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Polymer Supported Ni(salen) Catalysts and Ni(II)-salen zeolite Y as Catalysts for Heterogeneous Electrohydrocyclization Reactions

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Polymer supported Ni(salen) and zeolite encapsulated Ni(salen) were synthesized and investigated as electrocatalysis agents in the electrohydrocyclization reaction using a reticulated vitreous carbon electrode in dimethylformamide. Cyclic voltammetry was used to establish the reduction potentials of the heterogeneous catalysts using a modified glassy carbon electrode. Additionally, the corresponding homogeneous catalysts were also synthesized and studied. Bulk electrolysis experiments revealed that the heterogeneous catalysts were superior to the homogeneous catalysts with both shorter reaction times and cyclized product yields.

Keywords: electrocatalysis; organic electrochemistry; zeolite; nickel salen

1. INTRODUCTION

Electrosynthesis is a technique that can solve the problem of making complex organic molecules using green chemistry methodology. This is due to the idea that electrochemical organic synthesis uses electrical current as a reagent, replacing toxic or dangerous oxidizing or reducing agents. This is done by flowing an electrical current through a reaction which can activate a molecule through the addition or removal of an electron. [1] Electrochemistry can be thought of as a tool for constructing new bonds by reversing functional group polarity. This allows one to couple two electrophiles together or two nucleophiles together in ways in which it would be otherwise impossible to accomplish. The electrohydrocyclization (EHC) is a useful reaction that creates a carbocyclic ring that can be used in the synthesis of natural products. [2]

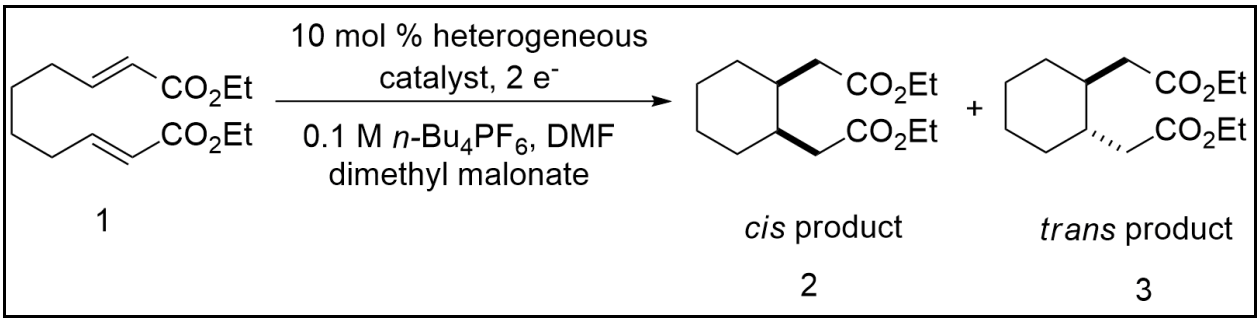
The EHC reaction, along with other electrochemistry reactions, can be done through a direct or indirect pathway. [3] The indirect pathway uses an electrocatalyst, such as metal-salen compounds, to be the source that transfers electrons to the substrate rather than directly from the cathode. [4,5] Previous

research in our group has studied the use of various transition metals such as cobalt, zinc, and nickel as the metal-salens. The biggest advantage of mediated (indirect) electrochemical reactions over direct electrochemical reactions is the use of a less negative potential than necessary in the direct substrate reduction. Running the reaction at a less negative voltage allows for the use of less electricity and in larger, industrial scale, reactions this can potentially be very cost efficient. However, the advantage of the more positive reaction potential is most important in complicated molecules with many different functional groups. Operating the reaction at a less negative potential allows the reduction of one part of the molecule while leaving other functional groups untouched, avoiding the need for cost and labor intensive protecting groups. [6] Only a catalytic amount of mediator is needed, thus resulting in reduced amount of chemical waste.

Polymer supported electrocatalysts have been used previously in organic reactions. One example, by Yoshida, is using a cross-linked poly-4-vinylpyridine as a heterogeneous catalyst. The heterogeneous catalyst was then successfully used in the electrochemical epoxidation of alkenes. [7]

Combining Ni-salen and zeolites has excellent literature precedent. [8] One example is the use of Co(salen) zeolite in a reaction in which phenylacetic acid was the major product from a mixture of benzyl chloride and carbon dioxide. [9] The homogeneous Co(salen) reaction and analogous heterogeneous Co(salen) zeolite reactions produced the same product with the same yield. However, the catalyst turnover was vastly improved with the Co(salen) zeolite catalyst. The efficiency of a catalyst is measured by its turnover, which is measured as moles of synthetic product per mole of Co-zeolite mediator. For the Co(salen) reaction, the ratio was 34, and for the Co(salen) zeolite reaction the ratio was 8 x 10^4 (or 2300 times the Co(salen) reaction). It was concluded that the improved catalyst turnover arose from the features of the zeolite framework. The frame of the zeolite allows a substrate to "dock" into the supercage of the zeolite and the reaction will occur inside a small confined space. In 2015, it was shown that Ni(salen) zeolite was used successfully in the electrooxidation of hydrazine. [10]

In this paper, we describe our efforts to synthesize several heterogeneous Ni(salen) catalysts, characterize the catalysts, and the use of the catalysts in the EHC reaction. Polymer supported Ni(salen) catalysts and Ni(salen) zeolite Y catalyst were specifically studied. The overall EHC reaction is shown in shown in Scheme 1.



Scheme 1. Mediated Electrohydrocyclization (EHC) reaction using heterogeneous Ni(salen) catalyst

Using a solid supported electrocatalyst provides an improved alternative to traditional homogeneous reactions. The main advantage this type of heterogeneous reaction would provide over

an analogous homogeneous reaction is product purification. After the reaction is complete, the solid mediator is filtered out of the reaction solution, washed and reused multiple times. [11] The soluble product is then left in the solvent for further isolation. [12,13] Two approaches were explored: anchoring the electrocatalyst to a polymer solid phase Merrifield resin and encapsulation of the electrocatalyst in a zeolite.

The three polymer solid phase Merrifield resin Ni(salen) catalysts that were synthesized are shown in Figure 1.

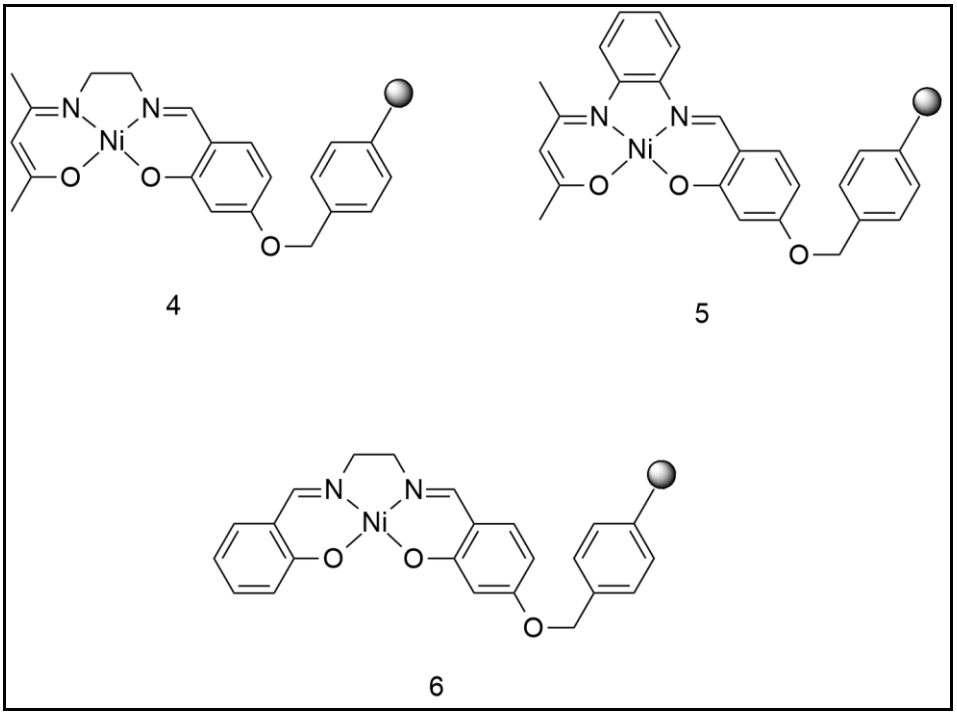


Figure 1. Solid Phase Merrifield resin Ni(salen) catalysts

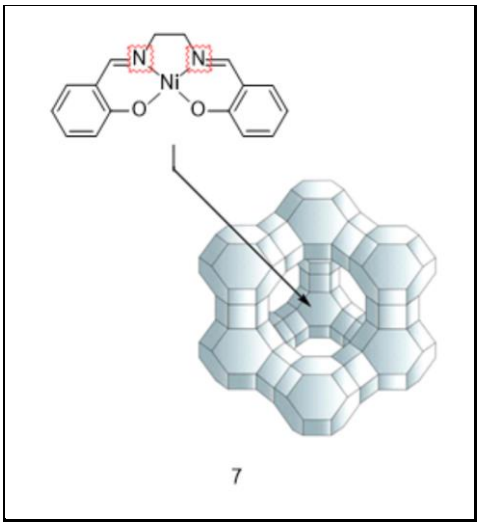


Figure 2. Ni(salen) zeolite Y catalyst

In addition to the polymer supported catalysts, we also studied a Ni(salen) zeolite Y catalyst 7 shown in Figure 2. This is a heterogeneous catalyst that has a Ni(salen) encapsulated into the crystalline lattice of a zeolite Y. It is the microporous property of zeolites that allows them to act as a catalyst in reactions. The framework of a zeolite allows the substrate to enter the cage, react with the mediator inside, then exit the super cage as the final product. For these reactions, Ni(salen) Zeolite Y was desired to be used as a heterogeneous catalyst in the EHC reaction.

Cyclic voltammetry (CV) was used to determine the necessary voltage potential needed for catalyst reduction and mediated EHC. The CV results were then used to set the potential for the mediated EHC reactions. We then performed bulk electrolysis (BE) reactions with each catalyst shown in Scheme 1. Yield and selectivity for each BE reaction was measured by GC/MS.

There were a total of eight catalysts that were synthesized and studied in the BE reactions. We studied four homogeneous mediators (Figure 3) and four heterogeneous mediators (Figures 1 and 2). The homogeneous catalysts were studied in order to compare the overall effectiveness of the heterogeneous catalysts to a typical solution phase reaction.

The electrohydrocyclization reaction has been used to make a sigma bond between two electrophilic carbons. As mentioned earlier, the reaction has been applied to the natural product 1-sterpurene as the key step. [2] 1-Sterpurene is a metabolite of the fungus *Stereum purpureum*, the cause of silver leaf disease that commonly affects fruit trees.

Another study in electrohydrocyclization reactions centered on investigating the effect of alkoxy substituents connected to the carbons of the forming ring. [14] Elimination or retention products can be formed preferentially. The product type is dictated by the type of oxygen functional group connected to the cyclization tether. If the functional group was a hydroxyl, the preferred product was elimination. If the functional group was an ether, such as a silyl ether, the preferred product was retention of the functional group.

Electrohydrocyclization reactions can also be performed using electrogenerated Sm(II), electrogenerated Yb(II) and magnesium ions that are generated at a sacrificial magnesium anode. [15] These studies showed that the diastereoselectivity of the cyclization reactions can be affected through a coordination effect of the metal ions with the Lewis basic reacting functional groups.

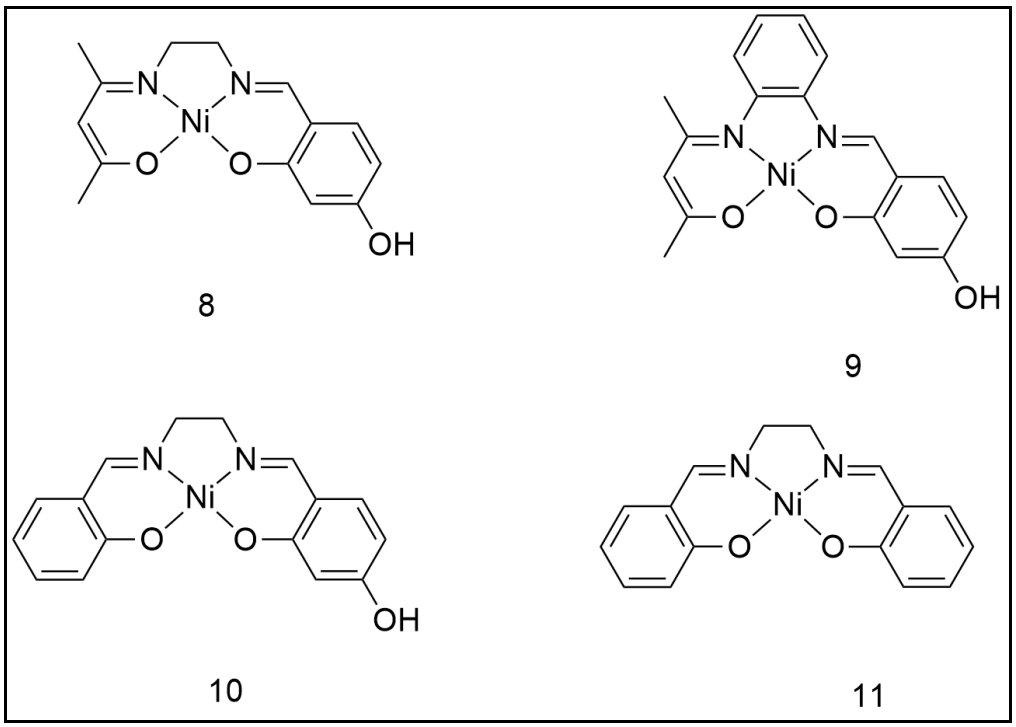


Figure 3. Homogeneous Ni(salen) type catalysts

2. EXPERIMENTAL

2.1. NMR

^{1}H NMR spectra were performed using a Bruker Avance III 500 NMR at ambient temperature. All chemical shifts are reported in ppm relative to TMS (0.00 ppm) or $CDCl_3$ (7.27ppm).

2.2. Electrochemistry

A BASi C-3 Cell Stand and an Electrochemical Analyzer/Workstation, model 600D, from CH Instruments were used for all electrochemical experiments (CV and BE).

2.3. Cyclic Voltammetry (CV) General Procedure

A standard single compartment glass cell vial was used for CV experiments. The working electrode was a glassy carbon electrode and a platinum electrode was used as the auxiliary electrode. The potentials were recorded against an Ag/AgCl reference electrode. This electrode has a potential of -0.045 V versus the saturated calomel electrode (SCE) at 25 ^{o}C. The voltage scan rate (VSR) was varied between 0.1 V/s and 0.2 V/s. All three electrodes were placed in solution of the mediator and 0.1 M NBu_4PF_6 in 5 mL of anhydrous dimethylformamide (DMF). The concentration of mediator was 5 mM for the heterogeneous CVs. The heterogeneous mediators were plated directly onto the surface of the

glass carbon electrode. Before the experiment, the solution was deoxygenated for 10 minutes by bubbling nitrogen in the solution and the cell contents were maintained under a nitrogen atmosphere during the experiment. CV was performed using a computer controlled potentiostat electroanalytical system. The data was collected and exported to MS Excel.

2.4. Bulk Electrolysis (BE) General Procedure

All reactions were carried out in a two compartment BE glass cell. The working electrode was a reticulated vitreous carbon (RVC) electrode. A coiled platinum wire within a fritted glass isolation chamber was used as the auxiliary electrode. The reaction was performed against an Ag/AgCl reference electrode. A 0.1 M solution of NBu_4PF_6 in 85 mL of DMF was poured into the cell containing all three electrodes. 75 mg of the EHC substrate, 2 equivalents of dimethyl malonate, and 10 mol % catalyst was added to the solution for each reaction. The solution was deoxygenated for 20 minutes by bubbling nitrogen in the solution and the cell contents were maintained under a nitrogen atmosphere during the experiment. The solution was stirred with a medium stir bar throughout the entire experiment. The reaction was monitored by GC/MS. Once complete, the catholyte solution was transferred to an Erlenmeyer flask. The catholyte solution was worked up by liquid-liquid extraction with 40 mL of water and extracted with diethyl ether (40 mL x 3). The combined organic layers were washed with brine (60 mL x 3) and dried over $MgSO_4$. The solvent was removed by rotary evaporation to give the crude BE product. The crude product underwent column chromatography with 50% hexanes/50% ethyl acetate solvent system. The collected fractions containing the cyclized product were combined and the solvents were removed by rotary evaporation to give the purified product.

2.5. Infrared Spectroscopy (IR)

A Thermo Scientific Nicolet iS50 – FT-IR Spectrometer with ATR accessory was used for all IR measurements. Each IR spectra was collected from 16 scans. For the zeolites, each IR spectra was collected from 100 scans.

2.6. GC/MS (Gas Chromatography/Mass Spectrometry)

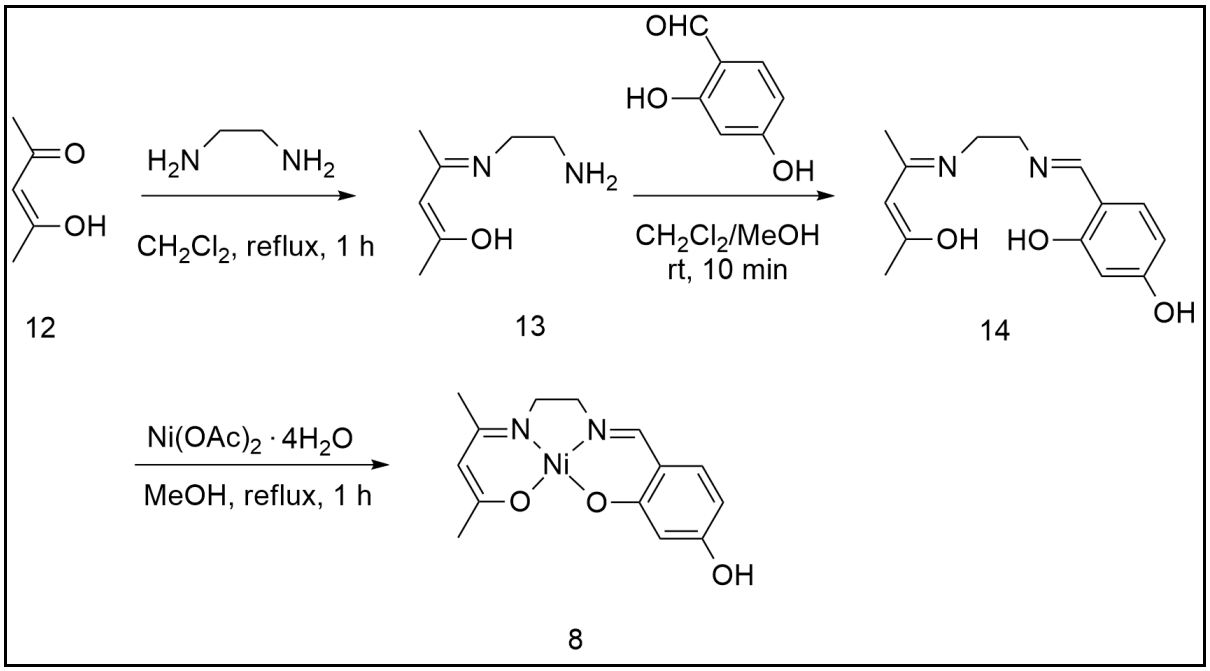
An Agilent Technologies 7890A GC system containing an Agilent J&W GC Column (stationary phase: HP5-MS, 30 m x 0.250 mm x 0.25 m) with a 5975 inert XL Ei/CI MSD with Triple Axis Detector was used to obtain all GC/MS data. The method used for all runs was 100 ^{o}C for 1 min, 45 ^{o}C/ min to 190 ^{o}C, 10 ^{o}C/min to 230 ^{o}C, hold for 1 min.

2.7. Graphite Furnace Atomic Absorption (GFAA)

A Perkin Elmer AAnalyst 800 high-performance atomic absorption spectrometer with WinLab32 for AA software was used to obtain all GFAA data. All samples were analyzed in the graphite furnace

mode using a Transversely Heated Graphite Furnace (THGF) with longitudinal Zeeman-effect background corrector. A nickel lamp at a wavelength of 232 nm was used for the detection of Ni in samples. In addition, an injection temperature of 20 ºC and a final furnace temperature of 2450 ºC was used.

2.8. Preparation of catalysts

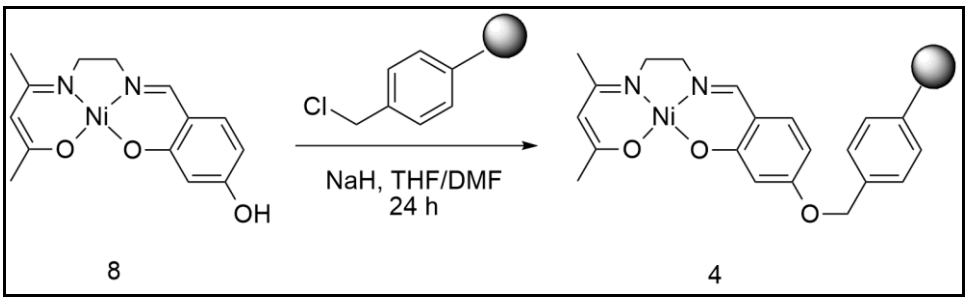


Scheme 2. Synthesis of Catalyst **8**

Eight catalysts (4 homogeneous and 4 heterogeneous) were synthesized to be used and studied in the bulk electrolysis reactions. The synthesis of catalyst 8 is described in Scheme 2. This catalyst was synthesized according to a procedure described by Styring. [16]

[9-(2',4'-Dihydroxyphenyl)-5,8-Diaza-4-Methyl-Nona-2,4,8-Trienato](2-)]Nickel(II) (8): A solution of 2,4-pentadione (1.06 g, 10.5 mmol) in dichloromethane (8 mL) was added dropwise to a stirred solution of 1,2-diaminoethane (1.22 g, 20.1 mmol) in dichloromethane (8 mL). The solution was heated at reflux for 1 hour. The solution was evaporated to remove excess 1,2-diaminoethane. 2,4-dihydroxybenzaldhyde (1.42 g, 10.3 mmol) was dissolved in 14 mL of solvent (50/50 methanol and dichloromethane). The orange colored 2,4-dihydroxybenzaldhyde solution was added dropwise to the liquid product from the first reaction after being dissolved in dichloromethane (16 mL). The resulting solution was stirred at room temp for 10 minutes. Nickel acetate tetrahydrate (2.50 g, 10.0 mmol) was dissolved in methanol (30 mL) and added to the reaction from the previous step. The solution was then heated at reflux for 1 hour, during which a precipitate formed. The solution was cooled to room temperature, followed by cooling in an ice bath for 15 minutes. The solids were then collected by vacuum filtration and recrystallized in methanol. After recrystallization 0.7770 g of compound **8** were collected (24.5 % yield).

^{1}H NMR: 9.723 (s, 1H), 7.629 (s, 1H), 7.066 (d, 1H), 6.054 (m, 3H), 3.340 (m, 10 H).
CV: E_{pc} = -1.7 V.
IR (neat): ~3200 (broad), 1606.55, 1542.91, 1448.86, 1227.35 cm^{-1}.



Scheme 3. Synthesis of heterogeneous catalyst **4**

Resin Bound [9-(2'-Hydroxyphenyl)-5,8-Diaza-4-Methyl-Nona-2,4,8-Trienato](2-)] Nickel(II) (4): Merrifield resin (2.59 g, 1.0 g resin per 0.8 mmol Cl^-) was preswelled in dimethylformamide (20 mL) for 20 min. Catalyst 8 (657 mg, 2.07 mmol) was dissolved into a solution of dry dimethylformamide (20 mL) and THF (10 mL). The solution was added dropwise to 0.10 g NaH (60 % dispersion in oil). The resulting mixture was stirred for 10 min under nitrogen gas. The preswelled Merrifield resin was added to the solution and stirred under the presence of nitrogen for 24 hours. The resin was collected by vacuum filtration and washed with water (3 x 50 mL), methanol (20 mL), and dichloromethane (3 x 50 mL). 2.49 g of Catalyst 4 was collected.

CV: E_{pc} = -2.4 V.
IR (neat): 3024.73, 2918.96, 1601.70, 1492.55, 1451.63 cm^{-1}.
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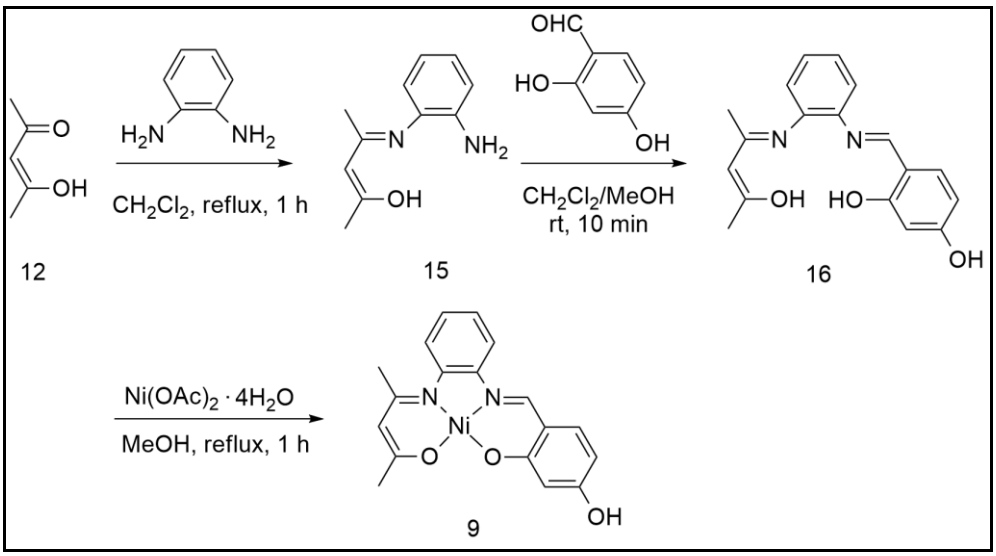


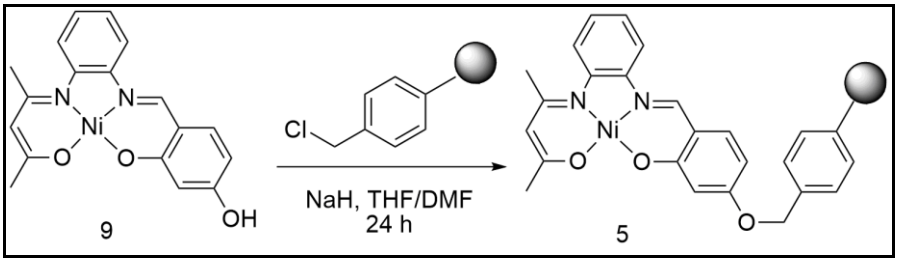
Scheme 4. Synthesis of Catalyst 9

[9-(2',4'-Dihydroxyphenyl)-5,12-Diaza-4-Methyl-Tridec-2,4,6,8,10,12-Hexeneato(2-)] Nickel(II) (9): A solution of 2,4-pentadione (1.06 g, 10.5 mmol) in dichloromethane (8 mL) was added dropwise to a stirred solution of *o*-phenylenediamine (2.18 g, 20.1 mmol) in dichloromethane (8 mL) and methanol (4 mL). The solution was heated at reflux for 1 hour. The solution was allowed to cool and then rotovaped down to remove excess 1,2-diaminoethane. 2,4-dihydroxybenzaldhyde (1.42 g, 10.3 mmol) was dissolved in 14 mL of solvent (50/50 methanol and dichloromethane). The orange colored 2,4-dihydroxybenzaldhyde solution was added dropwise to the liquid product from the first reaction after being dissolved in dichloromethane (16 mL). The resulting solution was stirred at room temp for 10 minutes. Nickel acetate tetrahydrate (2.50 g, 10.0 mmol) was dissolved in methanol (30 mL) and added to the reaction from the previous step. The solution was then heated at reflux for 1 hour, during which a precipitate formed. The solution was cooled to room temp followed by cooling in an ice bath for 15 minutes. 2.6045 g of catalyst 9 was collected by vacuum filtration (70.5 % yield).

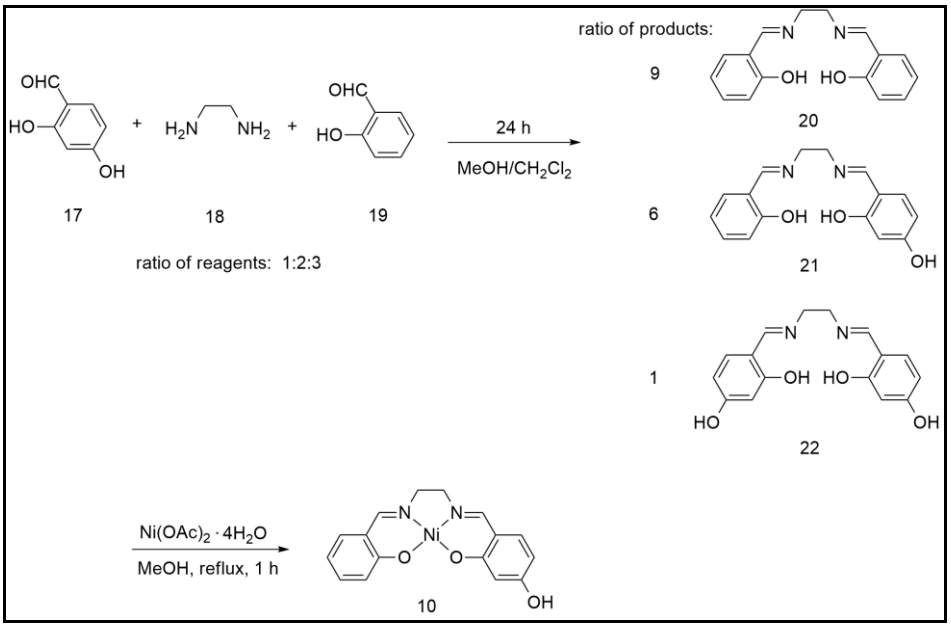
^{1}H NMR: 8.541 (s, 1H), 8.326 (s, 1H), 7.993 (m, 1H), 7.406 (m, 1H), 7.207 (m, 1H), 6.832 (m, 1H), 6.236 (m, 2H), 6.035 (d, 1H), 3.191 (m, 6H).

CV: E_{pc} = -1.8 V.

IR (neat): ~3200 (broad), 1603.39, 1539.57, 1446.08, 1229.71 cm^{-1}.



Scheme 5. Synthesis of heterogeneous catalyst **5**



Scheme 6. Synthesis of catalyst 10

Resin Bound [9-(2'-Hydroxyphenyl)-5,12-Diaza-4-Methyl-Tridec-2,4,6,8,10,12-Hexeneato(2-)]Nickel(II) (5): Merrifield resin (5.00 g, 1.0 g resin per 0.8 mmol Cl^-) was preswelled in dimethylformamide (20 mL) for 20 min. Catalyst 9 (1.47 g, 4.00 mmol) was dissolved into a solution of dry dimethylformamide (20 mL) and THF (10 mL). The solution was added dropwise to 0.20 g NaH (60 % dispersion in oil). The resulting mixture was stirred for 10 minutes under nitrogen gas. The preswelled Merrifield resin was added to the solution and stirred under the presence of nitrogen for 24 hours. The resin was collected by vacuum filtration and washed with D.I. water (3 x 50 mL), methanol (20 mL), and dichloromethane (3 x 50 mL). 4.57 g of catalyst 5 was collected.

CV: E_{pc} = -2.4 V.

IR (neat): 3024.62, 2919.77, 1600.59, 1492.32, 1451.47 cm^{-1}.

% Loaded: 11.4 %

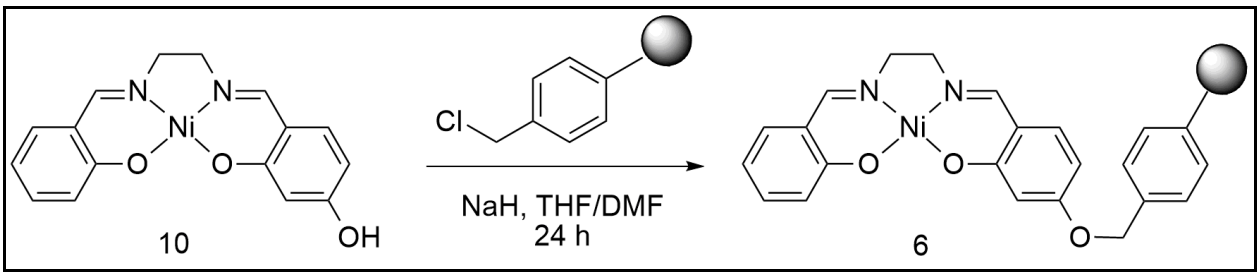
Catalyst 10 was synthesized according to a modified literature procedure by Jacobsen. [17] The procedure was modified to incorporate nickel as the metal instead of cobalt.

[N',N'-Bis(2',4'-Dihydroxyphenyl)-1,2-Ethylenediamine]Nickel(II) (10): 2,4-dihydroxybenzaldehyde (0.621 g, 5.50 mmol) was dissolved in 18 mL of DCM and 6 mL of methanol. Saliclaldehyde (1.65 g, 13.5 mmol) was added to the solution and allowed to mix thoroughly. Next, ethylene diamine (542 mg, 9.03 mmol) was added and the solution instantly turned bright yellow. The solution was stirred at room temp for 24 hours. The solution was then vacuumed filtered. 2.06 g of Catalyst 10 was collected (82.9 % yield).

^{1}H NMR: 9.750 (s, 1H), 7.898 (m, 2H), 7.271 (m, 1H), 7.255 (m, 1H), 7.180 (d, 1 H), 6.721 (m, 1H), 6.519 (m, 1H), 6.095 (m, 2H), 3.427 (m, 4H).

CV: E_{pc} = -2.0 V.

IR (neat): ~3200 (broad), 1602.04, 1536.61, 1446.48, 1225.66 cm^{-1}.



Scheme 7. Synthesis of heterogeneous catalyst **6**

Resin Bound [N',N'-Bis(2'-Hydroxyphenyl)-1,2-Ethylenediamine]Nickel(II) (6): Merrifield resin (5.00 g, 1.0 g resin per 0.8 mmol Cl^-) was preswelled in dimethylformamide (20 mL) for 20 min. Catalyst 10 (1.36 g, 4.00 mmol) was dissolved into a solution of dry dimethylformamide (30 mL) and THF (10 mL). The solution was added dropwise by an addition funnel to 0.20 g NaH (60 % dispersion in oil). The resulting mixture was stirred for 10 min under nitrogen gas. The preswelled Merrifield resin was added to the solution and stirred under the presence of nitrogen for 24 hours. The resin was collected

by vacuum filtration and washed with water (3 x 50 mL), methanol (20 mL), and dichloromethane (3 x 50 mL). 5.42 g of catalyst 6 were collected.

CV: E_{pc} = -2.2 V.

IR (neat): 3027.91, 2923.48, 1600.35, 1492.11, 1450.64 cm^{-1}.

% Loaded: 39.0 %

Ni(salen) catalyst 11 was synthesized according to a literature procedure. [18]

Ni(salen) Zeolite Y was synthesized according to the "flexible ligand method". [19]

Ni(salen) Zeolite Y (4): Na^+ zeolite Y (5.2 Si/Al ratio) was purchased from Sigma Aldrich and underwent a cation exchange by allowing the zeolite to stir in a 0.01 M nickel acetate solution for 4 weeks and periodically changing out the nickel acetate solution. The zeolite was subsequently washed with nano pure water and dried at 40 °C. Once the Ni^+ zeolite Y powder was obtained it was mixed with excess uncomplexed salen ligand at a 1:3 weight ratio. The two solids were placed in an oven at 170 °C overnight, then the molten mixture was removed from the oven and allowed to cool back into a solid. The solid was washed thoroughly to remove any excess ligand. Throughout the synthesis, the zeolite was characterized by infrared spectroscopy. Zeolites can change significantly from batch to batch and thus all work with zeolites were completed using only one batch of zeolites.

CV: E_{pc} = -2.2 V.

IR (neat): pyridine peak at 1490 cm^{-1} and Ni-pyridine peak at 1449 cm^{-1}.

% Nickel: 0.86 %

2.9. Determination of % nickel in heterogeneous catalysts

The heterogeneous mediators were characterized for the percent nickel content by digestion and detection of nickel using a Graphite Furnace Atomic Absorption (GFAA). The percent nickel characterization was needed to calculate the amount of catalyst needed in bulk electrolysis stoichiometry calculations. The percentage of nickel was obtained by digesting the solid-phase catalyst in nitric acid and then analysis of the solution by GFAA. Prior to sample preparation, all glassware was soaked in 5% nitric acid for at least 1 hour and rinsed with nano pure water. Nickel nitrate was used as a standard at a concentration of 10,000 ppm. A serial dilution of the standard was performed in 2 steps. First, the standard was diluted with nano pure water to 10 ppm and then again to produce a stock solution of 500 ppb Ni. The auto diluter on the instrument was set to run the 500 ppb stock solutions at concentrations of 25, 50, 100, and 200 ppb. The absorbance measurements were then used to construct a standard curve that was later used in determining the concentrations of the Merrifield resin catalysts. 3.3 mg of catalyst 4, 3.3 mg of catalyst 5, 3.0 mg of catalyst 6, and 11.2 mg of catalyst 7 were weighed into separate 50 mL round bottom flasks. 30 mL of HPLC grade concentrated nitric acid was added to each sample and the mixture was refluxed for 2 hours. The solution was then diluted with nanopure water and then vacuum filtered. The filtered solutions were then collected into 100 mL volumetric flasks. To evaluate whether all of the nickel was extracted during the first digestion, a second digestion was performed on all solids captured during filtration. A method blank consisting of 2.8 mg of the Merrifield resin (containing no nickel) was digested in nitric acid and filtered the same way as described for the other

samples. A 1% nitric acid solution was used as an instrument blank. A nickel lamp was used on the Perkin Elmer AA 800 Atomic Absorption Spectrometer at a wavelength of 232 nm. In addition an injector temperature of 20 ºC and a final furnace temperature of 2450 ºC was used. The standard absorption curve for the nickel standards is shown in Figure 4.

The results of the heterogeneous catalysts are shown in Table 1. A weight percentage of nickel was able to be determined for all heterogeneous catalysts. The method blank had a non-detectable nickel concentration, exhibiting that nickel contamination did not occur through digestion and contact with glassware.

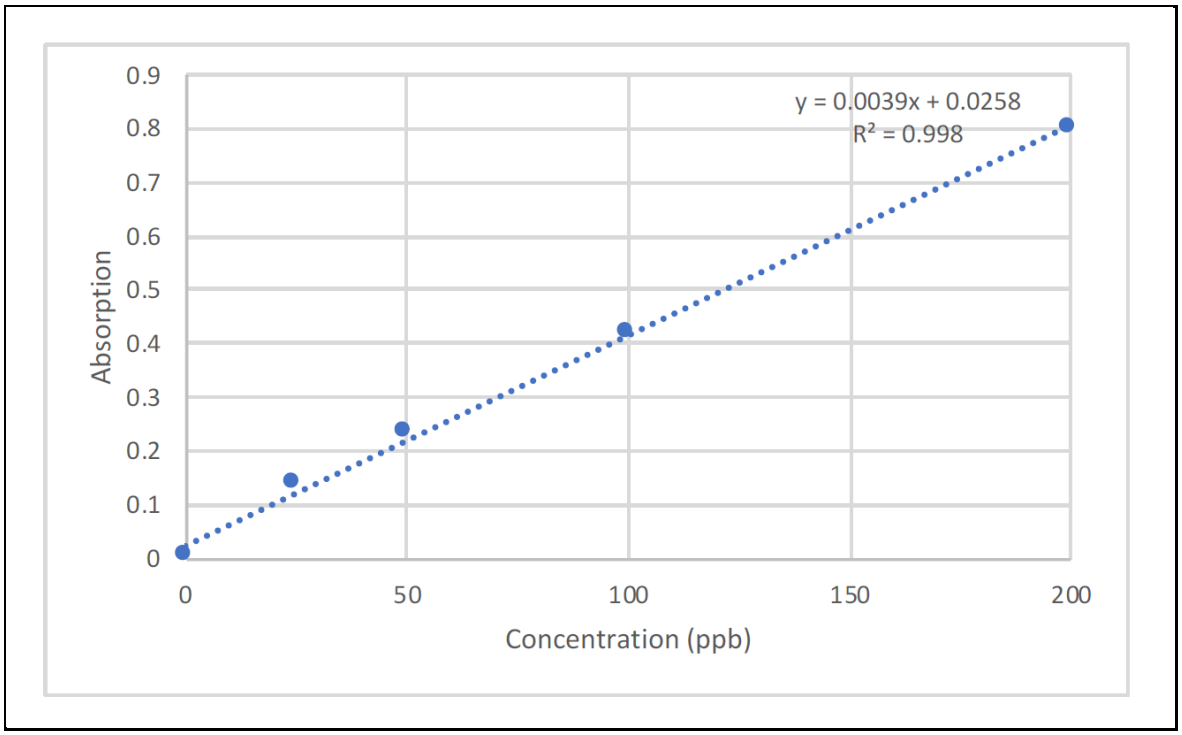


Figure 4. Standard Curve for Nickel Absorption by GFAA

Table 1. GFAA Results for Detection of Nickel in Heterogeneous Catalysts

Sample	Concentration (ppb)	Signal Response	% Nickel
Standard 4	200	0.0812	N/A
Standard 3	100	0.4212	N/A
Standard 2	50	0.2312	N/A
Standard 1	25	0.1362	N/A
Blank	0	0.0049	N/A
Catalyst **4**	39.77	0.1809	1.21%
Catalyst **5**	19.26	0.1009	0.58%
Catalyst **6**	50.51	0.2228	1.68%
Catalyst **7**	96.77	0.4032	0.86%
Method Blank	ND	0.0036	ND

Furthermore a loading percentage of the nickel catalyst onto the Merrifield resin was calculated for the polymer supported catalysts. The purchased Merrifield resin had a ratio of 1 g resin per 0.8 mmol Cl^-. A theoretical yield for the moles of nickel in each catalyst were calculated and compared to the results obtained by GFAA to produce the percent loading values shown in Figure 5. These values were consistent with literature values for catalyst 4. [16]

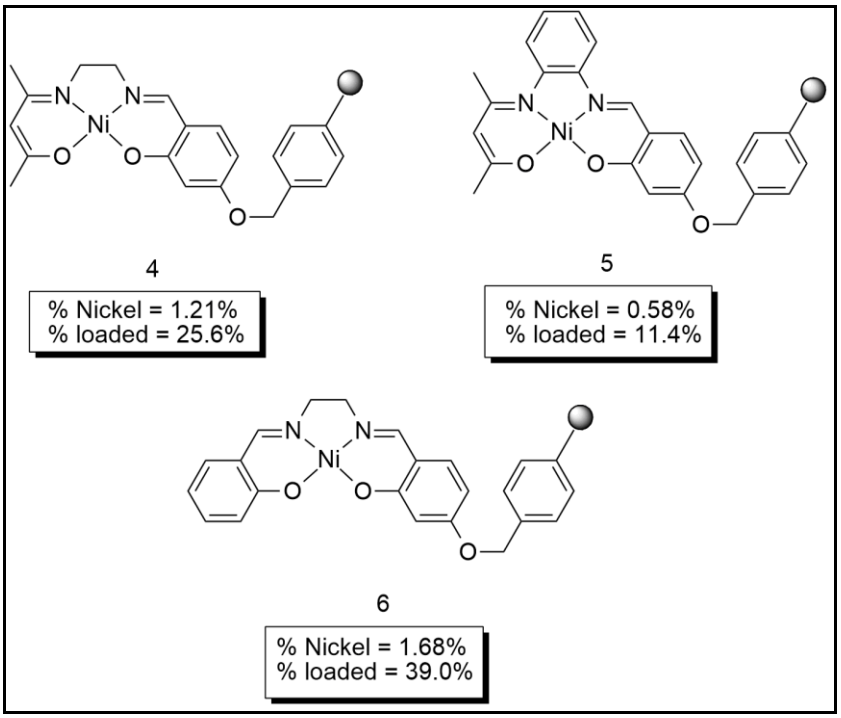


Figure 5. % Loaded Results for Synthesis of Polymer Supported Catalysts

2.10. Cyclic Voltammetry (CV)

Cyclic voltammetry on the homogeneous compounds (catalysts **8, 9, 10,** and **11**) was done by mixing 10 mM of each catalyst with 0.1 M tetrabutylammonium hexafluorophosphate in 5 mL of DMF. The results showed a reduction potential of -1.70 V (catalyst **8**), -1.80 V (catalyst **9**), -2.00 V (catalyst **10**), and -1.80 V (catalyst **11**). The reference electrode for each CV was Ag/AgCl.

The heterogeneous catalysts were analyzed by cyclic voltammetry using the glassy carbon plating method. Each heterogeneous catalyst was plated as follows: Before plating, the glassy carbon electrode was polished with alumina and water on polishing cloth and then rinsed with deionized water. The electrode was then cleaned on a sonicator in acetone, absolute ethanol, and HNO_3/H_2O (1:1, v/v) solution, lastly in deionized water, and then air dried. Next, 0.0312 g of graphite and 0.0316 g of catalyst **8** on polymer were dispersed in 1 mL of tetrahydrofuran (THF) ultrasonically to form a black suspension. Then 4 μL of this black suspension was pipetted directly on the polished surface of the glassy carbon electrode (GCE), forming a composite film. The film was air-dried overnight at room temperature. To plate the next film layer, polystyrene needed to be synthesized. This was done by reacing styrene with benzoyl peroxide at 135 ^oC. A Pasteur pipette was plugged with glass wool, filled halfway with alumina,

and 1.5 mL of styrene was poured in. 1 mL of styrene was collected into a test tube. Then, 0.0506 g of benzoyl peroxide and a boiling stone was added to the test tube.

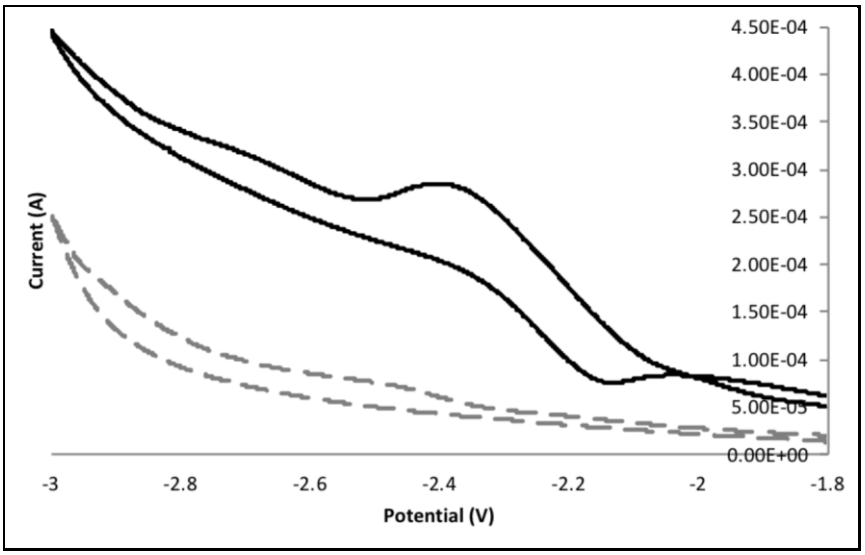


Figure 6. Cyclic Voltammetry of heterogeneous catalyst **4** (dashed line = blank solution, solid line catalyst **4**) Reference electrode = 0.1 M Ag/AgCl

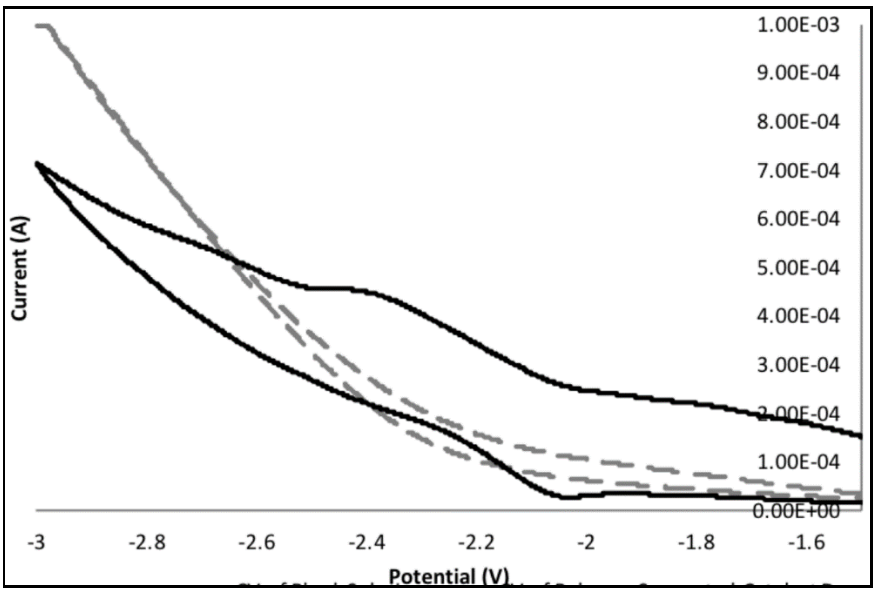


Figure 7. Cyclic Voltammetry of heterogeneous catalyst **5** (dashed line = blank solution, solid line catalyst **5**) Reference electrode = 0.1 M Ag/AgCl

The mixture was heated in a sand bath at 135 ^{o}C. Once polymerization occurred and the solution thickened, the product was cooled and then ground into a fine powder. Next, 0.0805 g of polystyrene was dissolved in 10 mL of THF. 10 μL (3x) of the polystyrene solution was placed on the surface of the electrode and then dried overnight at room temperature. The plated glassy carbon working electrode was then placed in a solution of 0.1 M tetrabutylammonium hexafluorophosphate in 5 mL of DMF. A

platinum auxiliary electrode and Ag/AgCl reference electrode was used in the experiment. Each CV contains a blank solution containing only supporting electrolyte with unmodified GCE for comparison. Each heterogeneous catalyst was plated using the same method described above.

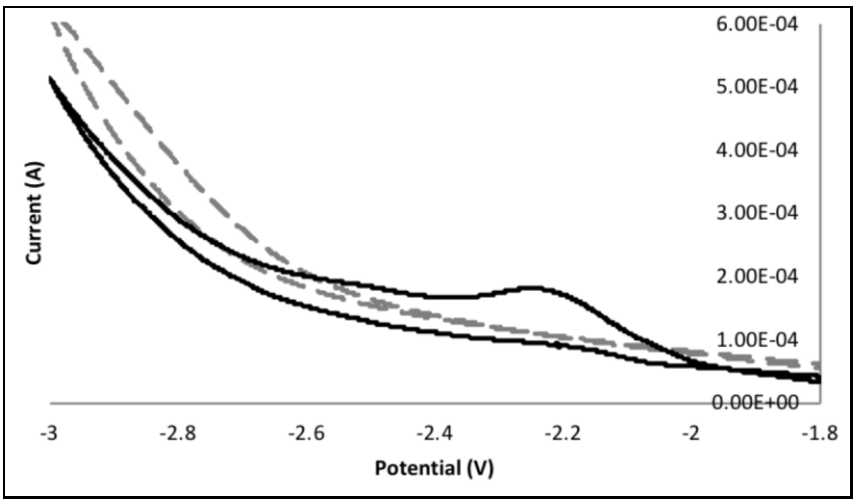


Figure 8. Cyclic Voltammetry of heterogeneous catalyst **6** (dashed line = blank solution, solid line catalyst **6**) Reference electrode = 0.1 M Ag/AgCl

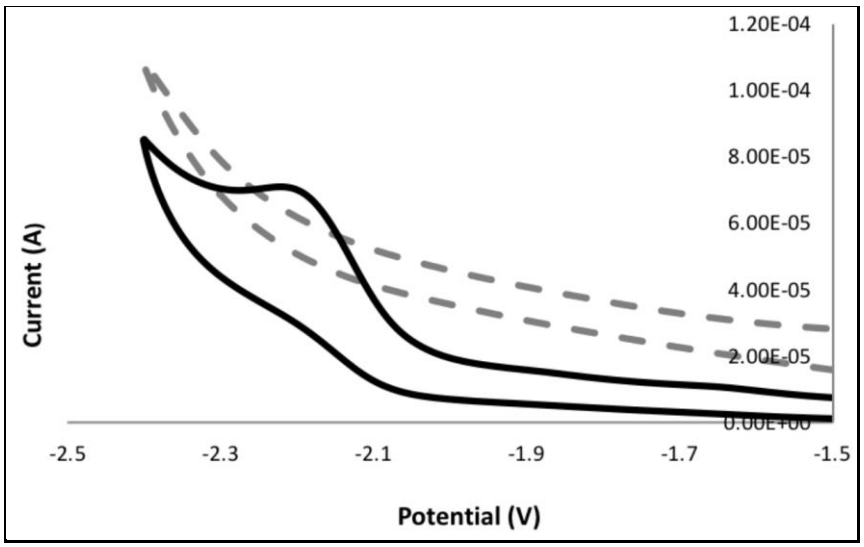


Figure 9. Cyclic Voltammetry of heterogeneous catalyst **7** (dashed line = blank solution, solid line catalyst 7) Reference electrode = 0.1 M Ag/AgCl

2.11. Synthesis of EHC substrate 1

The EHC substrate, compound 1, was synthesized by an *in situ* oxidative diol cleavage Wittig process. [20] Trans-1,2-Cyclohexanediol was reacted with sodium periodate, silica, and a Wittig reagent to produce compound 1 in a 76% yield.

2.12. Bulk Electrolysis (BE)

Bulk electrolysis was first performed via a direct pathway. Then, BE was performed via an indirect pathway using each of the eight catalysts (4, 5, 6, 7, 8, 9, 10, and 11). The BE reaction conditions have been described previously. [5] Each reaction was conducted inside a glass cell with a reticulated vitreous carbon (RVC) mesh working electrode, a platinum wire auxiliary wire electrode and an Ag/AgCl reference electrode. Each reaction solution consisted of DMF as the solvent, EHC substrate **1**, 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, and 2 equivalents of dimethyl malonate. During the indirect electrolysis, each catalyst was added at 10 mole %. The potential used in each bulk electrolysis reaction was determined from the reduction potential. Each BE reaction was set at 0.2 V more negative potential than the reduction potential for each catalyst indicated in CV. After the current stabilized and returned to background current, the reaction was stopped and underwent a liquid/liquid extraction. The DMF reaction solution was extracted with 40 mL of diethyl ether and 40 mL of saturated NaCl. All organic layers were combined and washed with deionized water three times. The organic layer was concentrated by rotary evaporation. Purification by column chromatography was accomplished with 50% hexanes/50% diethyl ether. The cyclized products were characterized by NMR and the *cis/trans* ratio was determined by GC/MS. The results of the BC experiments are shown in Table 2 and Table 3.

Table 2. Bulk Electrolysis results with heterogeneous catalysts

Catalyst	time (hours)	% yield	cis/trans
4	3	89.2	1:1.68
5	4	53.6	1:1.69
6	4	85.6	1:1.11
7	2.5	91.4	1:1.46
no catalyst	6	48.2	1:1.72

Table 3. Bulk Electrolysis results with homogeneous catalysts

Catalyst	time (hours)	% yield	cis/trans
8	8	72.1	1:1.85
9	8	51.9	1:1.72
10	12	64.3	1:1.65
11	6	76.8	1:1.47
no catalyst	6	48.2	1:1.72

3. RESULTS AND DISCUSSION

Every mediated bulk electrolysis reaction produced greater yields over the direct bulk electrolysis reaction with no catalyst. Furthermore, each heterogeneous catalyst produced higher product yields in

comparison to their analogous homogeneous catalyst. The solid supported catalysts increased yield percentages ranging from 1.7% to 21.3%. Catalyst **9** and **5** seemed to be the least performing mediators, only small increases in yield over the direct bulk electrolysis reaction were made. Catalyst **7**, (Ni(salen) encapsulated in zeolite Y) produced the highest yield. In addition to producing higher yields, the heterogeneous catalysts did so in shorter periods of time ranging from 1/3 to ½ the amount of time it took for the homogeneous catalysts.

After each BE reaction with the solid phase catalysts, the reaction solution was filtered to remove the solid catalyst. The recovered catalysts were washed, dried, and weighed to determine the catalyst recovery percent as shown in Table 4.

Table 4. Percent Recovery of Heterogeneous Catalysts after BE Reaction

Table 5. Percent Recovery of Heterogeneous Catalysts after BE Reaction

Catalyst	Catalyst Recovery (%)
4	99%
5	95%
6	93%
7	91%

The percent recovery for catalysts 4, 5, 6, and 7 were greater than 90%. This value is reported to show that these heterogeneous catalysts will remain as solids during bulk electrolysis and then can be simply filtered out of the solution and reused.

Our results highlighting the enhanced reactivity of Ni-salen zeolite Y in EHC are consistent with similar studies using catalysts encapsulated in zeolites. Five recent studies (2017-2019) all have shown that various metal-Schiff base type catalysts such as salen and salophen encapsulated in zeolites results in more efficient reactions when compared to their non-encapsulated counterparts.

First, in 2019, it was reported that palladium-salophen complexes that were encapsulated in a zeolite-Y acted very efficiently in cross coupling Heck reactions of bromobenzene with styrene.[21] The authors studied the steric interactions and electronic effect of substituents around the salophen ligand. It was found that the non-encapsulated complex with the electron donating substituent was the most reactive for the Heck reaction while the complex with the electron withdrawing substituent was the least reactive. After encapsulation in zeolite-Y, the reactivity order was reversed. The authors speculated that encapsulation had a significant steric effect on the guest complexes that dominated the electronic effect of the substituents. The encapsulated palladium complexes improved the percent yield of the reaction by 34% over the non-encapsulated palladium-salophen complex. The authors also found that the heterogeneous catalyst was easily separated from the reaction mixture and was capable of being reused after washing without loss in activity.

Second, in 2017, another study highlighted the use of Ni-salen zeolite Y in the styrene oxidation reaction using H_2O_2 as oxidant.[22] Benzaldehyde was the major product while styrene oxide was the minor product. The authors found that the percent conversion was lower for the encapsulated Ni-salen

zeolite Y when compared to the non-encapsulated catalyst. However, when an –OH substituent was added to the Ni-salen catalyst the encapsulated and non-encapsulated complexes had similar percent conversions. Additionally, the authors found that the selectivity for benzaldehyde as the major product was significantly enhanced by 45%. It was speculated that this was due to the distortion of the planar complex of the catalyst while encapsulated in the zeolite Y supercage.

Third, in 2019, a computational study of iron(III), nickel(II) and copper(II)-salophen complexes that were encapsulated in zeolite Y measured bond distance, bond angle, torsional angle, and HOMO-LUMO energy gap using density functional theory.[23] The calculated DFT-global descripts such as global hardness, global softness, electrophilicity, and chemical potential showed that the zeolite encapsulated metal complexes had higher reactivity when compared to the non-encapsulated complexes.

Fourth, in 2017, it was shown that palladium-Schiff base complexes encapsulated in zeolite Y resulted in enhanced product yields in the sulfoxidation of methyl phenyl sulfide in comparison to non-encapsulated complexes.[24] The authors studied Pd-salen as well as other catalysts with various electron withdrawing and electron donating substituents. In each case, the zeolite-encapsulated complex acted as a better heterogeneous catalyst in the sulfoxidation reactions. The authors also speculated that the distortion of the encapsulated complex was the key factor for the increased catalytic activity. Additionally, zeolite-Y catalysts were used for up to four cycles without loss of catalytic activity.

Fifth, in 2019, it was shown that Cu(II)-Schiff base complexes that were encapsulated in zeolite Y were effective catalysts in styrene oxidation using H_2O_2 as the oxidant.[25] The authors concluded that the rigid framework on the zeolite Y catalyst forced the guest complex into a distorted structure that plays a critical role in the enhanced reactivity of the overall system. This was supported by UV-Vis spectroscopy that showed that the metal center became more electropositive and disrupts conjugation around the metal center, resulting in enhanced reactivity. This rendered the metal center more likely to undergo nucleophilic attack by H_2O_2.

4. CONCLUSIONS

The EHC reaction has previously been studied using metal salens as mediators to facilitate electron transfer. This work improves upon these reactions by introducing heterogeneous catalysts that remain as solids while mediating the EHC reaction. Eight catalysts were successfully developed; 4 homogeneous mediators and 4 heterogeneous mediators. The amount of nickel loaded onto the Merrifield resin or Zeolite Y was detected by GFAA. The % loading values were then further used to calculate the amount of catalyst needed for each reaction. The EHC substrate **1** was successfully synthesized by an *in situ* oxidative diol cleavage Wittig reaction. CV experiments were performed on each catalyst to determine their redox potentials. Modified CV experiments with modified electrodes were performed to successfully measure the redox potential for each heterogeneous catalyst.

The bulk electrolysis reactions with the EHC substrate was accomplished in a direct and indirect pathway, resulting in both *cis* and *trans* cyclized product. Eight total catalysts were assessed for their ability to mediate the EHC reaction, the length of time for the reaction to complete, and *cis/trans* ratio of the resulting cyclized product. The various mediators had little effect on stereoselectivity in the EHC

reaction. The *trans* isomer was the major product in each reaction. Preliminary computational chemistry has indicated that reaction temperature could affect the *cis/trans* ratio of ERC and EHC reactions. Future work in this area includes investigations of kinetic vs thermodynamic product ratios in order to affect *cis/trans* ratio in these cyclization reactions for both heterogeneous and homogeneous mediators.

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