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## THESIS SUMMARY

In my time as an undergraduate chemistry major at the University of South Carolina I've had the opportunity to work as an undergraduate research assistant in the Vannucci Research Group, an inorganic chemistry lab that specializes in green chemistry. For the past two years I've gotten to assist with the synthesis of four new nickel-based catalysts which are bonded to silica supports. These catalysts are designed to more efficiently catalyze Suzuki-Miyaura cross-coupling reactions. This thesis project focuses on two of the catalysts: their synthesis, how they bond to the SiO<sub>2</sub> support, how successful they are at catalyzing a cross-coupling reaction, and how well they remain bonded to the SiO<sub>2</sub> after a reaction. Their performance is examined and compared to each other, as well as to other similar catalysts. These catalysts are part of a growing trend to move to more sustainable nickel-based catalysts for Suzuki-Miyaura. The success of this project is another step forward to create a more affordable, more effective, and more sustainable catalyst.

## ABSTRACT

Two molecular nickel-based catalysts, (2,2'-bipyridine-4,4'-carboxylic acid)nickel(II) chloride and (2,2'-bipyridine-4,4'-diamidopropylsilatrane)nickel(II) chloride, were synthesized and subsequently attached to a solid support in the form of amorphous silicon dioxide to create two hybrid molecular/heterogeneous catalysts. Characterization using ICP-MS and ATR-FTIR confirms that both catalysts are bonded to the SiO<sub>2</sub> support. The catalysts were both able to catalyze a Suzuki-Miyaura cross-coupling which their molecular counterparts were unable to; the carboxylate catalyst was able to achieve yields of 10% and the silatrane catalyst achieved yields of up to 50%. Post-reaction analysis indicated that while some catalyst desorption occurred in both complexes, active catalytic species remained adhered to the surface post-reaction, with the silatrane catalyst showing more resistance to leaching. These hybrid catalysts represent another advancement in the field of surface stabilized metal oxide catalysts using an earth abundant transition metal.

## INTRODUCTION

Suzuki-Miyaura cross-coupling was initially discovered in 1981 and traditionally involves the cross-coupling of an aryl halide electrophile with an organoborane nucleophile.<sup>4</sup> This type of reaction has quickly become one of the most widely used reactions in industrial chemistry.<sup>1,4</sup> In 2014, Suzuki-Miyaura couplings were reportedly the second most common reaction.<sup>4</sup> Suzuki-Miyaura reactions are important for various industrial applications, particularly within the pharmaceutical industry. These reactions require a metal-based catalyst to work. Palladium catalysts have been the standard but due to the large scale industrial chemistry runs on, there has been a push for a less expensive and more effective catalyst. The ACS

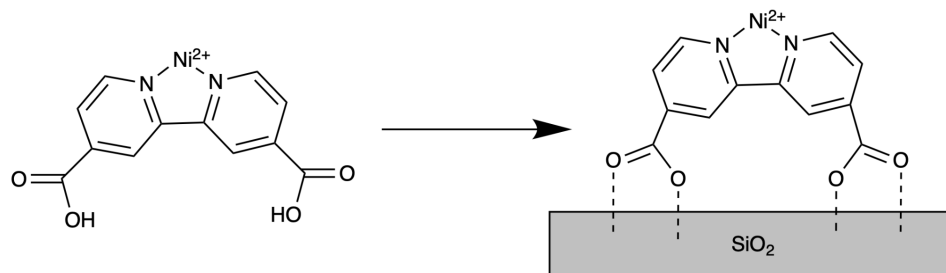
Pharmaceutical Round Table has advocated for increased exploration of both nickel catalysts and catalyst immobilization techniques.<sup>1,6</sup>

In an attempt to continue advancing the scope of hybrid molecular/heterogeneous catalysts, two new catalyst systems were designed and synthesized, each exploring a different method of attachment to the heterogeneous SiO<sub>2</sub> support. The first is based on the molecular catalyst [(2,2'-bipyridine-4,4'-carboxylic acid)Ni<sup>2+</sup>]Cl<sub>2</sub>, herein abbreviated as NibpyCOOH, which is then bound to the A300 SiO<sub>2</sub> to form NibpyCOOH[A300]. The second is based on the molecular catalyst [(2,2'-bipyridine-4,4'-diamidopropylsilatrane)Ni<sup>2+</sup>]Cl<sub>2</sub>, herein abbreviated as Nibpysil, which is then bound to the A300 SiO<sub>2</sub> to form Nibpysil[A300]. These catalysts are design to build on previous successes using immobilized polypyridinyl Ni catalysts for cross-coupling.<sup>1,6</sup>

Nickel is a more abundant transition metal than palladium and is therefore less expensive to work with.<sup>1,4</sup> Nickel catalysts have also demonstrated the ability to activate less reactive electrophiles, expanding the scope of traditional Suzuki-Miyaura reactions to include bonding to sp<sup>2</sup>-hybridized carbons.<sup>1,4</sup> They have also demonstrated good enantioselectivity when using an alkyl electrophile.<sup>4</sup> Nickel can more easily undergo both one and two electron reductions compared to palladium due to its lower field splitting, which means that nickel catalysts undergo the crucial oxidative addition step more readily than palladium catalysts.<sup>4</sup> All of these benefits make nickel catalysts seem like the future of catalysis. However, there are some drawbacks to contend with. Controlling the reactivity and catalyst stability are primary issues. Sensitivity to solvent and base choice is an issue for nickel catalysts.<sup>1</sup> Due to generally lower activity than palladium, nickel catalysts also require a larger amount of catalyst for effective product formation.<sup>1,4</sup> Not only is this inefficient, it gives rise to several other issues. High concentrations of nickel can cause issues such as metal poisoning in the product, a big concern for the pharmaceutical industry.<sup>1</sup> Additionally, large amounts of catalyst in solution can increase the rate of formation of undesired side products.<sup>1,2,4</sup>

One method being explored to combat these drawbacks is catalyst immobilization. By anchoring the catalytic complex to a solid metal oxide, a hybrid molecular catalyst is created. The hybrid catalyst is designed to combine all of the benefits of molecular catalysts (high activity and selectivity) and heterogeneous catalysts (longer lifetimes, greater stability, easier post-reaction separation, reusability, and less sensitivity to solvents) into one complex.<sup>1,2,6</sup> Catalyst immobilization also works to prevent unwanted side reactions, most notably, dimerization. Formation of the nickel dimer deactivates the catalyst, rendering it useless.<sup>2</sup> Dimers are also very difficult to convert back into active catalyst.<sup>6,8</sup> Preventing dimerization of the nickel catalyst is paramount to increasing catalyst performance. Immobilization should prevent dimer formation by physically separating the nickel complexes so that bonding is not possible. Catalyst activity has also shown to improve with immobilization, Key et al. has reported reaction yields of up to 75% using a catalyst loading of as low as 0.1 mol% of molecular nickel catalyst.<sup>1</sup> Amorphous SiO<sub>2</sub> was chosen as the metal oxide due to previous successes using it as a solid support for similar nickel polypyridyl complexes.<sup>1,2,6</sup>

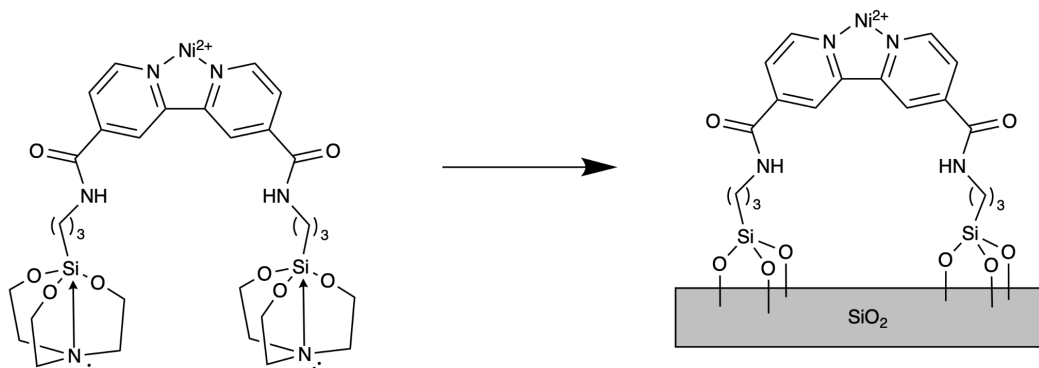
The method of attachment to the metal oxide surface is thought to play a significant role in determining the stability and longevity of the catalyst. The general method of immobilization is through the use of an anchoring group like a carboxylate. NibpyCOOH is bound to the surface using two carboxylate anchoring groups, shown in Figure 1.



**Figure 1.** Illustration of the catalyst NibpyCOOH being bonded to the  $\text{SiO}_2$

Carboxylate anchoring groups have been used for numerous applications from fuels cells, to organic reaction catalysts, and beyond.<sup>1,2,6,9,10</sup> They also have the advantage of being easily accessible with relatively simple precursors and synthetic routes.<sup>10</sup> The carboxylate group bonds to the metal oxide surface via hydrogen bonding. Computational studies have indicated that for amorphous  $\text{SiO}_2$  the carboxylate group can form hydrogen bonds to either the silanol or siloxane groups on the  $\text{SiO}_2$  surface.<sup>2</sup> Numerous studies on other metal oxides indicate that carboxylates anchoring groups can have a bidentate binding conformation using both the alcohol and carbonyl portions of the carboxylic acid.<sup>9,10</sup> However, Catalysts anchored via carboxylic groups have been shown to be susceptible to surface desorption.<sup>6,9,10</sup> This can be especially problematic for catalysts designed for their recyclability. Catalyst leaching has been found to contribute to progressively lower yields in subsequent reactions until no product can be formed.<sup>1</sup> Methods of improving catalyst anchoring are being explored in order to mitigate this. Previous works have focused on immobilization via one anchoring group, but by designing a nickel catalyst with two anchoring groups, it is hoped that the addition of another anchor point will increase the catalyst stability and help to combat leaching and dimerization.

An alternate method of immobilization being explored is the use of silatranes as an anchoring group, illustrated in Figure 2.



**Figure 2.** Illustration of the catalyst Nibpysil being bonded to  $\text{SiO}_2$

Silatrane anchoring groups have previously been used in dye-sensitized solar cells and photochemical cells, and have been shown to be highly effective at bonding to metal oxides.<sup>3,9,10</sup> The tripodal caged structure provides more points of attachment to the metal oxide and protects it from side reactions.<sup>3,10</sup> They have even been shown to be stable within a pH range of 2 to 11, further proving their durability, and expanding the scope of reactions for which this catalyst is useful.<sup>3</sup> Silatrane groups bond to the metal oxide via a covalent bond formed between the surface hydroxyl group and the Si of the silatrane group. The Si center undergoes a nucleophilic attack from a surface silanol to surface silanol to form the siloxane bond, subsequently releasing the protecting triethanolamine group.<sup>10</sup> Silatranes are thought to form bidentate or tridentate linkages to the surface with the bidentate conformation being theoretically favored on TiO<sub>2</sub>.<sup>9,10</sup> The free alcohol group is thought to be able to undergo intermolecular condensation to other silatranes to create intermolecular siloxane bonding, making surface linkage possibilities diverse.<sup>10</sup> One drawback to the use of silatranes is the complex synthetic process which is not easily achieved by laboratories not equipped to handle inorganic air-sensitive processes.<sup>10</sup> On an industrial scale, it may be difficult to scale up the synthetic process to the necessary level in a safe and environmentally friendly manner.

One of the overarching goals of this project is to create a more sustainable catalyst for Suzuki-Miyaura cross-couplings. Nickel is a cheaper and more abundant transition metal compared to palladium and on the whole, nickel catalysts are considered to be more sustainable than palladium ones.<sup>1</sup> Catalyst immobilization not only allows for easy separation from the reaction mixture for reuse, which reduces waste, it also allows for more selective reactions which can reduce side-product waste. Increased stability will expand solvent scopes, hopefully allowing for greener solvents like water or ethanol. The current challenge is that protic polar solvents disrupt catalyst binding to the solid support.<sup>6</sup> The hydrogen bonds of the carboxylate group are especially susceptible to interference from polar solvents. Though not explored in this work, it is hoped the covalent siloxane bonds might be resistant to polar interference. The larger applicability of binding a catalyst to a solid support has a significant impact beyond catalysis, the area of renewable energy — fuel cells, solar cells, photochemical cells — would benefit greatly from the improvement of metal oxide catalyst stability.<sup>3,9,10</sup>

## EXPERIMENTAL

**Materials.** All reagents are assumed to be pure and were used as they were received from the manufacturer. 2,2'-bipyridine-4,4'-diamidopropylsilatrane and 2,2'-bipyridine-4,4'-carboxylic acid were prepared by previously reported methods from Materna et. al. and Huang et. al., respectively.<sup>2,5</sup> The metal oxide support used throughout is amorphous SiO<sub>2</sub> purchased from Evonik (Aerosil 300, A300). A300 has a surface area of 300 m<sup>2</sup>/g and an average particle size of 20 nm.

**Instrumentation.** Inductively coupled plasma-mass spectrometry (ICP-MS) analysis was performed using a Finnigan ELEMENT XR with a double focusing magnetic field. A quartz

torch and injector from Thermo Fischer Scientific and a 0.2 mL/min Micromist U-series nebulizer from GE were used for sample introduction. ICP-MS was used to determine nickel catalyst loading on A300. Fourier transform infrared-attenuated total reflection (FTIR-ATR) was performed using a Nicolet iS FTIR spectrometer with an iD7 diamond crystal ATR attachment. A background scan was collected prior to sample analysis and was subtracted out. FTIR was used to characterize ligand binding to SiO<sub>2</sub>.

**Synthesis of NibpyCOOH catalyst.** In a round-bottom flask, 100 mg (0.41 mmol) of [2,2'-bipyridine]-4,4'-dicarboxylic acid and 1 equiv. of NiCl<sub>2</sub> · 6H<sub>2</sub>O were dissolved in 50 mL of ethanol. The solution was heated to 85 °C and refluxed overnight. The solution was placed on the rotary evaporator and evaporated to dryness. The resulting lime green solid was recrystallized in ethanol before use or characterization.

**Preparation of NibpyCOOH[A300]. Method 1:** Procedure is based on previous work with modifications.<sup>1</sup> 100 mg of A300 SiO<sub>2</sub> was dissolved in 50 mL of methanol. To this solution, 0.150 mmol of NiCl<sub>2</sub> · 6H<sub>2</sub>O and 0.100 mmol of 2,2'-bipyridine-4,4'-carboxylic acid were added. The solution was briefly sonicated and then allowed to settle overnight in a dark environment. The white (with a slight green tinge) solid was then vacuum-filtered, rinsed with hexanes, and dried before further use or characterization.

**Preparation of NibpyCOOH[A300]. Method 2:** Procedure is based on previous work with modifications.<sup>1</sup> 200 mg of A300 SiO<sub>2</sub> was dissolved in 100 mg of methanol. To this solution, 0.100 mmol of NiCl<sub>2</sub>[2,2'-bipyridine-4,4'-carboxylic acid] was added. The solution was briefly sonicated and then allowed to settle overnight in a dark environment. The white (with a slight green tinge) solid was then vacuum-filtered, rinsed with hexanes, and dried before further use or characterization.

**Synthesis of bpy-Sil catalyst.** In an inert nitrogen gas atmosphere 100 mg (0.15 mmol) 2,2'-bipyridine-4,4'-diamidopropylsilatrane was dissolved in 25 mL of warm acetonitrile in a round bottom flask. 1 equiv. of NiBr<sub>2</sub> · DME was added to the pink solution which turned teal upon addition. The reaction mixture was stirred overnight at room temperature. The reaction mixture was removed from the nitrogen atmosphere and vacuum filtered to produce a pink solid. Yield: 0.077 g (0.10 mmol).

**Preparation of bpy-Sil[A300].** Reaction was performed under constant flow of N<sub>2</sub> gas. In a round bottom flask, 100 mg of NiCl<sub>2</sub>[2,2'-bipyridine-4,4'-diamidopropylsilatrane] and 60 mg of A300 SiO<sub>2</sub> were dissolved in 10 mL anhydrous CH<sub>3</sub>CN. The green solid formed a vivid blue solution upon addition of solvent. The solution was heated to 70°C and refluxed for 24 hrs. Reaction mixture was allowed to cool to room temperature and then vacuum-filtered, washing with ethanol. The solid should be white with a slight green tint. If the solid had more than a slight tint of green, it was recrystallized in ethanol before use or characterization.

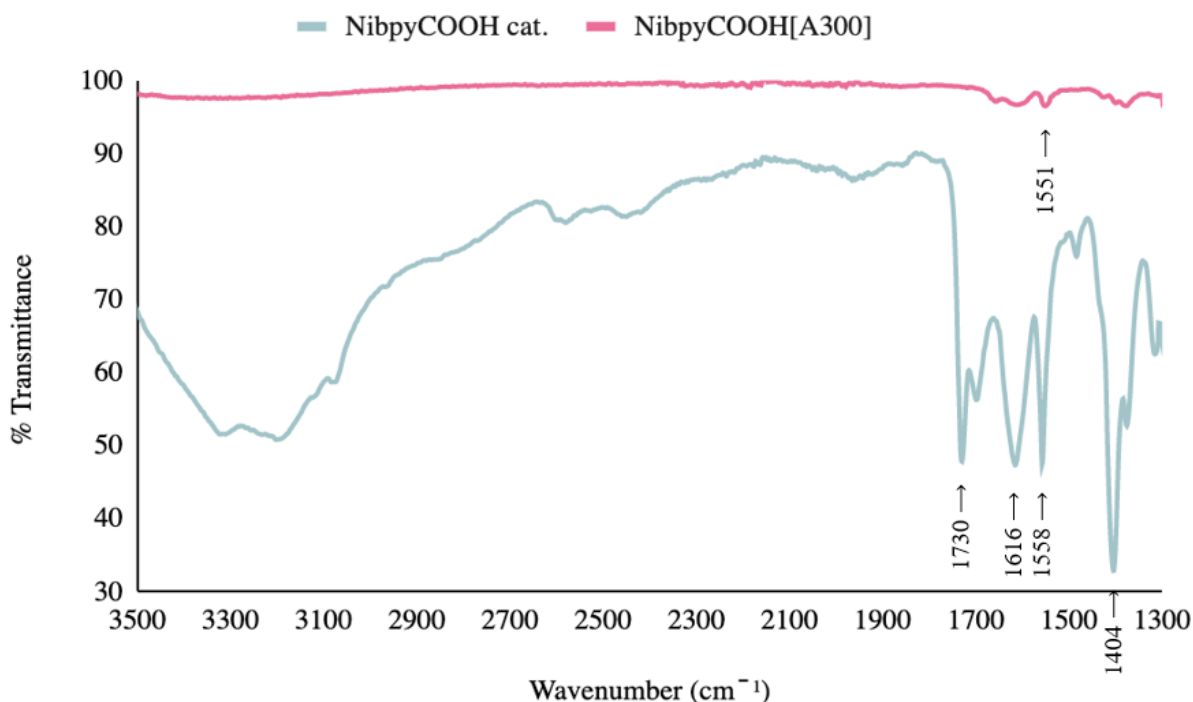
**Cross-Coupling Reaction Scheme.** In a round bottom flask, 100 mg of catalyst, 0.68 mmol of 4-Iodotoluene, 1.2 equiv of 4-methoxyphenylboronic acid, and 2.5 equiv of K<sub>3</sub>PO<sub>4</sub>, were added to 20 mL of dioxane. This reaction mixture was flushed with nitrogen gas for 15 minutes as it was brought to reflux at 115 °C for 24 hrs. Upon completion, the reaction mixture

was cooled to room temperature using a water bath. The mixture was centrifuged at 1500 rpm for 5 minutes. The liquid was decanted and the solvent was evaporated off via rotary evaporation. The resulting product was isolated using preparative scale thin layer chromatography. The resulting product was a clear crystalline solid. The solid catalyst separated via centrifugation was washed with hexanes and then allowed to dry. The dried post-reaction catalyst was stored for characterization or further reactions.

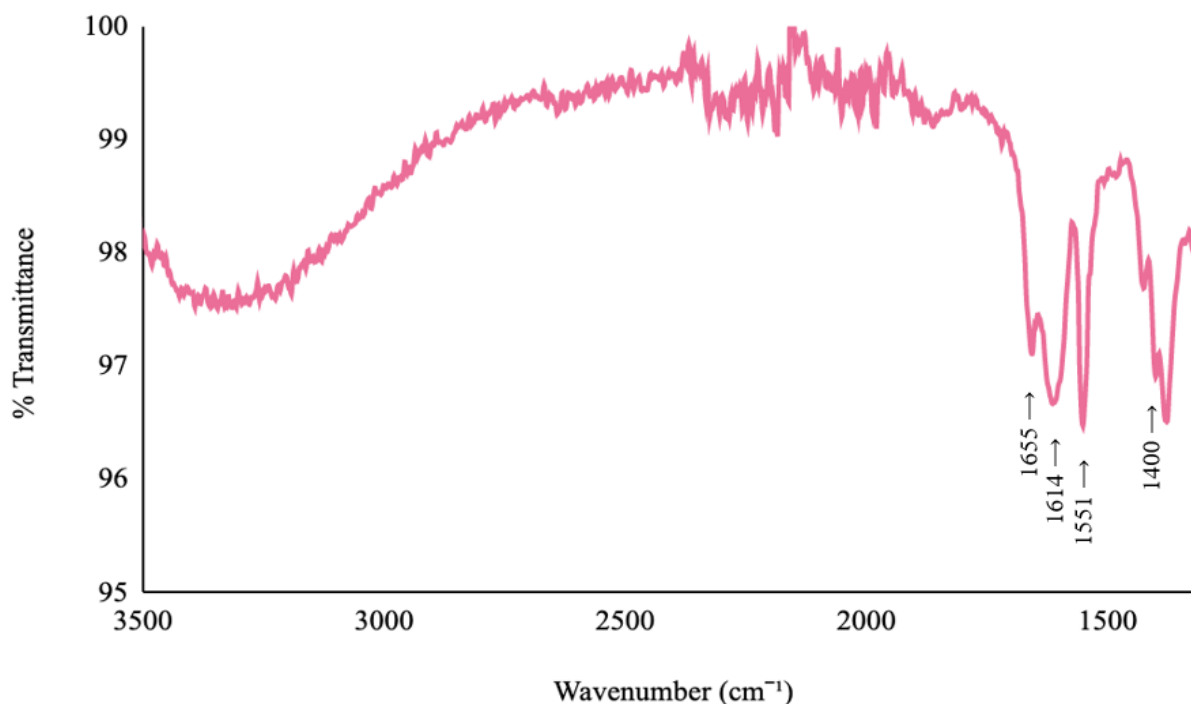
## RESULTS

### *Characterization*

Infrared attenuated total reflection (FTIR-ATR) spectroscopy was used to characterize the anchoring group ligand binding to the molecular support. Scans were conducted from 1300 - 3500  $\text{cm}^{-1}$ . Figure 3 shows the FTIR spectra of both the homogenous NibpyCOOH catalyst and the molecular NibpyCOOH[A300] catalyst while Figure 4 shows just the molecular catalyst. Key peaks are noted on each. The molecular catalyst is indicated in blue, while the loaded catalyst is indicated in pink.



**Figure 3.** NibpyCOOH and NibpyCOOH[A300] FTIR comparison

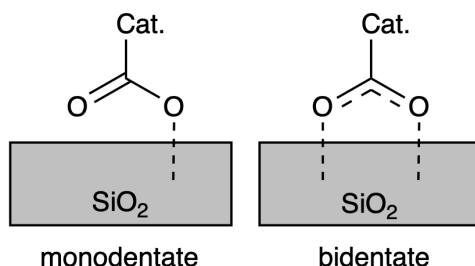


**Figure 4.** NibpyCOOH[A300] FTIR detailed view

The molecular catalyst has a strong C=O stretching peak at  $1730\text{ cm}^{-1}$  which, upon binding to A300, is absent. This is a strong indicator of carboxylate to metal oxide binding.<sup>6,9,10</sup> There is also a broad O-H peak around  $3203\text{ cm}^{-1}$  present for the molecule catalyst. Upon binding to  $\text{SiO}_2$ , it is shifted to  $3345\text{ cm}^{-1}$  and the intensity is significantly reduced. Most minor spectral features present in the NibpyCOOH spectra are reduced to transmittance values of greater than 98%. The characteristic bipyridine peaks at 1404, 1158, and  $1616\text{ cm}^{-1}$  still remain identifiable in the loaded catalyst spectra, slightly down-shifted, at 1400, 1551, and  $1614\text{ cm}^{-1}$ , respectively. The endurance of the bipyridine peaks indicates that loading the catalyst on A300 does not affect overall structure.

The conformation of the carboxylic acid anchor to  $\text{SiO}_2$  may have a monodentate or bridging bidentate conformation as shown in Figure 5. The bidentate binding conformation has been reported previously as the preferred binding mode for carboxylate anchoring groups bonded to  $\text{TiO}_2$  and is indicated by the disappearance of the C=O peak upon binding to the metal oxide.<sup>9,10</sup>

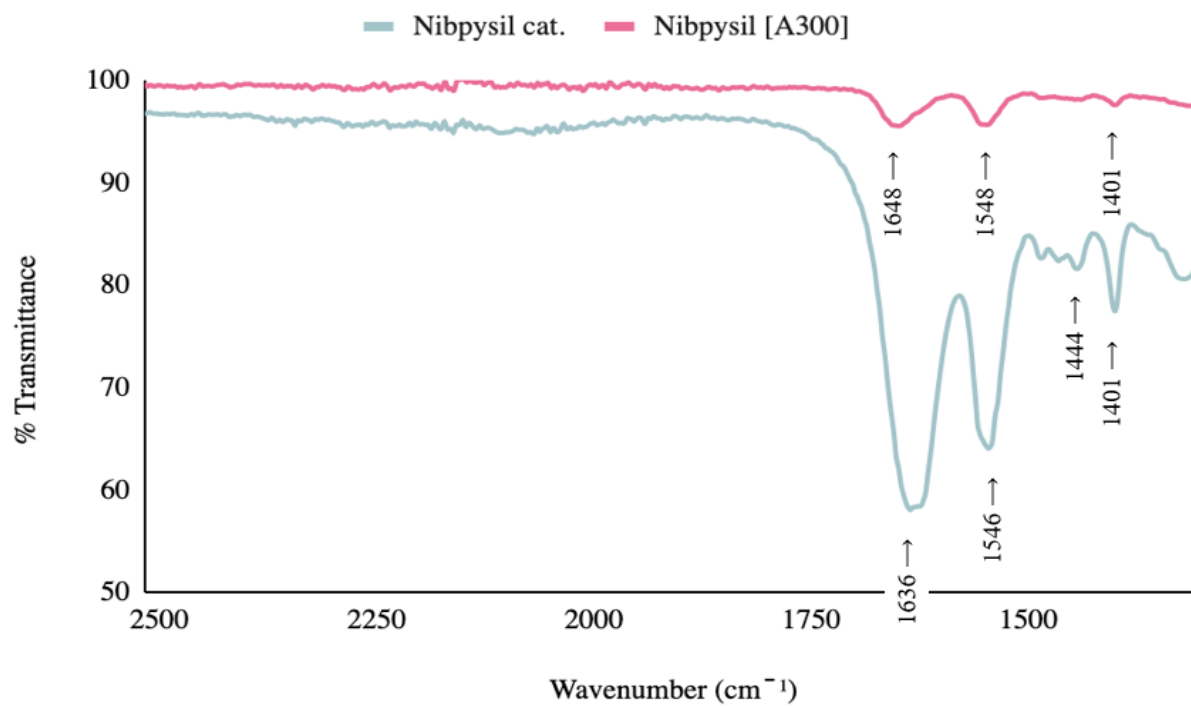




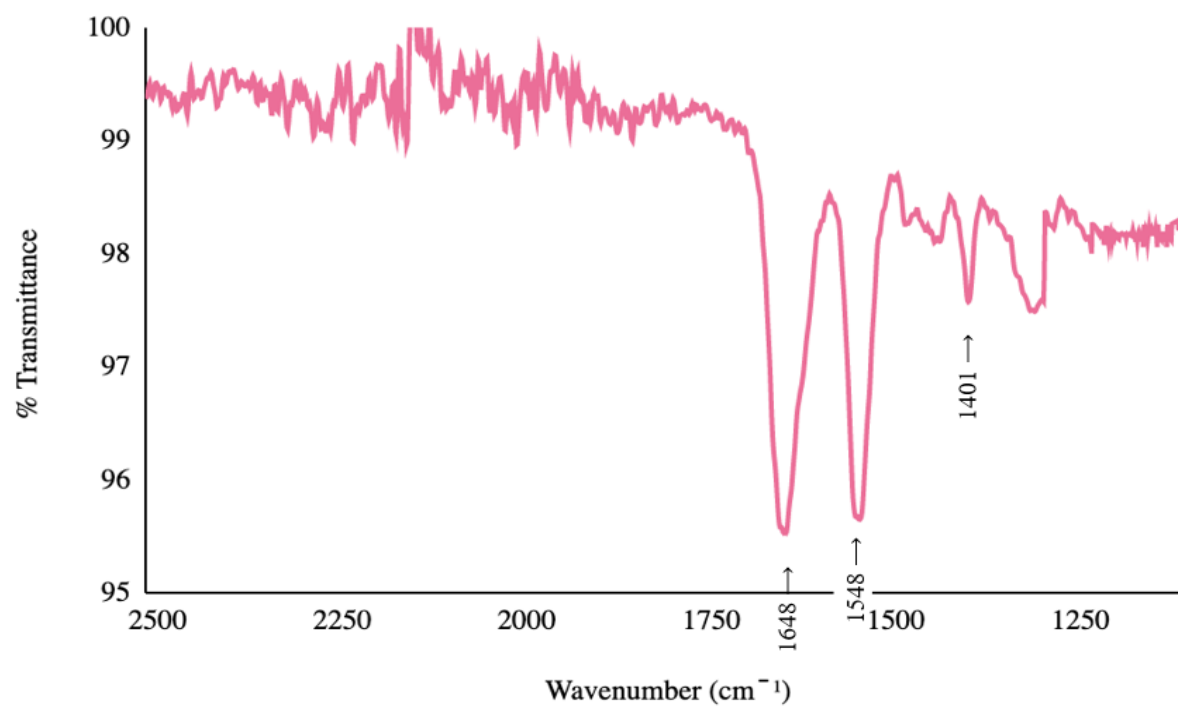
**Figure 5.** Carboxylate anchoring group binding configuration

However, a previous density functional theory (DFT) simulation of carboxylic acid groups bonded to amorphous silica oxide only predicted monodentate hydrogen bonding schemes.<sup>2</sup> Furthermore, the coordination of a surface silanol to the carbonyl oxygen was determined to not have a very strong interaction, which would be necessary for a bidentate binding conformation. Deeper investigations into the interaction between the carboxylic acid and the  $\text{SiO}_2$  surface are required to make a conclusion.

The FTIR spectra of the homogeneous Nibpysil catalyst and the Nibpysil[A300] catalyst are shown in Figure 6 while only the Nibpysil[A300] spectra is shown in Figure 7. Key peaks are noted. The molecular catalyst is indicated in blue, while the loaded catalyst is indicated in pink.



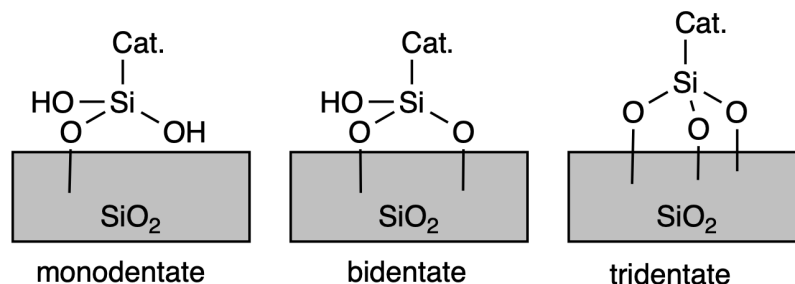
**Figure 6.** Nibpysil and Nibpysil[A300] FTIR comparison



**Figure 7.** Nibpysil[A300] FTIR detail view

The molecular catalyst has three strong bipyridine peaks at 1401, 1546, and 1636  $\text{cm}^{-1}$ . Upon binding to A300, these peaks are significantly reduced in intensity to around 95 percent transmittance but still remain identifiable; they appear at 1401, 1448, and 1648  $\text{cm}^{-1}$ . Two of the peaks do not experience a shift but one is shifted slightly upwards. The continued presence of these peaks indicates that binding to A300 does not significantly affect the bipyridine structure of the catalyst. Nibpysil also has a peak at 1444  $\text{cm}^{-1}$  which is related to the  $\text{CH}_2$  of the caged silatrane structure. This peak is not present in the Nibpysil[A300] spectra which indicates the deprotection of the cage structure, a key indication of surface binding.<sup>9,10</sup> Other characteristic silatrane peaks<sup>9,10</sup> occur at wavenumbers below 1300  $\text{cm}^{-1}$  which were not considered in this characterization. However, it can still be confirmed with reasonable certainty that the silatrane ligands have bonded to the surface without the additional confirmation of those peaks below 1300  $\text{cm}^{-1}$ .

The tripodal caged structure of the silatrane ligand is thought to lend itself to a bidentate or even tridentate binding conformation to  $\text{SiO}_2$ , as shown in Figure 8. Previous work by Materna et. al. with silatranes bound to  $\text{TiO}_2$  has indicated the bidentate conformation may be the most common,<sup>9</sup> and most stable<sup>10</sup>, even though silatrane is often depicted as binding triply. In a bidentate binding conformation it is possible for intermolecular condensation to occur between the free hydroxyl group and an adjacent silatrane center.<sup>10</sup> It is unknown if this cross-linking occurs in Nibpysil[A300].



**Figure 8.** Silatrane anchoring group binding configurations

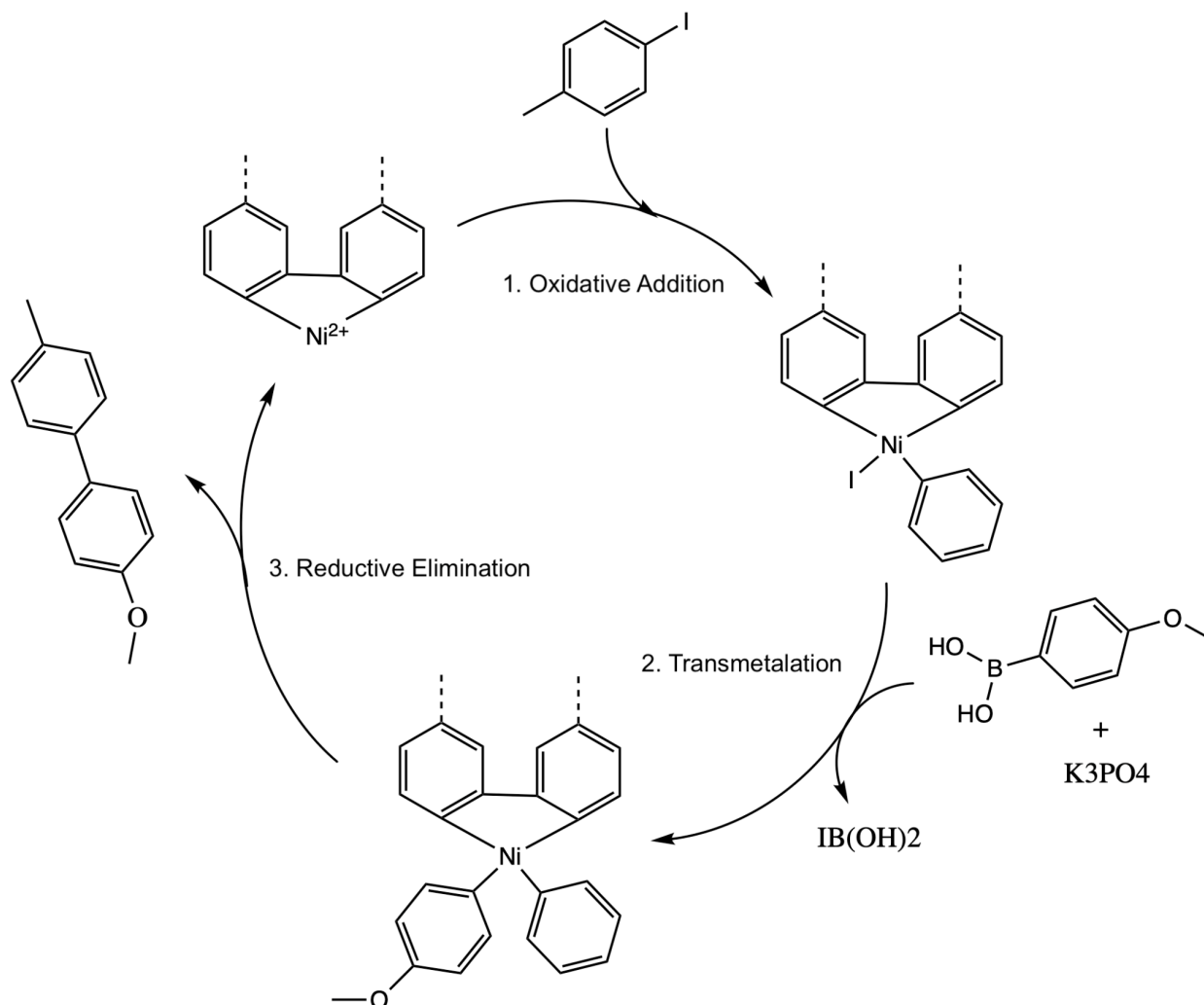
ICP-MS analysis indicates that NibpyCOOH[A300] contains 0.10 weight % Ni loading, which is approximately  $7.77 \times 10^{-9}$  mol of catalyst per  $\text{m}^2$  of A300.<sup>8</sup> The loading of the catalyst onto A300 does not require any increase in temperature nor any reductive/oxidative processes; it is therefore assumed that the Ni detected in ICP-MS is wholly due to the immobilized NibpyCOOH catalyst. A comparable nickel polypyridyl catalyst with a singular carboxylate binding moiety has shown four to five times the amount of wt% Ni compared to bpyCOOH[A300].<sup>1,6</sup> However, neither of those catalysts have comparable loading to the 2.1 wt% Pd achieved with a polypyridyl palladium catalyst.<sup>2</sup> This indicates there is still a gap in binding efficacy to be bridged between the nickel and palladium complexes. The use of an anchoring group with a stronger attachment to the metal oxide could overcome this deficit.

The ICP-MS analysis of Nibpysil[A300] indicates there is 2.03 weight% Ni loading, which is around  $1.6 \times 10^{-7}$  mol of catalyst per  $\text{m}^2$  of A300.<sup>8</sup> Compared to the carboxylate anchored catalyst, the silatrane catalyst has more than twenty times the amount of catalyst

bonded to the surface. Loading levels of this magnitude are comparable to those reported by DeLucia et. al. for their palladium terpyridine carboxylic acid catalyst on A300 SiO<sub>2</sub>.<sup>2</sup> It has been reported that silatranes will spontaneously hydrolyze to form Si-O linkages when in contact with a metal oxide surface,<sup>9</sup> which could lead to increased catalyst absorption on the metal oxide. The covalent linkage between the anchoring group and the metal oxide is also stronger than the hydrogen bond between the metal oxide for carboxylates.

#### Catalytic Performance

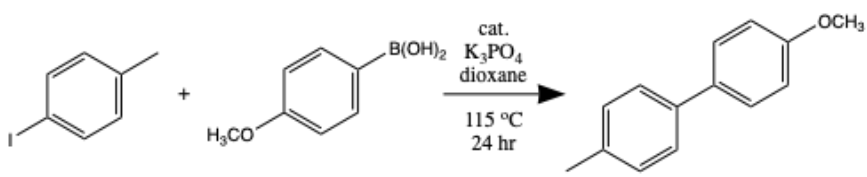
To illustrate the benefits of the hybrid molecular catalysts, a standard suzuki-miyaura coupling between iodotoluene and methoxyphenylboronic acid was chosen to be the benchmark reaction. The reaction was run in dioxane and under conditions (115°C, 24 hr, K<sub>3</sub>PO<sub>4</sub> base) which have been previously determined to be optimal for a comparable nickel catalyst.<sup>1,6</sup> The addition of the base is necessary for boronic acid activation in the transmetalation step of the catalyst cycle. Figure 9 shows the hypothesized catalytic cycle for both NibpyCOOH[A300] and Nibpysil[A300] based on the current mechanistic understanding of Suzuki-Miyaura reactions.<sup>4</sup> The limiting reagent in this reaction is iodotoluene. The rate limiting step is the transmetallation.<sup>4</sup>



**Figure 9.** Proposed Suzuki-Miyaura Cross-coupling mechanism using the Ni catalysts

The use of the molecular catalysts NibpyCOOH and Nibpysil were both unsuccessful in producing any product. This is unsurprising at such low catalyst amounts. The hybrid catalysts were both able to produce product. NibpyCOOH[A300] was able to achieve yields of up to 10% while Nibpysil[A300] produced yields of up to 50%. Percent yields are based on the limit reagent and are isolated yields. This data is summarized in Table I.

**Table I.** Catalytic Suzuki-Miyaura Cross-Coupling Reaction Yields

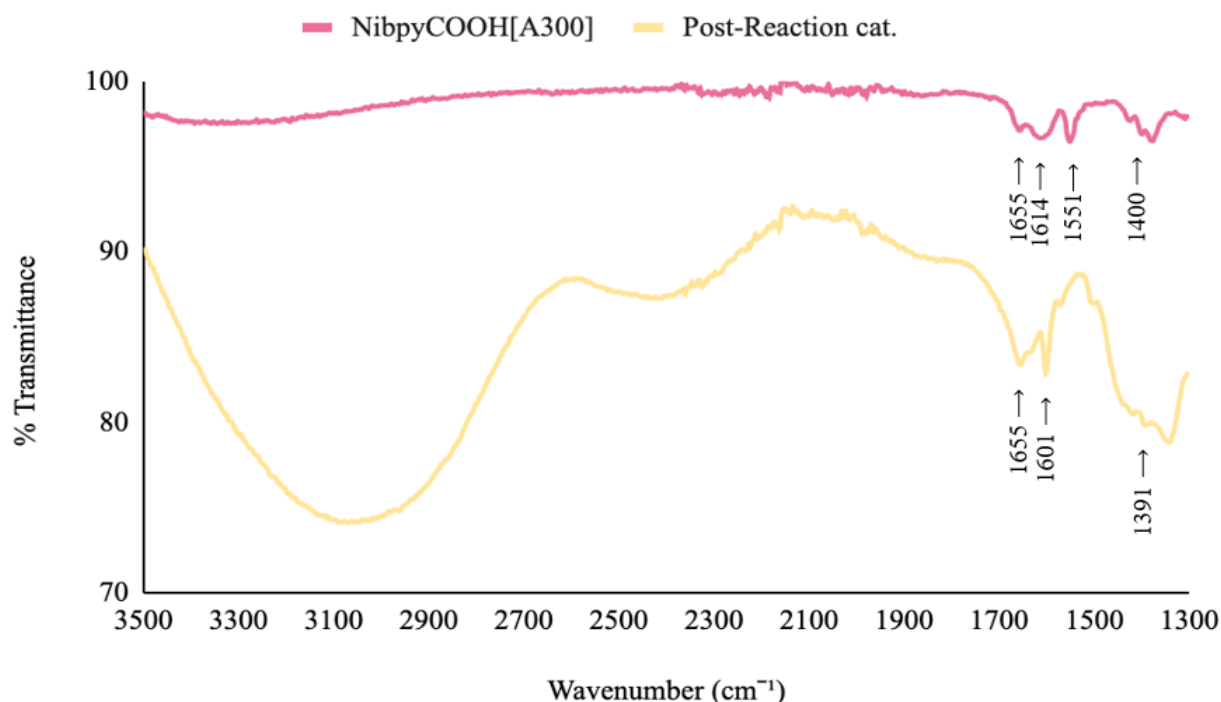


Catalyst	Yield
NibpyCOOH[A300]	10%
Nibpysil[A300]	50%
NibpyCOOH	0%
Nibpysil	0%

While yields are not up to the current standards for catalysts (>90%), these cross-coupling experiments are designed to serve primarily as a proof-of-concept that the hybridized catalysts are able to catalyze a reaction that their molecular counterparts are unable to at equivalent amounts of catalyst. Furthermore, while reaction conditions were based off of previously optimal conditions, no attempts were made to optimize this particular system. Regardless, a 50% yield on a non-optimized reaction is a promising starting place for the Nibpysil[A300] catalyst.

#### Post-Reaction Characterization

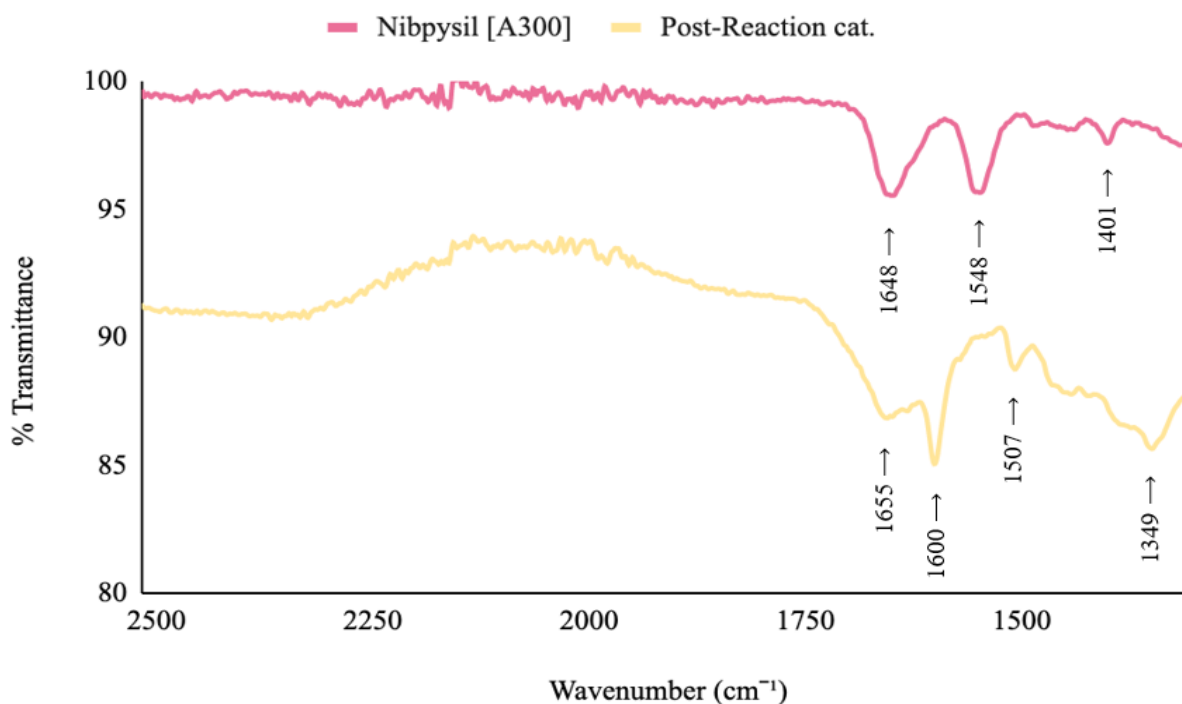
Of particular interest is how well the catalyst remains bonded to the SiO<sub>2</sub> support after catalytic use. Catalyst leaching from the surface has been a paramount issue in other metal oxide supported complexes.<sup>1-3,6,9,20</sup> FTIR scans were taken of each catalyst after being separated from a completed reaction cycle to determine how well the catalyst remained bonded to the silica. The pre- and post-reaction catalyst spectra are shown in Figures 10 and 11. The pre-reaction catalyst is indicated in pink, while the post-reaction catalyst is indicated in yellow; key peaks are noted.



**Figure 10.** Pre- and Post-Reaction NibpyCOOH[A300] FTIR Spectra

After one reaction, there is an obvious change in the binding of the carboxylate groups to the  $\text{SiO}_2$ , which can be attributed to some catalyst leaching occurring. There is a return of the general pattern exhibited by the molecular catalyst which can be seen in the increased transmission of the broad -OH peak at around  $3000 - 3200 \text{ cm}^{-1}$ . There is a general decrease in transmission by about 10 - 15% which suggests more ligand and catalyst are more exposed. The location of the bipyridine peaks at  $1601$  and  $1391 \text{ cm}^{-1}$  post-reaction appear downshifted even further than the pre-reaction, making them around  $15 \text{ cm}^{-1}$  lower than their molecular catalyst counterparts. The other bipyridine peak at  $1551 \text{ cm}^{-1}$  disappears in the post-reaction spectra. There is also the emergence of a stronger peak at  $1655 \text{ cm}^{-1}$  which was not present in the molecular catalyst but is seen in the loaded catalyst. These changes could be due to a number of things: leftover reaction materials may be contaminating the sample or catalyst degradation could have occurred either during the reaction or in the storage time between reaction completion and analysis. In the future, more thorough post-reaction separation techniques and prompt post-reaction analysis to minimize storage time could be employed to combat some of those effects and allow for a direct examination of catalyst degradation related to the cross-coupling reaction. Despite these concerns, the  $\text{C=O}$  peak at  $1730 \text{ cm}^{-1}$  does not return, which means at least some complex is still bound to  $\text{SiO}_2$  despite evidence of leaching. Catalyst that completely dissociated from the  $\text{SiO}_2$  during the Suzuki-Miyaura reaction would have been separated out in centrifugation and would not be detected by FTIR. Another ICP-MS analysis is necessary to

quantify the amount of NibpyCOOH still bonded to the surface, but qualitatively it can be concluded there is still NibpyCOOH bound to the A300.



**Figure 11.** Pre- and Post-Reaction Nibpysil[A300] FTIR Spectra

As with the carboxylate catalyst, there is also a general increase in transmission. The characteristic bipyridine peaks at 1548 and 1648 cm<sup>-1</sup> which were both present in the Nibpysil[A300] spectra prior to the reaction were more defined and appeared at 1600 and 1655 cm<sup>-1</sup>. In the post-reaction spectra, a new broad peak at 1349 cm<sup>-1</sup> can be seen, likely obscuring the signal of any bipyridine peak that would be seen around 1400 cm<sup>-1</sup>. An additional peak at 1507 cm<sup>-1</sup> can also be seen. There is no return of the peak at 1452 cm<sup>-1</sup> which would indicate the reformation of the silatrane cage. Due to the method by which the siloxane bond to SiO<sub>2</sub> forms, it would be extremely unlikely to see the re-emergence of this peak because the triethanolamine group is completely dissociated from the silatrane molecule. It has been reported that the triethanolamine group binds to some degree to the SiO<sub>2</sub> surface itself.<sup>10</sup> This might contribute to some of the irregularities noted above. Additional characterizations, like an ICP-MS analysis, would be beneficial to further examine silatrane stability post-reaction.

## DISCUSSION

The results using the NibpyCOOH[A300] catalyst were surprising. The two carboxylic acid moieties on the NibpyCOOH complex should, hypothetically, lead to a better attachment and higher loading when compared to a catalyst with single carboxylic acid moiety like

NitpybenzCOOH (Key et. al.) — and yet the opposite seems to be true. As for why this is happening, it is hypothesized that only one of the carboxylic acid groups is able to successfully bond to the SiO<sub>2</sub>, leaving the other group free. Amorphous silica dioxide is a non-ordered metal oxide; it is possible the second carboxylic acid moiety might not have an available binding site near enough to bind. This theory has been substantiated by computational work done by DeLucia et. al. where a density functional theory (DFT) model of amorphous SiO<sub>2</sub> was analyzed to determine the distribution of favorable binding sites.<sup>2</sup> They found the SiO<sub>2</sub> had hot spots of favorable interactions between the surface and a carboxylate and conversely had cold spots where it would be unfavorable to bind.<sup>2</sup> The inability to find two favorable surface binding sites could explain why there is relatively low nickel loading compared to other nickel catalysts and in turn why there is less catalytic activity. To further compound the issue, due to the unsymmetrical axis of binding, the strain from the unbound carboxylate would be greater than that experienced by a catalyst bound by a single carboxylate group symmetrically. This might be a contributor to catalyst instability and help explain the low catalyst loading for NibpyCOOH[A300]. If the catalyst does remain bound to the surface, the free carboxylate could also be interacting with other components in the reaction mixture, leading to decreased yields.

The lackluster performance of the NibpyCOOOH[A300] catalyst serves to further highlight the success of the Nibpysil[A300] complex. The covalently bound complex exhibited twenty times better catalyst loading and was able to produce five times the yields in the cross-coupling reaction than its carboxylate counterpart. The improved loading and reactivity can only be attributed to the binding group as the catalysts are identical otherwise. While both catalysts did suffer from some desorption post-reaction, Nibpysil[A300] displayed better resistance to desorption than NibpyCOOH[A300]. Whether the observed alternation in surface binding is directly due to wear-and-tear from catalyzing a reaction or caused partially by other factors it is not yet known. Ideally, prolonged storage of the catalyst (1-4 months) would not degrade its integrity but that cannot be ruled out. The increased resistance to desorption from the silatrane anchoring group can be attributed to the strength of the siloxane covalent bonds formed between the group and the surface. The success of the silatrane binding group on SiO<sub>2</sub> opens the door to further investigations into the scope of reactivity which is afforded by a covalent bond to the metal oxide support.

## CONCLUSION

Two molecular/heterogenous hybrid nickel catalysts for Suzuki-Miyaura cross-coupling have been synthesized and characterized. These catalysts utilize earth-abundant nickel and a solid support of inexpensive amorphous silicon dioxide. Two different binding motifs are presented for comparison: carboxylate and silatrane. Both the carboxylate and silatrane catalysts were successfully bound to the A300 SiO<sub>2</sub> surface using non-intensive synthetic techniques. Nibpysil[A300] exhibited catalyst loading on par with current palladium catalysts on SiO<sub>2</sub> and over twenty times the loading seen with the NibpyCOOH[A300] complex. Despite the



carboxylate catalyst suffering from unexpectedly poor binding to the SiO<sub>2</sub> surface, it still shows enhanced reactivity compared to its molecular counterpart. The catalysts were both successful in catalyzing a Suzuki-Miyaura cross-coupling reaction for which their molecular counterparts are not active. The silatrane catalyst was able to produce yields of up to 50% for an unoptimized reaction scheme, while the carboxylate was able to produce yields of 10%. Post-reaction analysis found the silatrane catalyst to be more resistant to catalyst leaching as well. The better performance of the silatrane catalyst in all key areas demonstrates the crucial role the anchoring group plays in catalyst stability and activity.

The next steps of this project are to optimize the Suzuki-Miyaura cross-coupling reaction conditions with hopes to improve yields up to industrial standards, particularly with the silatrane catalyst. Beyond that, a key feature of the hybrid catalyst scheme is catalyst reusability, which was not explored in this work. Additionally, further work is already being undertaken to explore the possibility of functionalizing the SiO<sub>2</sub> surface using an acid pre-treatment to create more favorable binding sites for catalysts. There has also been preliminary success in stabilizing the carboxylate catalyst using atomic layer deposition which has shown previous success in improving the longevity of a similar nickel carboxylate catalyst.<sup>6</sup>

The impacts of this project reach far beyond organic catalysis. The shift to alternative energy relies heavily on fuel cells and dye sensitized solar cells, both of which operate using a catalyst bonded to a metal oxide.<sup>1,3,7-10</sup> This style of catalyst have also been utilized to break down biomass into usable components like energy dense liquid fuels.<sup>3</sup> Improvements in immobilized catalysts will have effects in these key alternative energy areas as well as improving industrial-scale green catalysis. The catalysts presented in this comparative study are a step forward in the progress to create a more sustainable, highly efficient, and reusable catalyst.

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