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

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ABSTRACT

Ni-supported hydroxyapatite catalyst (Ni/HAP) was characterized and evaluated for propanol amination to propylamine at 423 K. The reaction proceeds via dehydroamination, a process that involves sequential dehydrogenation, condensation, and hydrogenation. Kinetic and isotopic studies indicate that α-H abstraction from propoxide species limits the rate of the dehydrogenation step, and hence the overall rate of reaction. The rate of propanol dehydrogenation depends on the composition of the support and on the concentration of Ni sites located at the interface between the Ni nanoparticles and the support. Ni/HAP is an order of magnitude more active than Ni/SiO_2 and displays a higher selectivity towards the primary amine. The superior performance of Ni/HAP is attributed to the high density of basic sites on HAP which are responsible for stabilizing alkoxide intermediates and suppressing the disproportionation and secondary amination of amines.

Keywords: hydroxyapatite, HAP, dehydroamination, alkylation, C-N coupling

INTRODUCTION

Alkylamines are valuable precursors for many rubbers, herbicides, and pharmaceuticals, and are typically produced by the amination of alcohols with ammonia.[1,2] Although this reaction can be performed over solid acid catalysts, the process requires high temperatures (573 – 773 K) and can lead to the formation of unwanted side products, such as olefins.[2,3] An alternative approach is to use a catalyst that dehydrogenates the alcohol to the corresponding alkanal. The alkanal then reacts with ammonia to form the alkylimine which is then hydrogenated to the alkylamine. Suitable catalysts for this approach are Ni, Cu, Co, Pt, and Pd supported on a metal oxide.[4,5,6,7,8,9,10,11,12] These catalysts can operate at lower temperatures (373 – 623 K) due to the higher reactivity of the alkanal compared to the corresponding alcohol. Ni-containing catalysts in particular are promising because they exhibit high activity and stability for a variety of alcohols.[7,13,14,15]

A number of supports for Ni have been investigated for alcohol amination. These include SiO_2, Al_2O_3, CeO_x, La_2O_3, ZrO_2, TiO_2, and combinations thereof; however, the role of the support remains unclear.[7,9,11,12,13,14,15,16] Šolcová et al. have evaluated Ni supported on SiO_2, Al_2O_3, ZrO_2, TiO_2, and Nb_2O_5 and found that the rates of diethylene glycol amination to diethlyene glycol amine varied only with the number of surface Ni sites, independent of support composition.[15] Based on these results, they concluded that the support affects Ni dispersion but does not play a direct role in the reaction. On the other hand, Shimizu et al. have found that the support has a significant effect on the rate of 2-octanol amination with NH_3.[7] Of the catalysts tested, Ni/γ-Al_2O_3 was the most

active. However, the reported turnover frequencies were based on the total number of Ni atoms instead of the number of surface Ni atoms, which makes comparison of the intrinsic rates unclear. In a later study of 1-octanol amination with aniline over Ni/Al_2O_3, Shimizu et al. determined that the amination rate per surface Ni atom decreases with increasing Ni particle size, which suggests that Ni atoms located on the corners or edges of the nanoparticles are more active.[17] Cho et al. have studied 2-propanol amination with NH_3 over a series of Ni/Al_2O_3 catalysts with different alumina phases.[18] They observed that 2-propanol conversion increases with decreasing particle size, even though no clear trend was found between 2-propanol conversion and Ni surface area. Large variations in monoisopropylamine selectivity were observed, which was attributed to differences in Lewis acid site densities of the alumina supports.

We have previously shown that hydroxyapatite (HAP) is an active catalyst for the Guerbet reaction of ethanol, which follows a mechanism similar to that proposed for alcohol amination.[19] This suggests that HAP would be an excellent support for Ni-catalyzed amination of alkylamines. The present work was undertaken with the aim of elucidating the mechanism and kinetics of alcohol amination over Ni/HAP and the role of the support composition. To this end, we synthesized and characterized Ni/HAP and compared its activity to Ni/SiO_2 for a series of Ni particle sizes. The results show that for a given Ni surface area and particle size, Ni/HAP is significantly more active than Ni/SiO_2. We propose that the active site is located at the interface between the Ni nanoparticles and the support. The support does not affect the activation barrier for the rate-limiting step, α-H abstraction from a propoxide group, and instead, is responsible for the formation of surface alkoxides, which are key intermediates in the reaction.

EXPERIMENTAL METHODS

Catalyst Synthesis

SiO_2 (Silicycle) and MgO (Sigma-Aldrich) were used without further treatment. Hydroxyapatite (HAP) was synthesized using a modification of the procedure reported by Tsuchida *et al.*[20] and Hanspal *et al.*[21] Aqueous solutions of 0.25 M $Ca(NO_3)_2 \cdot 4H_2O$ and 0.55 M $(NH_4)_2HPO_4$ were prepared and brought to a pH of 11 by addition of ammonium hydroxide. The calcium solution was added dropwise to the phosphorus solution at room temperature and stirred for 0.5 h before heating to 353 K for an additional 3 h. The resulting slurry was filtered and washed with DI water. γ-Al_2O_3 was synthesized by calcining boehmite (Süd-Chemie) in 100 mL min^{-1} of air at 823 K for 3 h.

Ni-supported catalysts were prepared by incipient wetness impregnation using an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ on a support that had been dried at 393 K for 1 h. After impregnation, the sample was dried at 298 K overnight and subsequently calcined in 100 mL min^{-1} of air at 823 K for 2 h. All Ni-supported catalysts contain 4wt% nickel unless otherwise specified.

Dipropylimine was synthesized by stirring stoichiometric amounts of propanol and propylamine at 298 K. After 5 min, K_2CO_3 was added to adsorb water and drive the reaction to completion. The product was extracted by centrifugation and stored until later use.

Characterization Techniques

Powder X-ray diffraction (PXRD) patterns were acquired with a Bruker D8 GADDS diffractometer equipped with a Cu-Kα source (40kV, 40mA). BET surface areas were calculated from nitrogen adsorption isotherms obtained using a Micromeritics Gemini VII 2390 surface area analyzer after degassing the catalyst overnight at 393 K. Raman spectra were obtained using a LabRam HR Horiba Jobin Yvon spectrometer equipped with a 532 nm laser. Elemental compositions were measured by Galbraith Laboratories (Knoxville, TN) using ICP-OES.

Ni reducibility was measured by H_2 temperature-programmed reduction (TPR) using a Micromeritics AutoChem II 2920 instrument equipped with a thermal conductivity detector (TCD). Samples were pretreated under He flow at 823 K for 1 h before cooling to 313 K. Catalyst reduction was performed by flowing 4%H_2/Ar (50 mL min^{-1}) and raising the temperature from 313 K to 973 K at 10 K min^{-1}. For H_2-TPR of Ni/HAP, the TCD response due to CO_2 desorption from bulk HAP was corrected for by using the H_2-TPR spectra of HAP as a reference. Elemental maps of Ni/HAP were obtained using an FEI Quanta FEG 250 scanning electron microscope (SEM) equipped with a Bruker Quantax energy dispersive X-ray spectrometer (EDXS).

Static chemisorption of H_2 was performed using a Micromeritics 3 flex chemisorption analyzer. Samples were evacuated at 383 K for 0.5 h and then reduced in H_2 at the chosen reduction temperature (823 K unless otherwise specified) for 0.5 h. After evacuation at 723 K for 1 h, the samples were cooled to 313 K to measure the adsorption isotherm. Afterwards, the samples were evacuated at 313 K for 1 h and a

subsequent isotherm was obtained to quantify the amount of weakly bound H_2. The total amount of chemisorbed H_2 was determined by taking the difference between the two isotherms. O_2 titration was performed by evacuating the same sample at 723 K for 0.5 h and pulsing in O_2 at 723 K. A Ni site density of 0.0677 nm^2/atom and adsorption stoichiometry of 1H:1$Ni_{surface}$ were used to calculate the Ni surface area.[22] Average crystallite size was determined by assuming a spherical crystallite geometry.[22]

Measurements of Catalytic Activity

Measurements of reaction rates were carried out using a quartz-tube, packed-bed reactor (10 mm inner diameter). Quartz wool was placed below the catalyst bed to hold the catalyst in place. The reactor temperature was maintained using a tube furnace equipped with a Watlow temperature controller and a K-type thermocouple. Prior to reaction, the catalyst was treated in 30 mL min^{-1} of H_2 at the chosen reduction temperature (823 K unless otherwise specified) for 0.5 h before cooling to the reaction temperature.

In a typical experiment, propanol was introduced into a stream of He, H_2, and NH_3 using a syringe pump (World Precision Instruments, SP100I). Other liquid reactants were also fed in a similar manner. All experiments were carried out at atmospheric pressure. Product streams were analyzed by gas chromatography using an Agilent 6890A GC fitted with a HP-5 capillary column (30 m x 0.32 mm x 0.25 μm) and a flame ionization detector. Measurements of the rate of propanol amination were carried out at <10% conversion, where the only products observed were propylamine, dipropylamine, and tripropylamine. The reported amination rates were calculated by assuming that

dipropylamine and tripropylamine are formed by amination of two and three equivalents of propanol, respectively.

Theoretical Calculations

Calculations of the thermodynamics of selected gas phase reactions were carried out using the Q-Chem simulation package.[23] Optimization and frequency calculations were performed at the ωB97X-D/6-31G** level of theory while single point calculations were performed at the ωB97X-D/6-311++G(3df,3pd) level of theory.

RESULTS AND DISCUSSION

Characterization of IE-HAP catalysts

The synthesized HAP support has a Ca/P ratio of 1.66 as determined by elemental analysis, which is consistent with a stoichiometric composition ($Ca_5(PO_4)_3OH$). The BET surface areas of HAP and Ni/HAP are 91 and 77 m^2/g, respectively. PXRD patterns for HAP and Ni/HAP are shown in Figure 1. The diffraction peaks associated with HAP are identical for both samples, indicating that the addition of nickel does not alter the crystal structure or lattice parameters of HAP. The HAP particle size is 21 nm for the bare support and 22 nm for Ni/HAP, as estimated by the Scherrer equation using the (002) diffraction peak. The weak diffraction peaks at 38° and 42° for Ni/HAP are characteristic of NiO, and the presence of NiO was verified by Raman spectroscopy (Figure S1). To gauge the reducibility of Ni species on HAP, H_2-TPR was performed (Figure 2). All nickel was fully reduced by 850 K, assuming a 1:1 H_2:Ni reduction stoichiometry. The large reduction peak at 590 K corresponds to reduction of

bulk NiO species while the shoulder peak at 490 K is due to reduction of very small NiO particles.[24] The high temperature peak at 750 K is indicative of the reduction of isolated Ni^{2+} species stabilized by the HAP framework, likely due to substitution of two protons or Ca^{2+} in HAP by Ni^{2+}.[25]

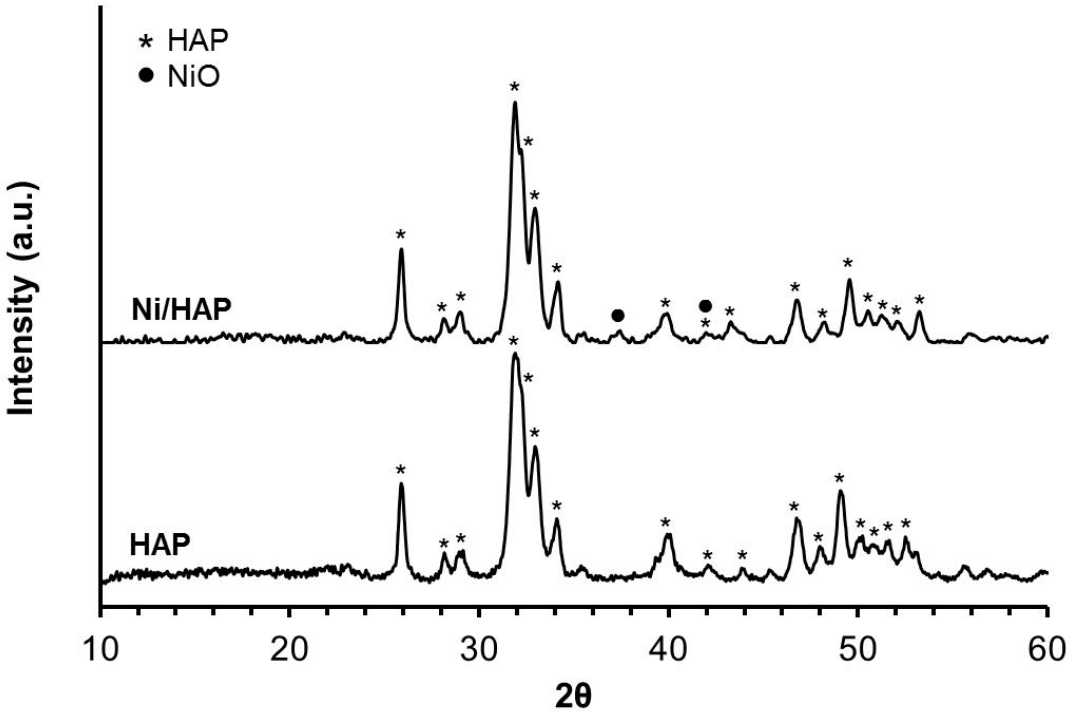


Figure 1: PXRD spectra of HAP and Ni/HAP

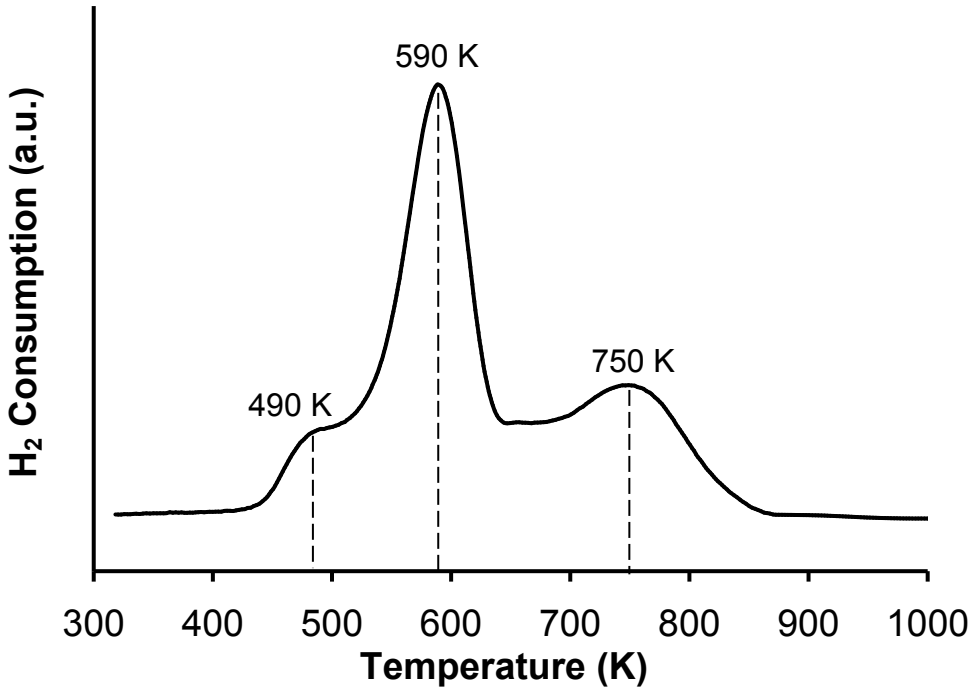
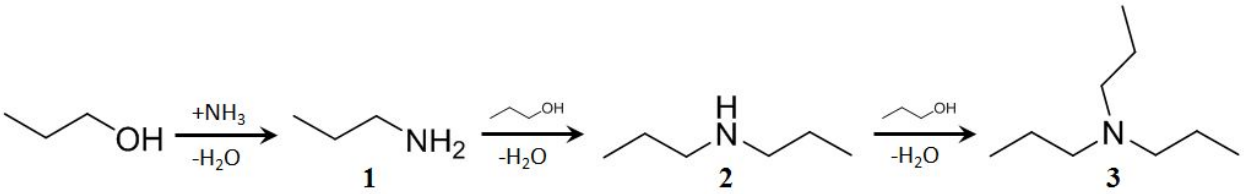


Figure 2: H_2-TPR spectra of Ni/HAP

Propanol amination over supported Ni catalysts

HAP, Ni/HAP, Ni/SiO_2, Ni/Al_2O_3 and Ni/MgO were initially screened for propanol amination at 423 K (Scheme 1). All catalysts except the bare HAP support were active for the reaction, and the only products observed were propylamine **1**, dipropylamine **2**, and tripropylamine **3**. Ni-supported catalysts were inactive without H_2 pretreatment, showing that metallic Ni is necessary for the reaction to proceed. Ni/HAP was the most active catalyst tested, with a propanol conversion of 10.8% (Table 1). Ni/HAP also demonstrated a high selectivity towards propylamine (92%), with the major side product being dipropylamine. Ni/MgO was the least active catalyst with a conversion of 3.3%, while Ni/SiO_2 was the least selective towards propylamine. The differences in conversion and selectivity show that the support composition affects the catalytic activity.



Scheme 1: Propanol amination to primary, secondary, and tertiary amines

Table 1: Propanol amination with NH_3 over nickel supported catalysts[a]

Catalyst	Ni Particle Size (nm)	Ni Dispersion[b]	Ni surface area[c] (m^2/g)	Conversion (%)	TOF[d] (s^{-1})	Selectivity (%)		
						1	**2**	**3**
HAP	-	-	-	~0	-	-	-	-
Ni/HAP	16.5	0.042	3.9	10.8	1.7	92	8	<1
Ni/MgO	10.4	0.014	0.3	3.3	1.1	84	16	<1
Ni/SiO_2	6.3	0.065	1.6	4.4	0.1	74	24	2
$Ni/\gamma\text{-}Al_2O_3$	4.9	0.041	1.0	4.5	0.2	88	12	<1

[a] Reaction conditions: T = 423 K; catalyst mass = 0.02 g; $P_{Propanol}$ = 1 kPa; P_{NH3} = 5 kPa; P_{H2} = 95 kPa; total gas flow rate at STP = 30 mL min^{-1}
[b] Dispersion defined as number of surface Ni^0 atoms over the total loading of Ni
[c] Based on H_2 chemisorption and O_2 titration measurements
[d] Turnover frequencies (TOF) defined as rates per perimeter Ni atom as determined by H_2 chemisorption and O_2 titration

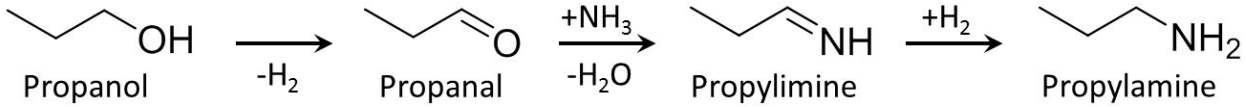
A list of Ni-catalyzed amination rates for aliphatic alcohols have been compiled from literature in Table S3. Direct comparison of rates is difficult since different authors used different reactants and reaction conditions. However, for the reaction of low molecular aliphatic alcohols at similar temperatures, the Ni/HAP catalyst demonstrates a higher TOF than other catalysts reported in literature. We note, however, that Table 1

clearly shows that under identical reaction conditions and dispersion of Ni, the TOF for propanol amination is an order of magnitude higher for Ni/HAP than for Ni/Al_2O_3.

Mechanism of propanol amination over Ni/HAP

In order to understand the role of the support, it is first necessary to establish the reaction mechanism of propanol amination over Ni/HAP. Previous studies have shown that alcohol amination over Ni/SiO_2 and Ni/Al_2O_3 proceeds via a dehydroamination pathway, which involves sequential dehydrogenation, C-N coupling, and hydrogenation steps (Scheme 2).[7,13,26] For aliphatic alcohols, the initial dehydrogenation step has been reported to be rate-limiting.[4,5] An alternative pathway involves direct coupling of alcohol and ammonia in one step, which occurs over solid acid catalysts such as zeolites.[27] One key difference between the two pathways is that hydroamination requires an alcohol reactant with an α-H for the initial dehydrogenation step. To determine which pathway occurs over Ni/HAP, the amination of tert-butanol was investigated. Prior work has shown that tert-butanol will readily couple with NH_3 via direct amination but cannot occur through dehydroamination because tert-butanol lacks an α-proton necessary to undergo dehydrogenation.[27] When tert-butanol and NH_3 were fed over 4%Ni/HAP at 423 K under flowing H_2, no products were formed (Table S1), suggesting that direct amination does not occur over Ni/HAP. The mechanism was further probed by feeding NH_3 and H_2 with propanal, which is an intermediate in the dehydroamination pathway. Propanal converted quantitatively to propylamine (Table S1), indicating that the amination of propanol follows a dehydroamination pathway. Moreover, the rapid rate of

propanal conversion indicates that the initial dehydrogenation step is slow, consistent with previous literature reports for Ni-supported catalysts.[17]



Scheme 2: Hydroamination pathway for propanol amination to propylamine

Kinetic isotope experiments with ethanol were performed to verify the pathway and shed more light on the reaction mechanism. The rate of reaction was unaffected when H_2/ethanol was replaced with D_2/ethanol-D1 (Table S2), showing that the dissociation of H_2 and cleavage of the O-H bond in propanol are not rate-limiting. However, a kinetic isotope effect (KIE) was observed when D_2/ethanol-D6 was used (k_H/k_D=1.5). This result is in agreement with prior studies suggesting that α-H abstraction is rate-limiting in the dehydrogenation step. The magnitude of the KIE is similar to what Baiker et al. have reported for octanol amination over Cu/Al_2O_3.[5]

The dependences of the rate propanol amination on reactant partial pressures are shown in Figures 3 and 4. The amination rate is positive order with respect to propanol at low propanol partial pressures and approaches zero order with increasing propanol partial pressures for the range of partial pressures tested (P_{PrOH} = 0.2-1.0 kPa). In contrast, the rate is zero order with respect to NH_3 for all NH_3 partial pressures tested (3.4-16.8 kPa). The results suggest that the sites responsible for propanol dehydrogenation are predominantly empty or are occupied by propanol-derived species. NH_3 has been proposed to aid in alcohol dehydrogenation over a Ni(111) surface.[28]

However, the rate over Ni/HAP does not vary with NH_3 partial pressure. Thus, an NH_3-mediated pathway may not be relevant for supported Ni catalysts.

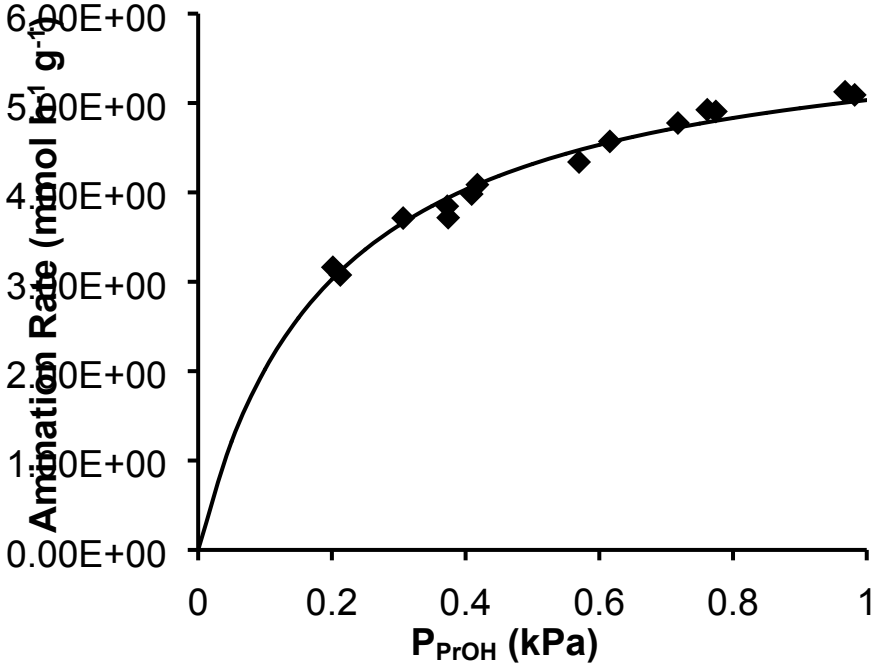


Figure 3: Effect of propanol partial pressure on amination rate. Reaction conditions: T = 423 K; Ni/HAP = 0.02 g; P_{NH3} = 5 kPa; P_{H2} = 95 kPa; total gas flow rate at STP = 60 mL min^{-1}.

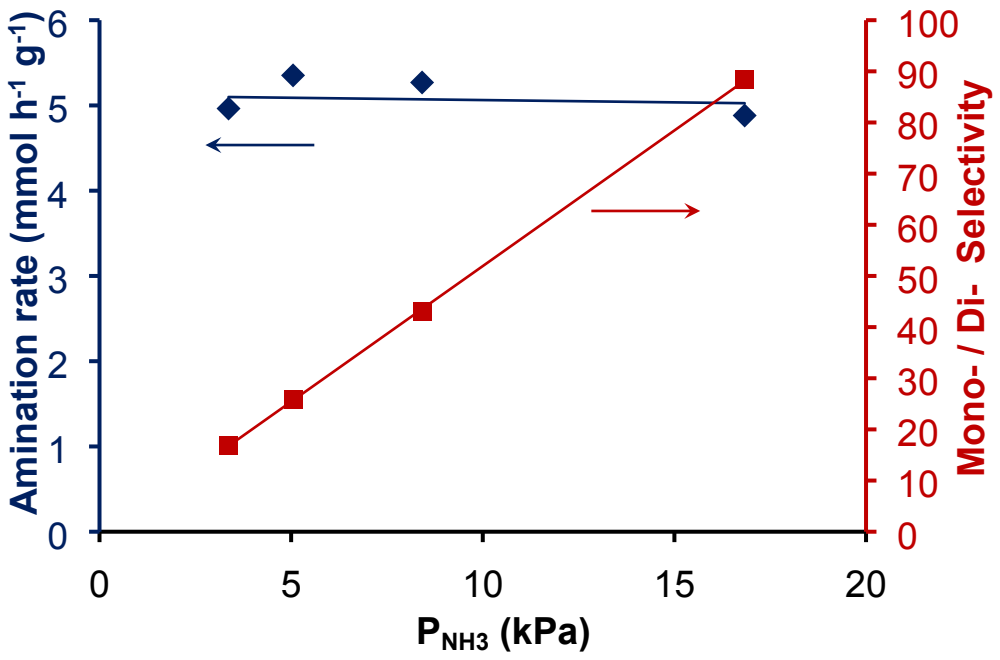


Figure 4: Effect of NH_3 partial pressure on propanol amination rate and selectivity of propylamine vs. dipropylamine. Reaction conditions: T = 423 K; Ni/HAP = 0.01 g; $P_{Propanol}$ = 1 kPa; P_{H2} = 83-96 kPa; total gas flow rate at STP = 30 mL min^{-1}.

As seen in Figure 4, the ratio of the production of propylamine to dipropylamine shows a strong dependence on NH_3 partial pressure. This finding is consistent with the proposed mechanism in which a propanal intermediate can react with either NH_3 to form propylamine or with propylamine to form dipropylamine. One interesting question is whether C-N bond formation takes place in the gas phase or on the surface. Several groups have reported that the C-N coupling reaction in the liquid phase is facile and can occur spontaneously in solution, while others have hypothesized that the reaction takes place on the catalyst surface based on the observation of a dependence of the product selectivity on catalyst composition.[29,30] To probe for C-N coupling in the gas phase, propanal and propylamine were fed through a blank reactor. Quantitative conversion to

dipropylimine was observed, showing that the reaction does not require a catalyst (Table S1). However, when a similar experiment was conducted with propanal and ammonia, no products were formed (Table S1). Primary imines are known to be unstable, so the lack of reaction could be due to the inherent thermodynamics instead of a kinetic limitation. Gas phase DFT calculations reveal that the Gibbs free energy of reaction, ΔG_{rxn}, for propanal and NH_3 to form propylimine is +33 kJ/mol while the ΔG_{rxn} for the reaction of propanal and propylamine to form dipropylimine is -0.6 kJ/mol (Scheme S1). The subsequent hydrogenation of propylimine (ΔG_{rxn} = -62 kJ/mol) or dipropylimine (ΔG_{rxn} = -39 kJ/mol) are both highly favorable. Based on these Gibbs free energy calculations, the equilibrium conversion of propanal and NH_3 to propylimine is approximately 1%. It is therefore tempting to suggest that coupling of propanal and NH_3 requires a catalyst, since no propylimine was detected in the product stream. However, we cannot rule out the possibility that small amounts of propylimine are formed but hidden beneath the propanal signal in the chromatogram, since the retention time of propylimine could only be estimated due to lack of a stable propylimine standard.

The amination rate and product selectivity are invariant with H_2 partial pressure for P_{H2} = 5-95 kPa (Figure S2). However the catalyst quickly deactivates if H_2 is not present due to the formation of metal nitrides and carbonaceous species.[8,11,31] Although H_2 does not play a direct role in the dehydrogenation reaction, a small amount is necessary to keep the Ni nanoparticles in their active metallic state. Possible product inhibition was investigated by co-feeding H_2O, butanal (as a proxy for propanal), diethylamine (as a proxy for dipropylamine), or triethylamine (as a proxy for tripropylamine). In all cases, no significant change in reaction rate was observed,

indicating that none of the above products or intermediates compete with propanol for the active site. (Figure S3).

Role of support in propanol amination over Ni catalysts

To gain more insight into the site requirements and role of the support, a series of Ni/HAP and Ni/SiO_2 catalysts with different Ni particle sizes were synthesized by varying the metal loading and reduction temperature (Table 2). Larger Ni particles were obtained at higher Ni loadings and higher reduction temperatures. Propanol amination rates were measured for all catalysts and are shown in Figure 5. When the rates are normalized by the number of surface Ni atoms, the rates decrease with increasing Ni particle size, suggesting that the Ni atoms located at the edges or corners are the active sites. Shimizu et al. have reported a similar observation for cyclodecanol dehydrogenation over Ni/θ-Al_2O_3.[32] An alternative hypothesis is that the support plays a direct role in alcohol dehydrogenation, in which case the active sites would be Ni perimeter sites located at the interface of the metal and the support. This would explain why Ni/HAP is more active than Ni/SiO_2 for a given particle size. The number of perimeter Ni particles were determined by assuming the Ni nanoparticle has the shape of a truncated cuboctahedron and then calculating the number of perimeter sites based on the nanoparticle size and number of Ni surface sites, as demonstrated by Cargnello et al.[33] Note that since particle surface area is proportional to the square of a characteristic radius, and particle perimeter is proportional to its radius, the relationship between perimeter sites, surface sites, and particle size should be similar for various particle geometries. When the rates are normalized by the number of perimeter Ni sites

(Figure 5b), the turnover frequencies become invariant with particle size, suggesting that the Ni perimeter sites are the ones active for propanol dehydrogenation.

Table 2: Synthesis conditions and characterization of Ni/HAP and Ni/SiO_2 catalysts

Catalyst	Ni loading[a] (wt %)	Reduction temperature (K)	Ni surface area[b] (m^2/g)	Fraction of Ni reduced[b] (%)	Ni particle size[a] (nm)
Ni/HAP-8.3	4.02	623	2.2	69	8.3
Ni/HAP-9.9	4.02	673	2.3	82	9.9
Ni/HAP-13.0	4.02	723	2.0	95	13.0
Ni/HAP-16.5 (Ni/HAP)	4.02	823	1.6	99	16.5
Ni/SiO_2-6.3 (Ni/SiO_2)	3.95	823	3.9	93	6.3
Ni/SiO_2-7.6	3.95	923	3.4	97	7.6
Ni/SiO_2-12.5	11.3	823	6.7	98	12.5
Ni/SiO_2-16.6	22.9	823	8.8	94	16.6

[a] From ICP-OES conducted by Galbraith Laboratories
[b] Based on H_2 chemisorption and O_2 titration measurements

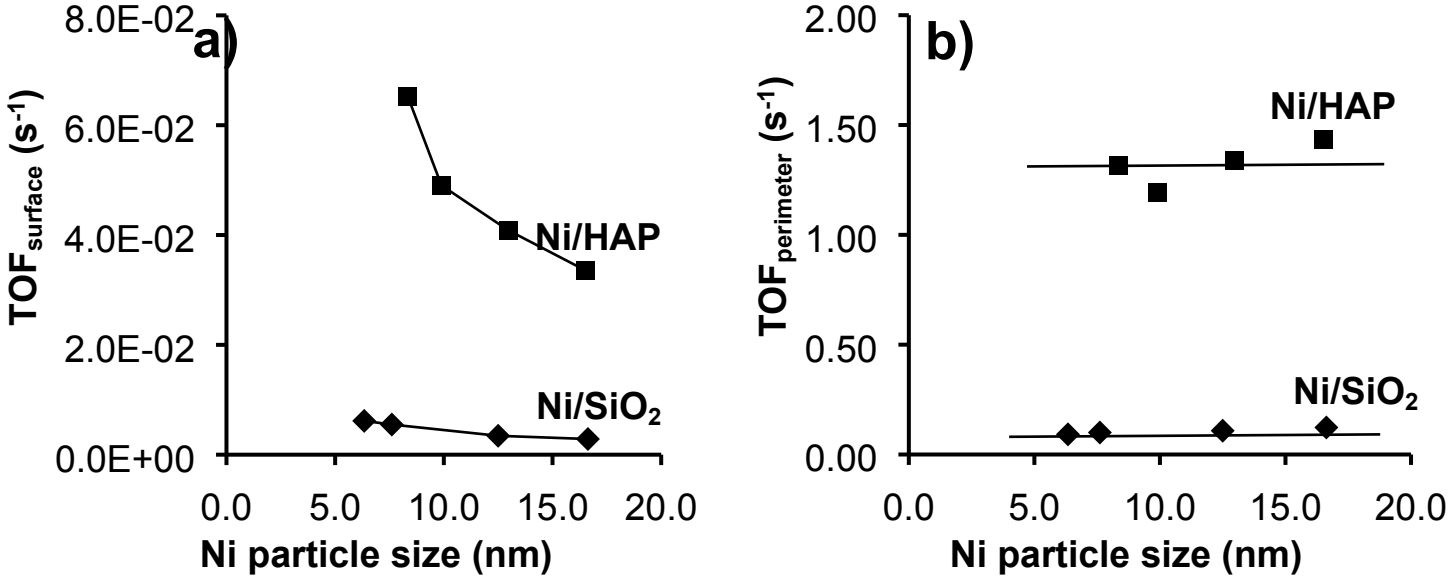
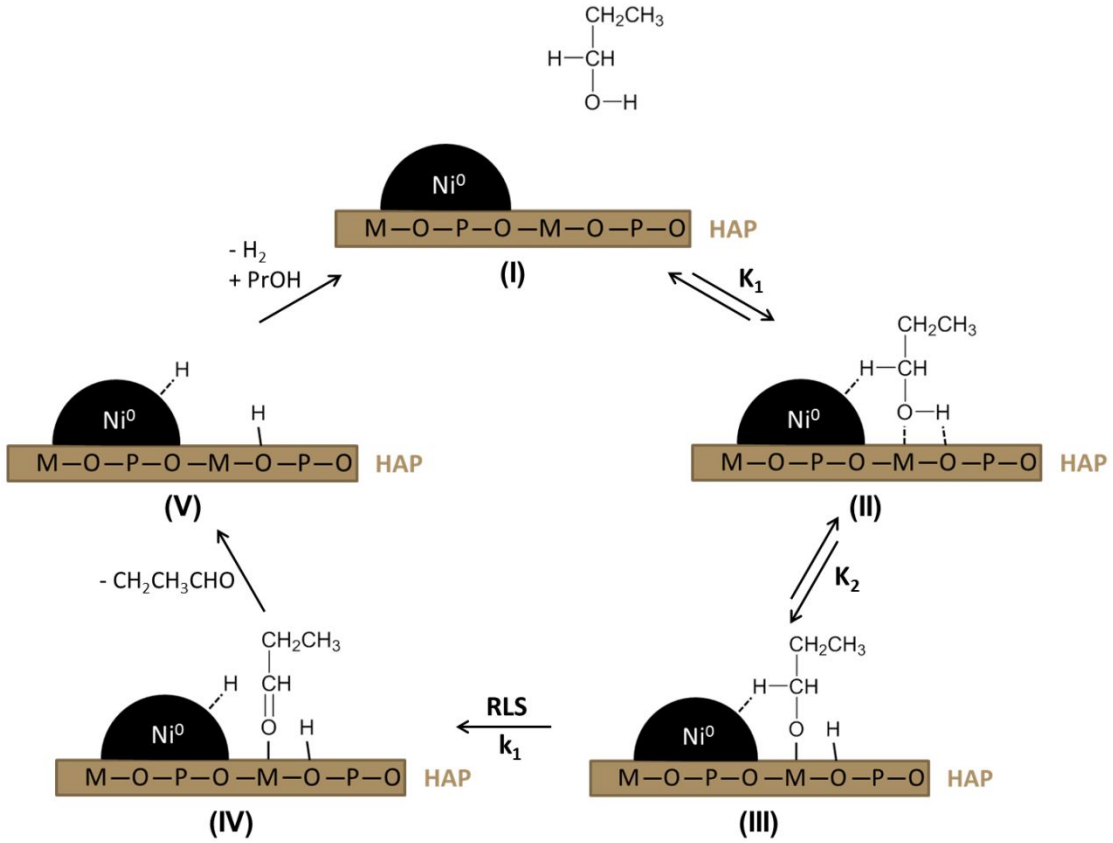


Figure 5: Effect of support and Ni particle size on turnover frequencies (TOF) of propanol amination. a) TOF is based on the number of surface Ni sites. b) TOF is based on the number of perimeter Ni sites. Reaction conditions: T = 423 K; $mass_{catalyst}$ = 0.02 g; $P_{Propanol}$ = 1 kPa; P_{NH3} = 5 kPa; P_{H2} = 95 kPa; total gas flow rate at STP = 60 mL min^{-1}.

To determine why the support affects reaction rates, it is helpful to construct a plausible mechanism for propanol dehydrogenation over Ni/HAP (Scheme 3). The adsorption of propanol and formation of the corresponding propoxide are facile over HAP, suggesting that gas phase propanol (**I**), molecularly adsorbed propanol (**II**), and surface propoxide (**III**) are in pseudo-equilibrium with each other.[34] The subsequent rate-limiting α-H abstraction occurs on a neighboring Ni site (**IV**), since dehydrogenation does not proceed in the absence of Ni at 423 K. Recombination of the surface hydrogen atoms (**V**) and desorption of the products complete the catalytic cycle.



Scheme 3: Proposed reaction mechanism for propanol dehydrogenation over Ni/HAP

An alternative mechanism is that dehydrogenation takes place exclusively on Ni, and the support only serves to modify the electronic properties of the metal. In this case, the activation barrier for α-H abstraction would depend on the nature of the support. To test this possibility, the activation energy was measured over Ni/HAP-16.5 and Ni/SiO_2-12.5 at P_{PrOH} = 2.0 kPa, where all interfacial sites are covered predominantly with propanol derived surface species (Figures S4, S5). As shown in Figure 6, The activation energies over both catalysts are similar ($E_{a,Ni/HAP}$ = 68 kJ/mol; $E_{a,Ni/SiO2}$ = 70 kJ/mol), indicating that the support does not affect the electronic properties of the Ni

nanoparticles and, hence, the rate of the α-H abstraction step. Instead, the difference in turnover frequencies between Ni/HAP and Ni/SiO_2 suggest that the properties of the support affect the concentration of the active surface propoxide species. Several groups have shown that alcohol adsorption on SiO_2 leads mainly to molecularly adsorbed alcohol, and only a small fraction of surface species are alkoxides which form by condensation of alcohol/silanol groups or opening of the siloxane bridges.[35,36,37] On the other hand, HAP is known to have a high density of basic sites that can activate alcohols.[21,38] This is evident when looking at adsorption microcalorimetry of ethanol. The differential heat of ethanol adsorption over HAP ($\Delta H_{EtOH} \approx 100$ kJ/mol) remains constant up to a surface coverage of 4 μmol m^{-2}, which is indicative of a surface that contains strongly chemisorbed ethanol species.[21] For SiO_2, the differential heat of ethanol adsorption decreases rapidly from ~100 kJ/mol to ~60 kJ/mol as the surface coverage increases to 1 μmol m^{-2}, consistent with the idea that most alcohols on SiO_2 are weakly bound, physisorbed species.[35] Shimuzu et al. have proposed a similar role for the support in 2-propanol dehydrogenation over Ni/Al_2O_3.[32] Based on catalyst screening and FTIR studies, the group hypothesized that the basic sites in θ-Al_2O_3 were responsible for the formation of 2-propoxide species.[32] This conclusion parallels that drawn from studies of alcohol amination carried out with homogenous catalysts, in which alcohol dehydrogenation and amination over metal complexes typically require the addition of a base such as K_2CO_3 to deprotonate the alcohol and form the alkoxide.[39,40] Although MgO is a basic support that can catalyze alkoxide formation, the Ni/MgO catalyst exhibited a lower TOF than Ni/HAP (Table 1). This is likely due to the higher density of base sites on the HAP support, which translates to a higher

concentration of propoxide species on the surface, and hence, to a higher TOF even after normalizing rates per perimeter Ni atom.[21]

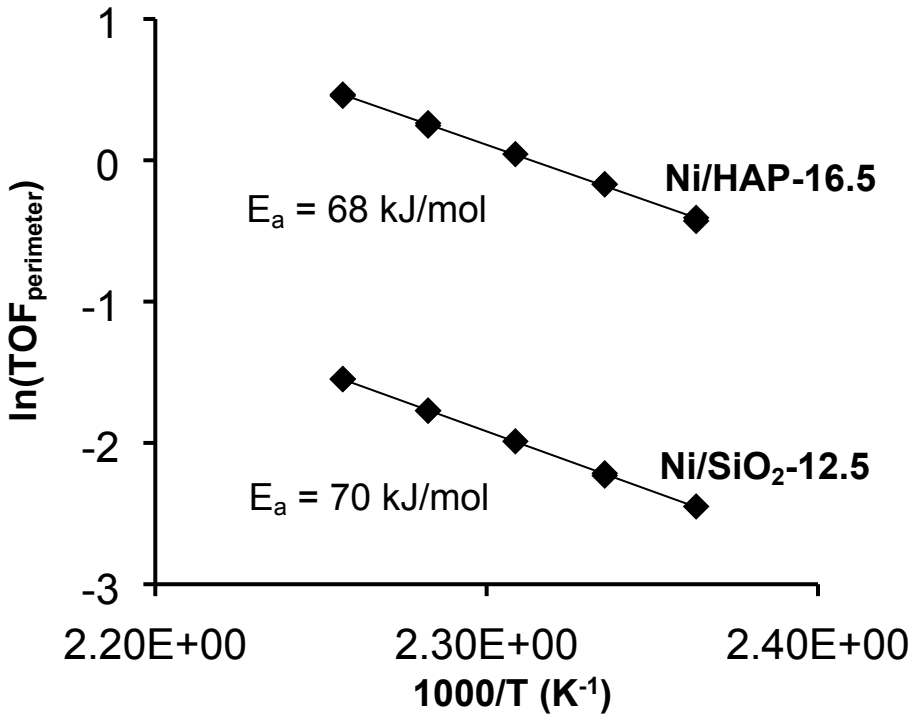


Figure 6: Arrhenius plots of propanol amination over Ni/HAP-16.5 and Ni/SiO_2-12.5. Reaction conditions: T = 423 K; $mass_{catalyst}$ = 0.02 g; $P_{Propanol}$ = 1 kPa; P_{NH3} = 5 kPa; P_{H2} = 95 kPa; total gas flow rate at STP = 60 mL min^{-1}.

An additional factor that could explain the large difference in activity between Ni/HAP and Ni/SiO_2 is the ability of Ni/HAP to catalyze hydrogen transfer reactions, since HAP is known to be active for hydrogen transfer reactions between alcohols and aldehydes.[19,41,42,43] These hydrogen transfer reactions are rapid in comparison to dehydrogenation and can accelerate condensation rates by providing an alternate pathway for producing aldehydes.[19] To determine whether Ni/HAP is active for hydrogen transfer between alcohols and imines, propanol and dipropylimine were fed to

the reactor. No dipropylamine was observed in the product stream, indicating that hydrogen transfer to a C=N bond is much more difficult than the corresponding reaction over the more polar C=O bond.

Space time studies over Ni/HAP and Ni/SiO_2 were performed to evaluate the effect of support on product selectivity. For both catalysts, propylamine selectivity decreased and dipropylamine selectivity increased with increasing propanol conversion, as shown in Figure 7. This is consistent with a mechanism in which propylamine is a primary product that can react further to form dipropylamine. There are two main pathways for dipropylamine formation. One pathway is a consecutive amination reaction, wherein propylamine and propanol react to give dipropylamine and water. The other pathway is the disproportionation of two equivalents of propylamine to give dipropylamine and NH_3. For a given propanol conversion, Ni/HAP is more selective towards propylamine than Ni/SiO_2.

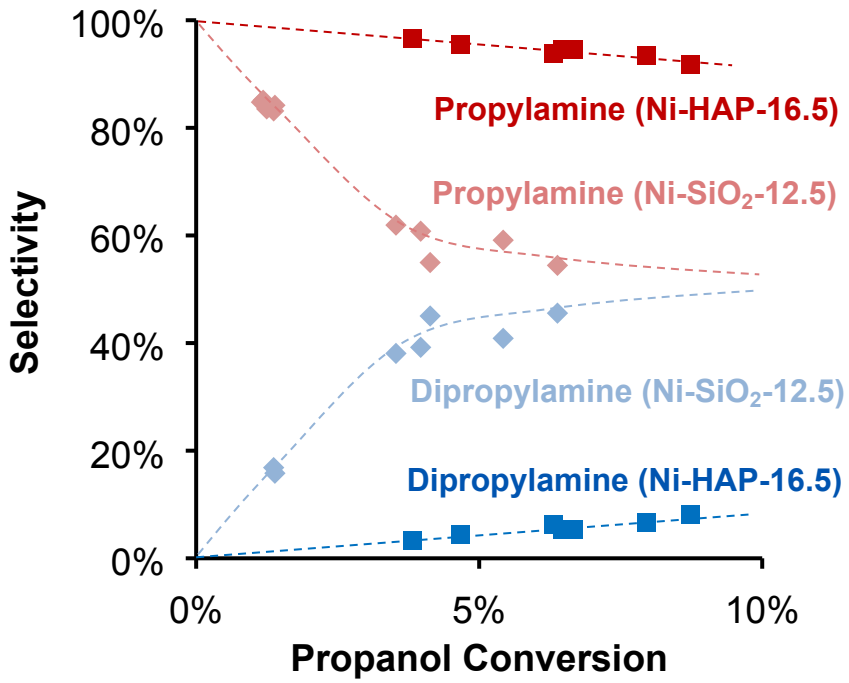
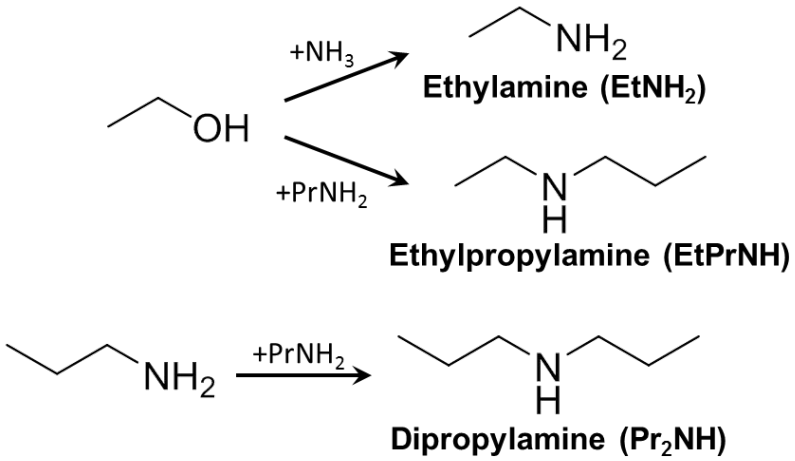


Figure 7: Spacetime studies showing how the selectivity of propylamine and dipropylamine as a function of propanol conversion over Ni/HAP-16.5 and Ni/SiO_2-12.5. Reaction conditions: T = 423 K; $mass_{catalyst}$ = 0.02 g; $P_{Propanol}$ = 1 kPa; P_{NH3} = 5 kPa; P_{H2} = 95 kPa.

To determine whether this difference in selectivity is due to differences in secondary amination or disproportion rates, experiments with ethanol/NH_3/propylamine feeds were performed to decouple the amination and disproportion rates. Primary amination of ethanol yields ethylamine, secondary amination of ethanol yields ethylpropylamine, and disproportionation of propylamine yields dipropylamine (Scheme 4). The disproportion rate was three times higher over Ni/SiO_2 compared to Ni/HAP, which partly explains why Ni/HAP is more selective for the primary amine than Ni/SiO_2 (Table 3). The reason for the low disproportion rates over Ni/HAP is likely due to a lack of strong Lewis acid sites, which are known to be active for disproportionation.[31] The

small fraction of unreduced Ni in Ni/SiO_2 can lead to the generation of Lewis acid sites, and Verhaak et al. have demonstrated that Ni/SiO_2 is an active catalyst for disproportionation.[31]



Scheme 4: Possible amination and disproportionation reactions for an ethanol/NH_3/propylamine feed

Table 3: Disproportionation of propylamine over Ni/HAP-16.5 and Ni/SiO_2-12.5. Reaction conditions: T = 423 K; $mass_{catalyst}$ = 0.01 g; P_{PrOH} = 0.1 kPa; $P_{Ethylamine}$ = 0.1 kPa; P_{NH3} = 5 kPa; P_{H2} = 95 kPa; total gas flow rate at STP = 30 mL min^{-1}.

Catalyst	Formation rate (mmol h^{-1} g_{cat}^{-1})		
	Ethylamine	Ethylpropylamine	Dipropylamine
Ni/HAP-16.5	1.90	1.39	0.62
Ni/SiO_2-12.5	0.69	1.50	1.79

The relative rates of primary and secondary amination also depend on the support. Ethylamine and ethylpropylamine are both formed from a common ethanal intermediate, and the ratio of their formation rates is proportional to the ratio of NH_3 and propylamine partial pressures. This is illustrated in eq 1, where k represents a rate constant, P represents the partial pressure, and $[CH_3CHO*]$ represents the surface concentration of propanal on the support. This expression is consistent with the observed trends in product selectivities and in the NH_3 kinetics of propanol amination (Figure 4).

$$\frac{r_{EtNH_2}}{r_{EtPrNH}} = \frac{k_{EtNH_2}P_{EtNH_2}[CH_3CHO*]}{k_{EtPrNH}P_{EtPrNH}[CH_3CHO*]} \quad (1)$$

Coupling of ethanal is more facile with propylamine than with NH_3 since propylamine is a stronger nucleophile and secondary imines are more stable than primary imines. The ratio of rate constants for ethanal coupling with propylamine vs NH_3 $\left(\frac{k_{EtPrNH}}{k_{EtNH_2}}\right)$ is 37 over Ni/HAP and 109 over Ni/SiO_2. The different rate constants for the two catalysts indicate that the support plays an important role in the condensation step. Furthermore, this is evidence that C-N coupling occurs on the support surface and not exclusively in the gas-phase. We hypothesize that $\frac{k_{EtPrNH}}{k_{EtNH_2}}$ is higher over Ni/HAP because of the basic nature of the HAP support, which lowers the effective concentration of adsorbed propylamine compared to SiO_2. Thus, Ni/HAP is more selective towards the primary amine than Ni/SiO_2 because both the secondary amination and disproportionation reactions are suppressed more greatly over HAP.

One question that arises is whether the density of active Ni sites affects the product selectivity. Propanol amination with propylamine has the same mechanism and site requirements as propanol amination with NH_3, so the number of active Ni sites should not affect the relative selectivity of these two reactions, as long as results are compared at isoconversion. However, the density of active Ni sites could affect the relative rate of amination and disproportionation.

While a detailed mechanistic understanding of amine disproportionation is outside the scope of this work, it has been generally proposed that disproportionation occurs in a 3-step process that involves dehydrogenation of the propylamine to proyplimine, coupling of propylimine with another propylamine, and hydrogenation of the resulting secondary imine to form dipropylamine.[4,31] Starting from a propylimine intermediate, hydrogenation would yield propylamine, while disproportionation would yield dipropylamine. Thus, the density of active Ni sites could affect the rate of propylimine hydrogenation, which would impact product selectivity.

To investigate this possibility, the selectivity to propylamine at a given propanol conversion (~10% for Ni/HAP, ~3.5% for Ni/SiO_2) was plotted as a function of the number of Ni perimeter sites for all supported Ni catalysts (Figure S7). The selectivity to propylamine appears to be invariant with the number of perimeter Ni sites for a given support. To explain this result, we note that disproportionation of propylamine occurs under reaction conditions (Table 3), indicating that propylamine dehydrogenation to propylimine is a relevant process. Thus, increasing the density of Ni sites will increase both the rate of propylimine hydrogenation and propylamine dehydrogenation, which

would explain why the density of Ni perimeter sites does not significantly affect product selectivity (Scheme S2).

However, for a catalyst with a low density of active Ni sites, increasing the number of Ni sites could lead to an increase in selectivity. For example, the basic 4%Ni/MgO exhibits a lower selectivity to propylamine compared to the acidic 4%Ni/Al_2O_3. This appears to contradict the idea that Lewis acidic supports are more active for disproportionation and secondary amination. However, close inspection of the 4%Ni/MgO catalyst revealsa that only 14% of Ni is reduced after treatment in H_2 at 773 K. This is due to the difficulty of reducing Ni on a MgO support. The 4%Ni/MgO catalyst has fewer active Ni sites compared to 4%Ni/Al_2O_3 (0.3 vs 2.2 μmol/g_{cat}). In addition, the unreduced NiO on MgO can serve as Lewis acid sites. These two factors could explain why Ni/MgO has a lower selectivity to propylamine than 4%Ni/Al_2O_3.

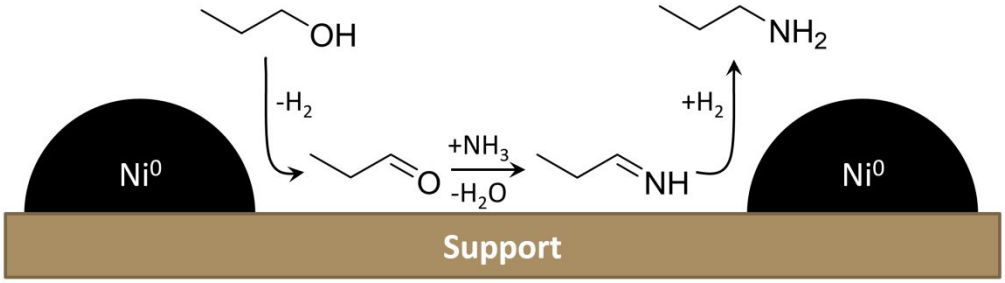
To test this hypothesis, a 12%Ni/MgO catalyst was synthesized by an impregnation method. Compared to 4%Ni/MgO, the 12%Ni/MgO catalyst has a higher Ni loading and larger NiO particles, which results in a higher fraction of reduced Ni after H_2 treatment. As a result, the 12%Ni/MgO catalyst has more active Ni sites and fewer Lewis acid sites than 4%Ni/MgO, which should lead to an increase in propylamine selectivity. Indeed, at a conversion of ~3.5%, the propylamine selectivity over the 12%Ni/MgO (89%, Table S1) was higher than that of 4%Ni/MgO (84%). Thus, propylamine selectivity can be improved by increasing the number of Ni sites and decreasing the number of Lewis acid sites. Unfortunately, the contribution due to the two effects could not be decoupled. A similar trend has been observed by Cabello et al.

over Ni/hydrotalcite, where the Ni reducibility and support basicity depend on the Ni and Mg loadings.[44] For a more comprehensive review of support effects on selectivity, the authors refer Gomez et al.[30]

CONCLUSIONS

We have demonstrated that Ni/HAP is an active catalyst for propanol amination to propylamine. The reaction proceeds through a dehydroamination pathway and is limited by the rate of α-H abstraction from propanol. The turnover frequency for this reaction is invariant with Ni particle size when normalized by the number of perimeter Ni atoms, suggesting that the active sites for dehydrogenation are located at the interface between the metal and the support. Ni/HAP is more active and selective towards the primary amine than Ni/SiO_2, highlighting the importance of the support. Although Ni is solely responsible for the α-H abstraction step, the support affects the reaction rate by deprotonating the alcohol to form active alkoxide intermediates. The subsequent coupling of propanal with ammonia is rapid and quantitative, independent of the ammonia partial pressure. While propylimine formed by this reaction is thermodynamically unstable, its rapid hydrogenation over the Ni nanoparticles leads to the thermodynamically favorable formation of propylamine. Experimental evidence suggests that the reaction of propanal with ammonia occurs on the surface of HAP, whereas the hydrogenation of propylimine occurs on the surface of the Ni nanoparticles (Scheme 5). The secondary reaction of product propylamine with propanal to form dipropylamine also occurs on the surface of HAP but is increasingly suppressed as the

partial pressure of ammonia is increased. This secondary reaction occurs to a much lower degree over Ni/HAP than Ni/SiO_2. Finally, we have found that the disproportionation of propylamine to dipropylamine and ammonia is disfavored over Ni/HAP compared to Ni/SiO_2.



Scheme 5: Proposed reaction mechanism for propanol amination over Ni/HAP

SUPPORTING INFORMATION

Raman spectra and EDX analysis of Ni/HAP, additional catalytic testing, KIE studies, DFT calculated gas-phase enthalpies and free energies of reactions, comparison of TOF values with literature.

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GRAPHICAL ABSTRACT