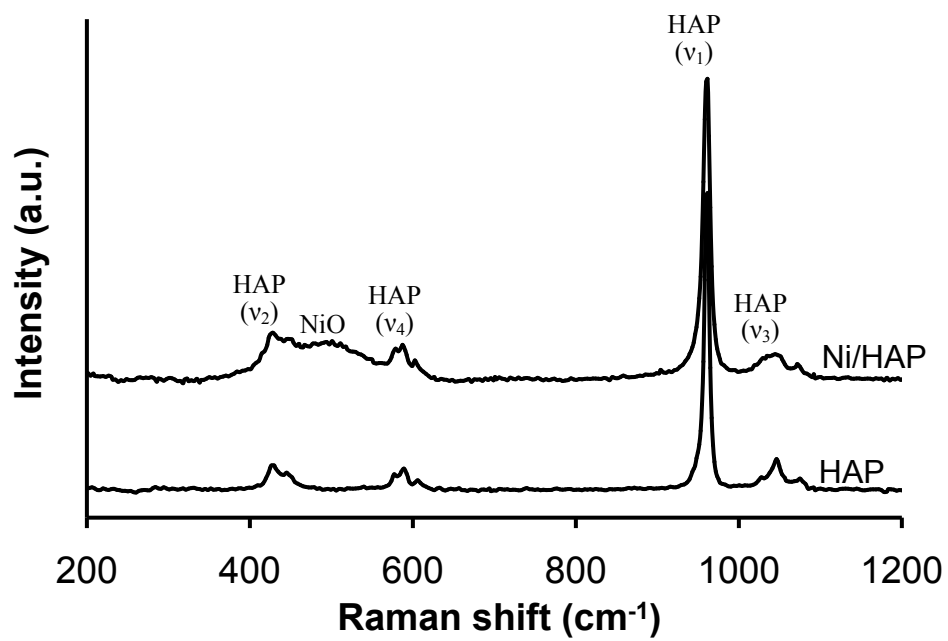

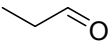

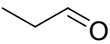
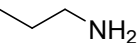
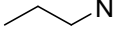
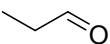
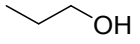



Figure S1: Raman spectra of ion-exchanged HAP catalysts.

Table S1: Miscellaneous reactions with alcohols, aldehydes, and amines

Reaction Conditions	Reactant	Catalyst	Conversion (%)	Selectivity (%)
[a]		Ni/HAP	0	-
[b]		Ni/HAP	100	 $\text{NH}_2 > 99$
[c]	 + 	-	100	 > 99
[d]	 + NH_3	-	0	-
[e]	 + NH_3	12%Ni/MgO	3.5	 $= 89$

[a] $P_{\text{t-BuOH}} = 0.5 \text{ kPa}$; $P_{\text{NH}_3} = 5 \text{ kPa}$; $P_{\text{H}_2} = 95 \text{ kPa}$.

[b] $P_{\text{propanal}} = 0.06 \text{ kPa}$; $P_{\text{NH}_3} = 5 \text{ kPa}$; $P_{\text{H}_2} = 95 \text{ kPa}$; $P_{\text{EtOH}} = 1.5 \text{ kPa}$ to simulate alcohol coverage under amination conditions

[c] $P_{\text{propanal}} = 0.6 \text{ kPa}$; $P_{\text{propylamine}} = 0.6 \text{ kPa}$.

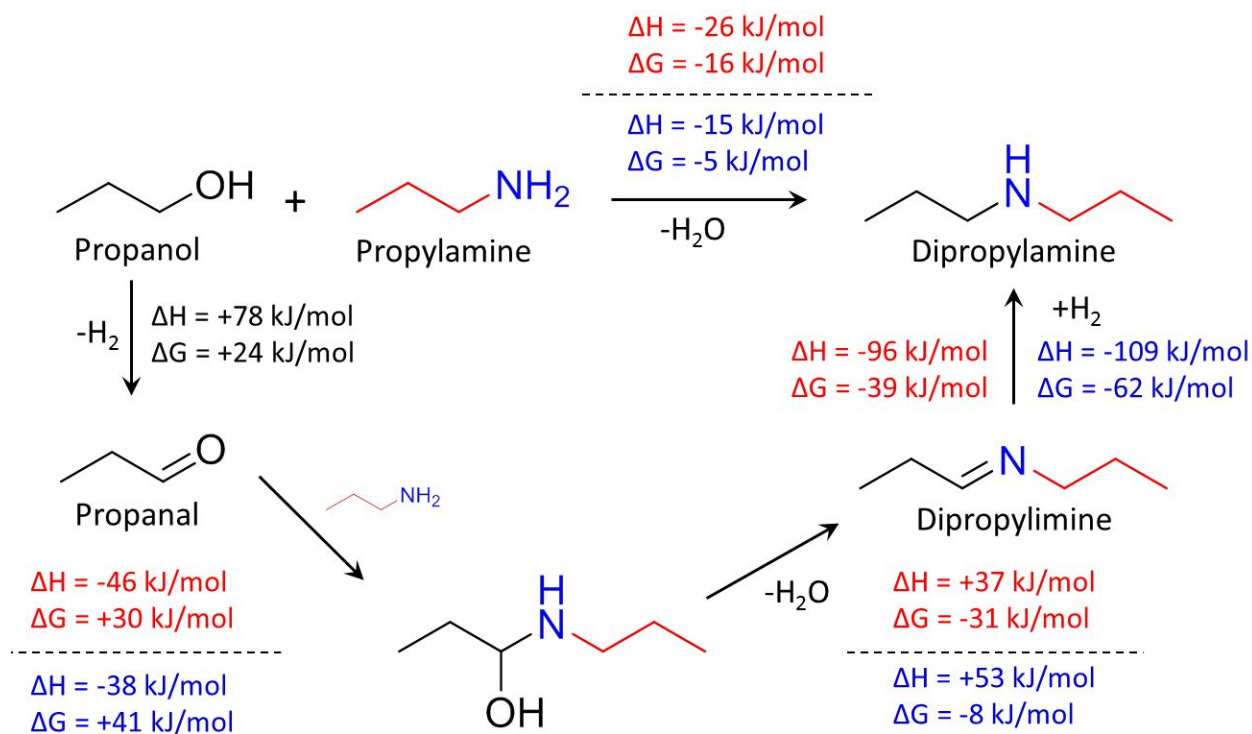
[d] $P_{\text{propanal}} = 0.6 \text{ kPa}$; $P_{\text{NH}_3} = 5 \text{ kPa}$.

For all above reactions: $T = 423 \text{ K}$; $\text{mass}_{\text{catalyst}} = 0$ or 0.02 g ; total gas flow rate at STP = 30 mL min^{-1}

[e] $T = 423 \text{ K}$; catalyst mass = 0.005 g ; $P_{\text{Propanol}} = 1 \text{ kPa}$; $P_{\text{NH}_3} = 5 \text{ kPa}$; $P_{\text{H}_2} = 95 \text{ kPa}$; total gas flow rate at STP = 30 mL min^{-1}

Table S2: KIE experiments with deuterated ethanol

Reactants	Observed k_H/k_D
$R-\overset{\text{H}_2}{\text{C}}-\text{OH} + \text{NH}_3 + \text{D}_2$	1.0
$R-\overset{\text{H}_2}{\text{C}}-\text{OD} + \text{NH}_3 + \text{D}_2$	1.0
$R-\overset{\text{D}_2}{\text{C}}-\text{OD} + \text{NH}_3 + \text{D}_2$	1.5



Scheme S1: Gas phase enthalpies and free energies of reaction for propanol amination based on DFT calculations. Values in red represent the thermodynamics of propanol amination to dipropylamine while values in blue represent the thermodynamics of propanol amination to propylamine.

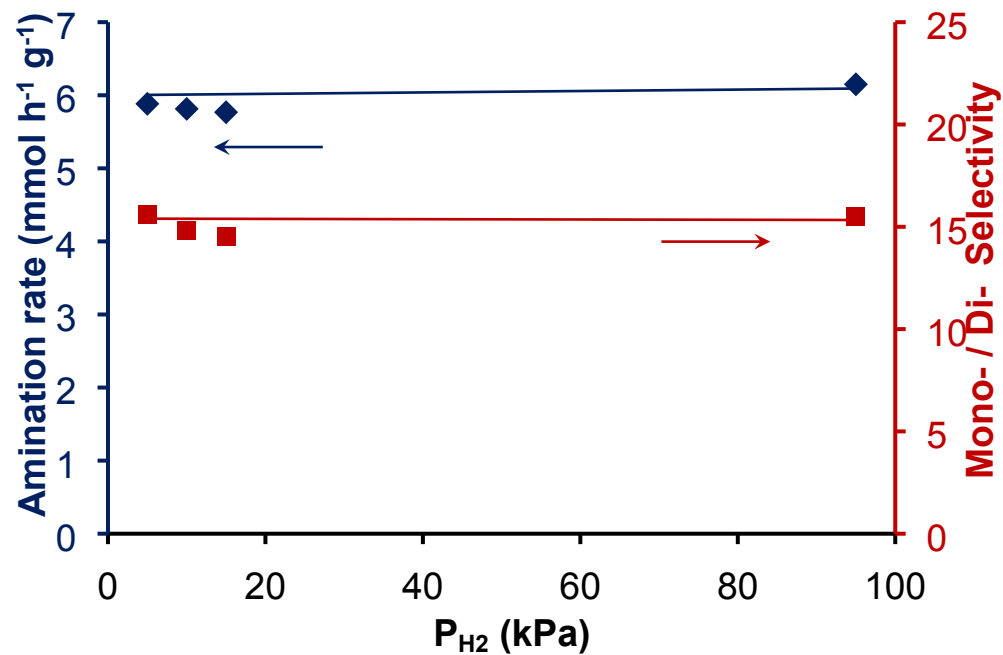


Figure S2: Effect of NH_3 partial pressure on propanol amination rate and selectivity of propylamine vs. dipropylamine. Reaction conditions: $T = 423 \text{ K}$; $\text{mass}_{\text{catalyst}} = 0.01 \text{ g}$; $P_{\text{Propanol}} = 1.4 \text{ kPa}$; $P_{\text{NH}_3} = 5 \text{ kPa}$; total gas flow rate at STP = 30 mL min^{-1} .

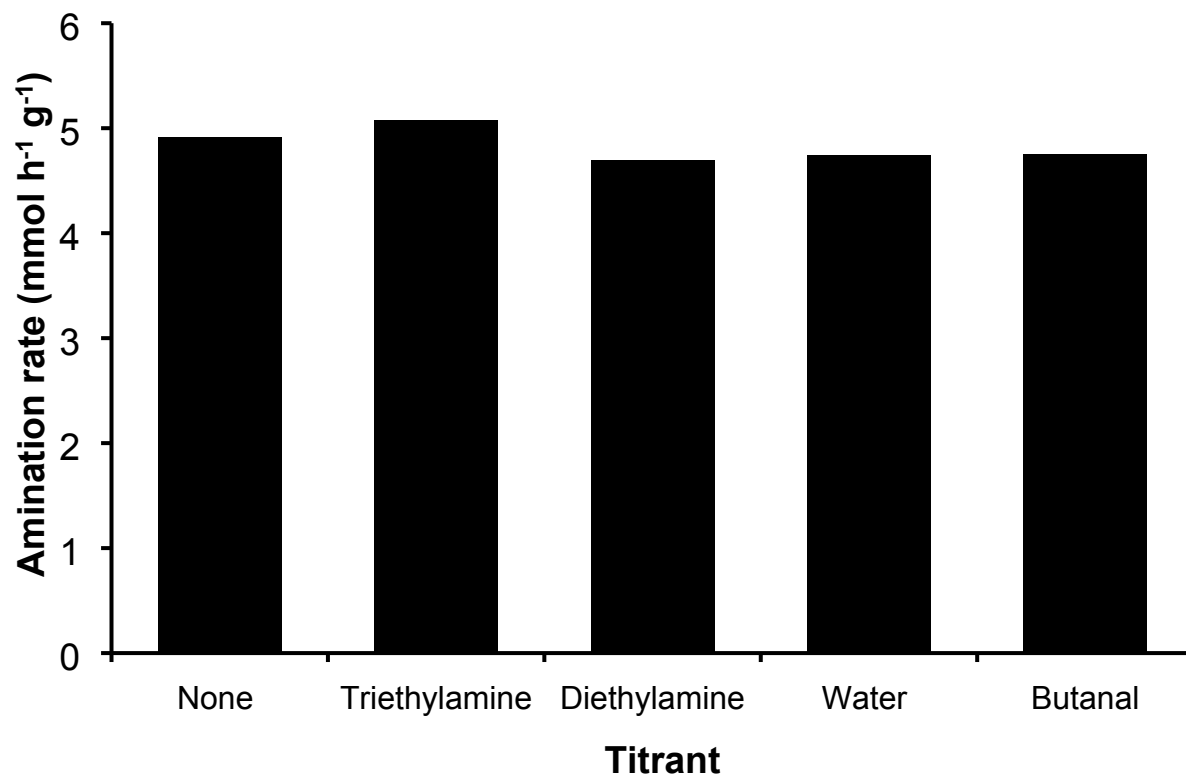


Figure S3: Effect of various titrants on propanol amination. Reaction conditions: $T = 423 \text{ K}$; $\text{mass}_{\text{catalyst}} = 0.01 \text{ g}$; $P_{\text{Propanol}} = 1.4 \text{ kPa}$; $P_{\text{NH}_3} = 5 \text{ kPa}$; total gas flow rate at STP = 30 mL min^{-1} . Titrant partial pressures: $P_{\text{triethylamine}} = 0.1 \text{ kPa}$; $P_{\text{diethylamine}} = 0.1 \text{ kPa}$; $P_{\text{H}_2\text{O}} = 0.7 \text{ kPa}$; $P_{\text{butanal}} = 0.1 \text{ kPa}$

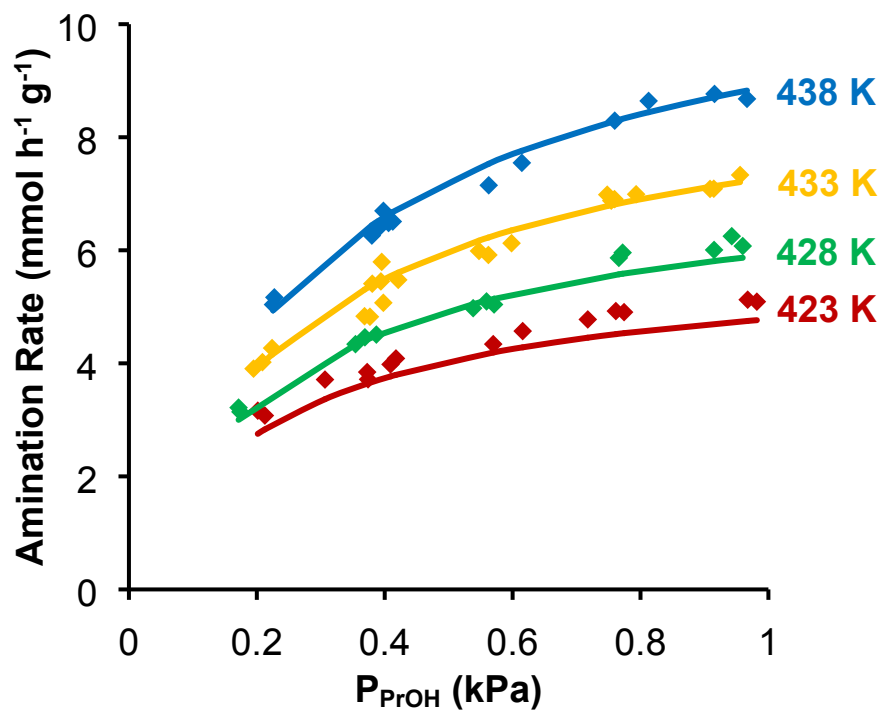


Figure S4: Effect of propanol partial pressure on amination rate over Ni/HAP-16.5 at various temperatures. Reaction conditions: Ni/HAP-16.5 = 0.02 g; P_{NH3} = 5 kPa; P_{H2} = 95 kPa; total gas flow rate at STP = 60 mL min⁻¹.

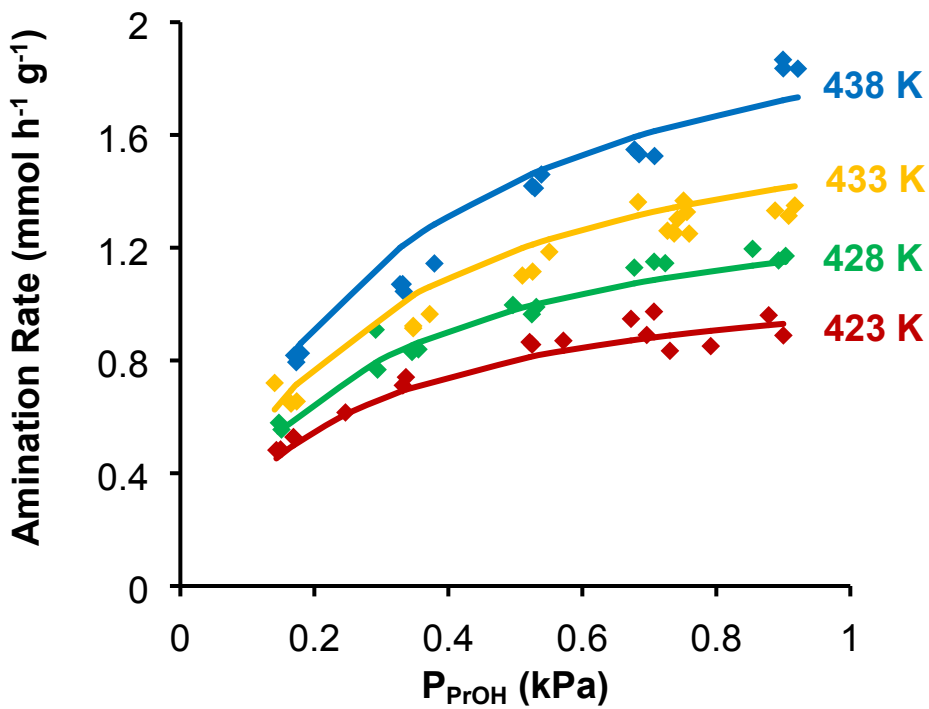


Figure S5: Effect of propanol partial pressure on amination rate over Ni/SiO₂-12.5 at various temperatures. Reaction conditions: Ni/SiO₂ = 0.02 g; P_{NH₃} = 5 kPa; P_{H₂} = 95 kPa; total gas flow rate at STP = 60 mL min⁻¹.

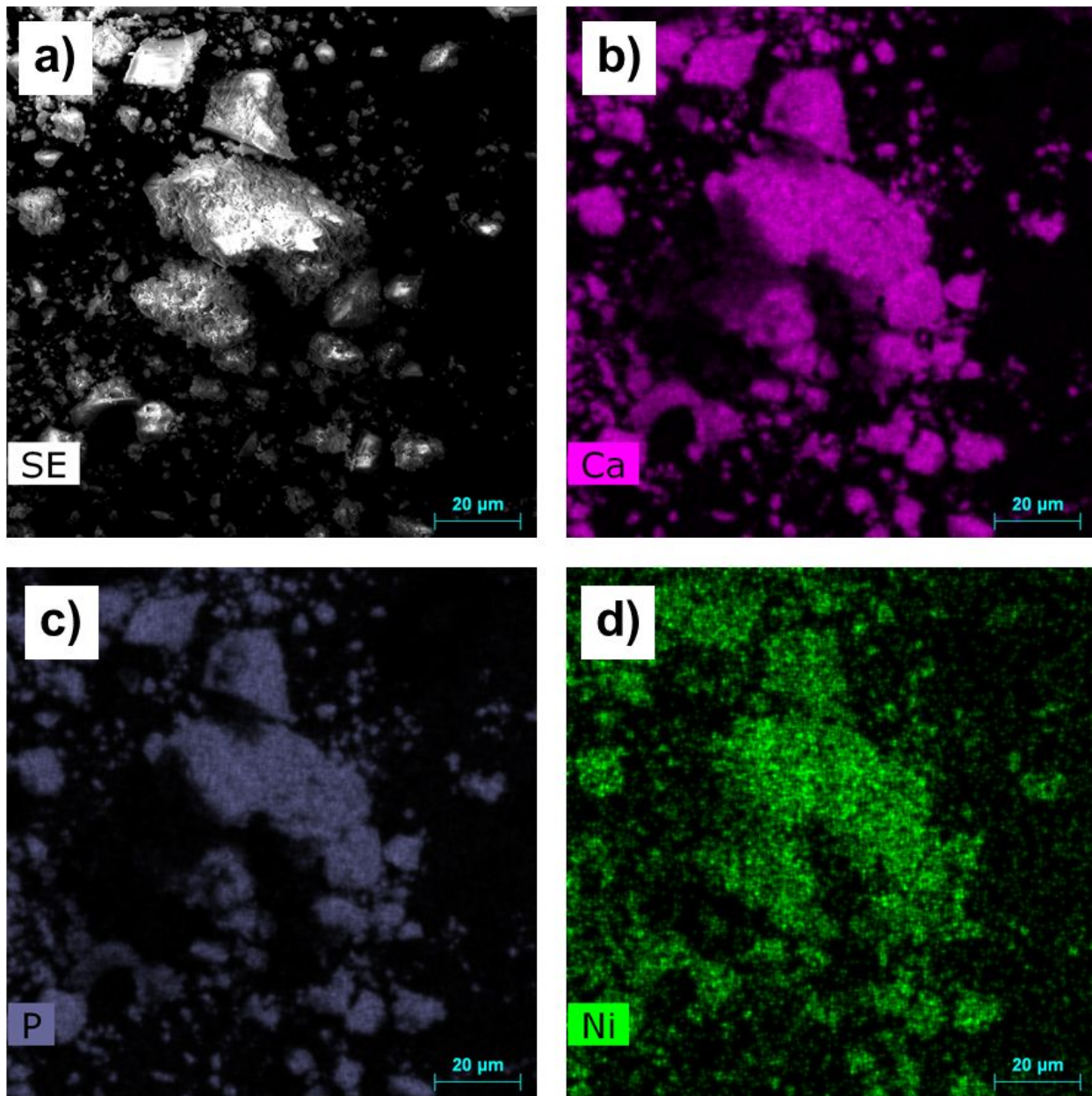


Figure S6: a) SEM micrograph of Ni/HAP and the corresponding EDXS maps for b) calcium, c) phosphorus, and d) nickel

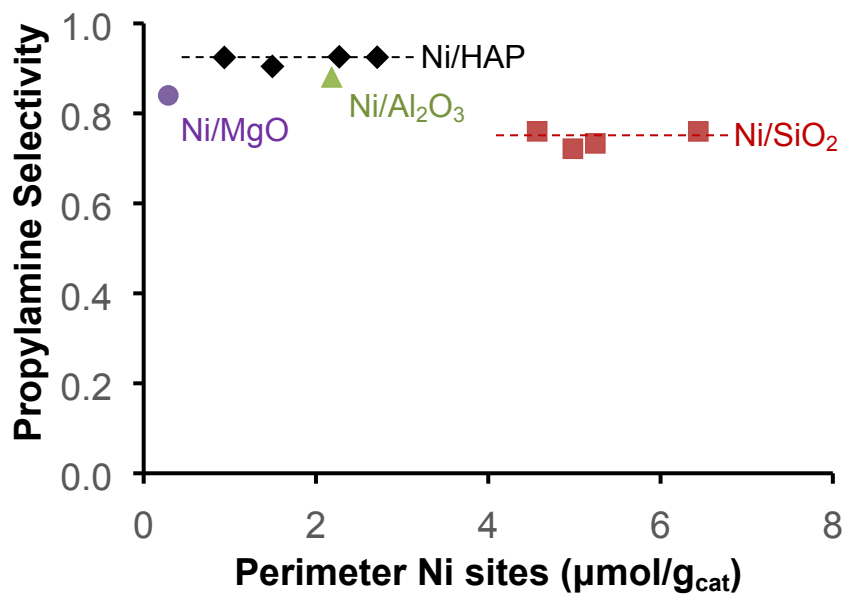
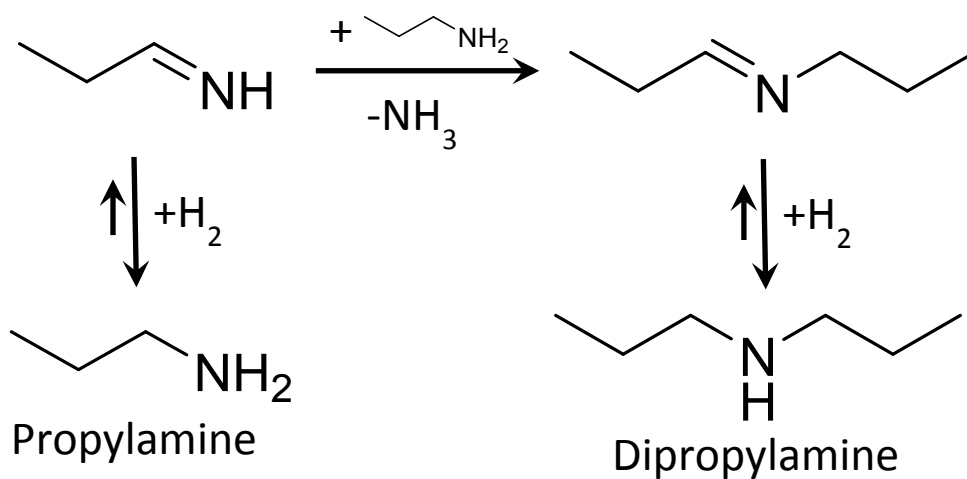







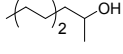
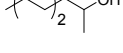
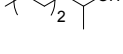
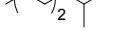




Figure S7: Selectivity of propylamine as a function of the number of perimeter Ni sites. Conversion over Ni/HAP is ~10% and conversion over Ni/SiO₂ is ~3.5%.



Scheme S2: Pathways for propylimine conversion to propylamine and dipropylamine via hydrogenation and disproportionation pathways, respectively.

Table S3: Ni-catalyzed amination of aliphatic alcohols

Catalyst	Reactant	Temp (K)	Reaction rate (mmol h ⁻¹ g _{cat} ⁻¹)	TOF ^[b] (s ⁻¹)	TOF ^[c] (s ⁻¹)	Selectivity to primary amine (%)	Reference
4%Ni/HAP		423	4.8	0.040	1.7	92	this work
4%Ni/MgO		423	1.5	0.041	1.1	84	this work
4%Ni/SiO ₂		423	1.9	0.013	0.1	74	this work
4%Ni/γ-Al ₂ O ₃		423	2.0	0.018	0.2	88	this work
60%Ni/AlSiO		453	46	0.014	-	99	[12]
60%Ni/LaO		453	8.8	0.008	-	~100	[12]
60%Ni/LaAlSiO		453	94	0.026	-	99	[12]
10%Ni/θ-Al ₂ O ₃		433 ^[a]	35	0.012	0.18 ^[d]	96	[7]
5%Ni/ZrO ₂		433 ^[a]	15	-	-	76	[7]
5%Ni/MgO ₂		433 ^[a]	0	-	-	-	[7]
Raney Ni		433 ^[a]	9.4	-	-	~100	[7]
6.5%Ni/γ-Al ₂ O ₃		453	26	0.056	0.71 ^[d]	84	[28]
10%Ni/SiO ₂		433	1.1	0.002	0.03	~40	[9]

[a] Reaction performed in liquid phase in absence of H₂

[b] Turnover frequencies (TOF) defined as rates per **surface** Ni atom

[c] Turnover frequencies (TOF) defined as rates per **perimeter** Ni atom

[d] Estimated based on reported particle size