Supporting Information

Lanthanide promoted nickel catalysts for the integrated capture and conversion of carbon dioxide to methane via metal carbonates

Christopher J. Koch, Zohaib Suhail, Prince, Anushan Alagaratnam, Matthew Coe, Alain Goeppert, G.K. Surya Prakash*

Contents

Additional Optimization Data

Table S1 corresponds to the data shown in Figure 5, where various carbonate salts were tested for the conversion to methane with the 50% Ni/12.5% Yb/Al_2O_3 catalyst.

Table S1. Conversion of various carbonate salt to methane over 50% Ni/12.5% Yb/Al_2O_3.

Carbonate Salt	**Products[b]**		**Methane Productivity ($g_{methane}$·h^{-1}·kg_{cat}^{-1})**
	CH_4 (mmol)	CH_4 yield (%)	
Li_2CO_3	7.3	73	16.3
Na_2CO_3	10	100	22.3
K_2CO_3	10	100	22.3
K_2CO_3[a]	1.1	11	58.8
$K_2{}^{13}CO_3$	10	100	22.3
Cs_2CO_3	5.6	56	12.5
$MgCO_3$	4.6	46	10.2
$CaCO_3$	0.5	5	1.11

Conditions: 10 mmol carbonate salt, 10mL DI H_2O, 225°C, 300 mg 50% Ni/12.5% Yb/Al_2O_3, 50 bar H_2 at room temperature, 24 hours, [a] 6 hours, 50 mg 50% Ni/12.5% Yb/Al_2O_3, 250°C, 50 bar H_2, 10 mL H_2O. [b] No CO or CO_2 detected in any of the reactions. Yields calculated from the gas phase by gas chromatography are within ±5% error.

Gas Chromatography Data

A gas Chromatogram (GC) of the gaseous phase was collected after each experiment to quantify the gases produced during the reaction. An example of a chromatogram obtained after the reaction of K_2CO_3 in 10 mL DI H_2O over 50% Ni/12.5% Yb/Al_2O_3 at 225°C, 50 bar H_2 and 24h is shown in Figure S1 and Figure S2. Figure S1 shows the full chromatogram, while Figure S2 excludes the H_2 for increased visibility of the CH_4 peak. In the chromatogram, H_2 appears at 1.8 minutes, N_2 at 2.3 minutes, and CH_4 at 4.5 minutes. If CO and CO_2 were present they would show at 2.5 and 8.6 minutes, respectively. N_2 originates from the atmosphere during the injection and is therefore present in the chromatogram. The peaks in these chromatograms were then integrated and the amount of CH_4 produced (in mmol) was calculated using the gas law equation as shown in Equation S1.

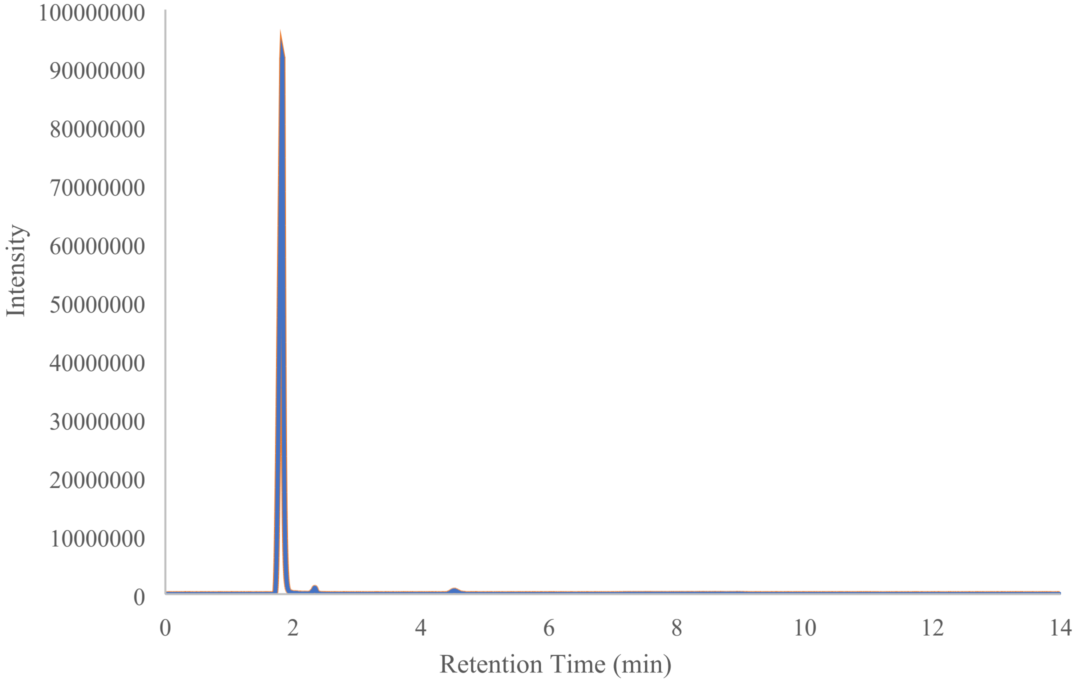


Figure S1. Gas Chromatography of a high yielding reaction from 0 to 14 minutes (conditions: 300 mg 50% Ni/12.5% Yb/Al_2O_3, 225°C, 50 bar H_2, 10 mL DI H_2O, 10 mmol K_2CO_3, 24 h). Expansion for CH_4 is shown in Figure S2.

Figure S2 showcases more clearly that the only peaks present are at 2.3 and 4.5 minutes, which correspond to N_2 and CH_4 respectively. There was no CO or CO_2 observed.

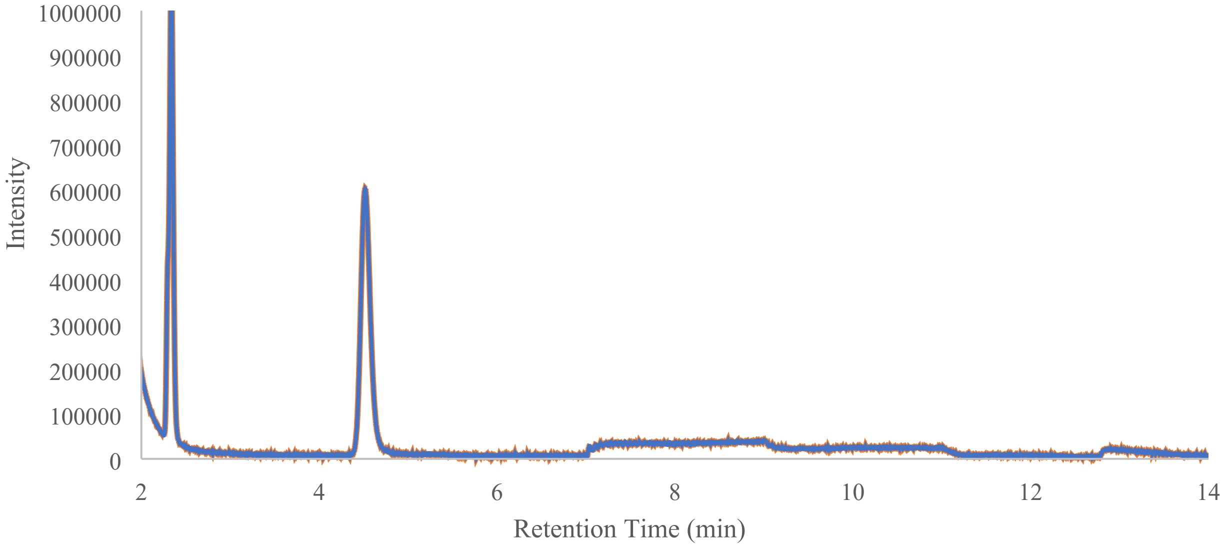


Figure S2. Gas Chromatography of high yielding reaction from 2 to 14 minutes (conditions: 300 mg 50% Ni/12.5% Yb/Al_2O_3, 225°C, 50 bar H_2, 24 h, 10 mL DI H_2O, 10 mmol K_2CO_3).

The amount of methane was quantified through the integration values obtained from the GC. For example, in the chromatograms shown in Figure S1 and Figure S2 there is 98.71% H_2 and 1.29% CH_4. Nitrogen is excluded from the calculation (it is due to air present during the injection using a gas syringe). The integration values were normalized to account for the different response factors of the gases. The normalized integration values were 95.20% H_2 and 4.80% CH_4. The pressure prior to releasing the gas was recorded and used for the next step to calculate the partial pressure of CH_4. The pressure prior to release for this experiment was 585 psi, which equates to there being 28.05 psi of CH_4 in the reactor. The unit of pressure was then converted to atm (1.91 atm CH_4). Then this partial pressure was used in gas law (Equation S1) to calculate the mmol of CH_4 obtained in the reaction, which is shown in Equation S2. The temperature that is used for the calculation is the temperature at the time of the release of the gas. After using gas law equation, there was 10 mmol of methane in the gas released from the reactor, which corresponds to the observed 100% yield.

$$n = \frac{PV}{RT}$$

Equation S1. Gas Law equation, where the known variables (P (pressure of reactor), V (volume of reactor), R (gas constant), and T (temperature of reactor in Kelvin) are on the same side of the equation.

$$mol\ of\ methane = \frac{(1.91\ atm)(0.130\ L)}{(27.0\ ℃ + 273.15)(0.0821\ \frac{atm * L}{mol * K})}$$

Equation S2. Example calculation showing the amount of methane (mol) produced, where the volume is the volume of the reactor was 0.130 L, the temperature is the temperature at which the gas is released, and R is the ideal gas constant.

NMR Data

Nuclear Magnetic Resonance (NMR) spectra were collected for the experiment with $K_2{}^{13}CO_3$ to determine if $^{13}CH_4$ had been obtained. Figure S3 shows the ^1H NMR of the gas mixture after the reaction of $K_2{}^{13}CO_3$ with H_2 over 50% Ni/12.5% Yb/Al_2O_3. This was done by bubbling parts of the reaction gas mixture through toluene-d_8. Both H_2 and H_2O are present in the spectrum as H_2 was used in excess during the reaction and water is the reaction's solvent and its vapors are also present in the gas phase. CH_4 is also present in the ^1H NMR and appears as a doublet centered around 0.17 ppm, indicating that $^{13}CH_4$ had been synthesized.

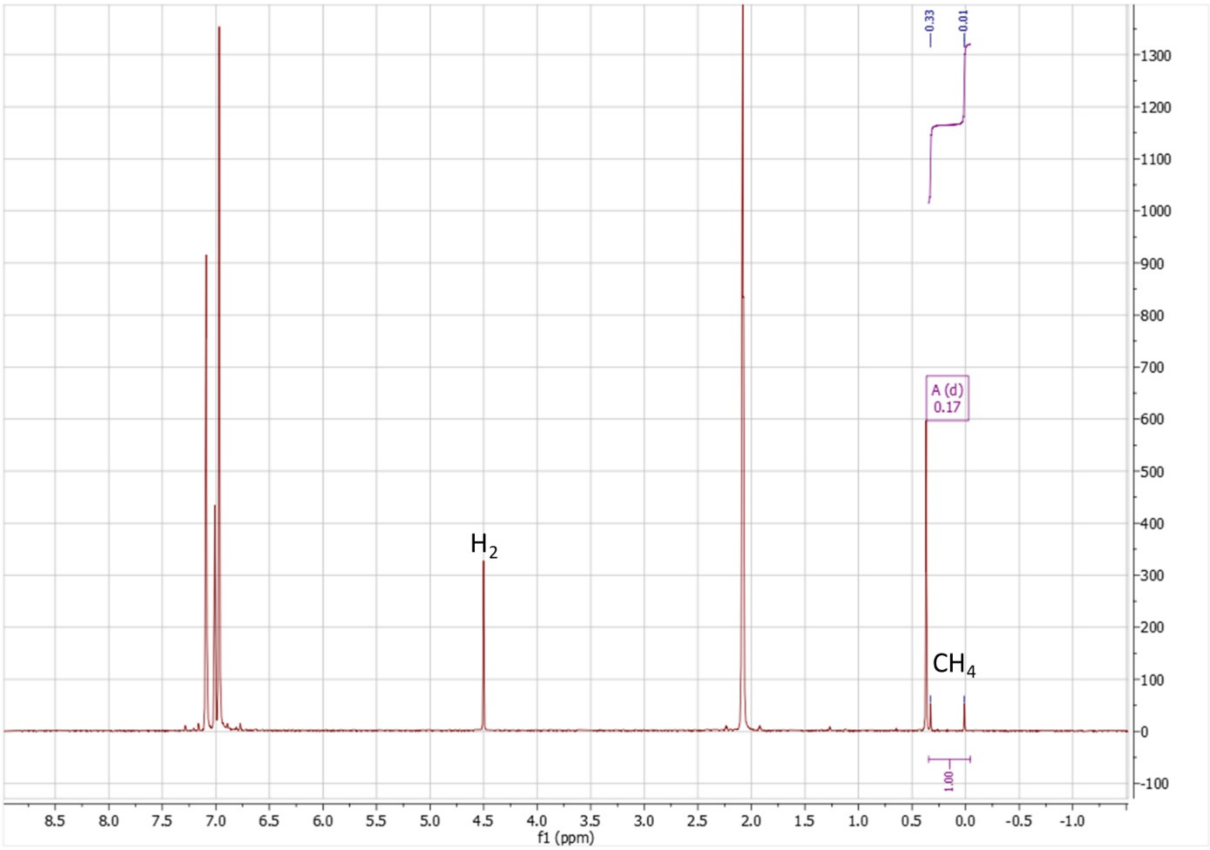


Figure S3. ^1HNMR of the gas mixture after the reaction with $K_2{}^{13}CO_3$ (conditions: 300 mg 50% Ni/12.5% Yb/Al_2O_3, 225°C, 50 bar H_2,24 hours, 10 mL DI H_2O, 10 mmol $K_2{}^{13}CO_3$).

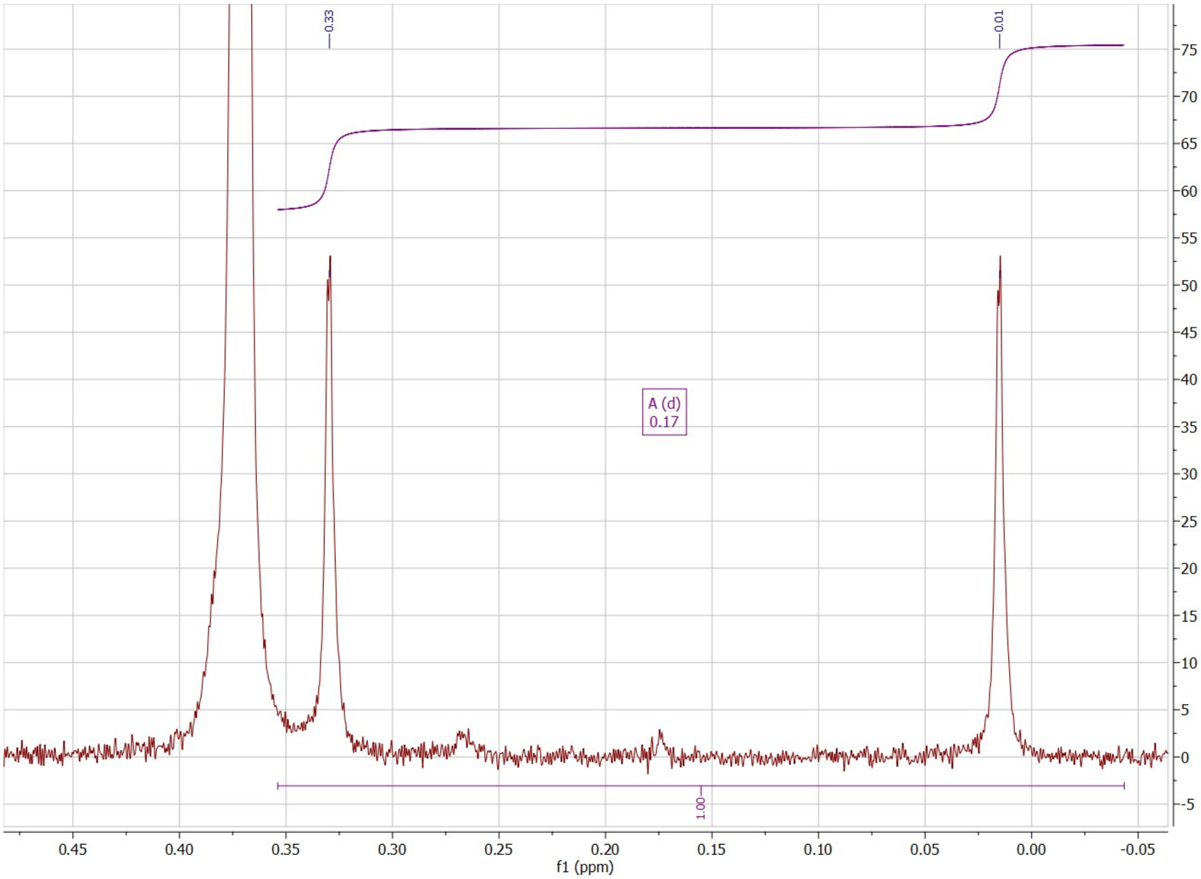


Figure S4. ^{1}HNMR zoomed between -0.05 and 0.5 ppm of the gas mixture after the reaction with $K_2{}^{13}CO_3$ (conditions: 300 mg 50% Ni/12.5% Yb/Al_2O_3, 225°C, 50 bar H_2,24 hours, 10 mL DI H_2O, 10 mmol $K_2{}^{13}CO_3$).

Figure S5 shows the ^{13}C NMR of the gas phase for the same reaction, where methane is present at 0.34 ppm. No other carbon containing gas was present in the spectrum, indicating $^{13}CH_4$ was synthesized selectively.

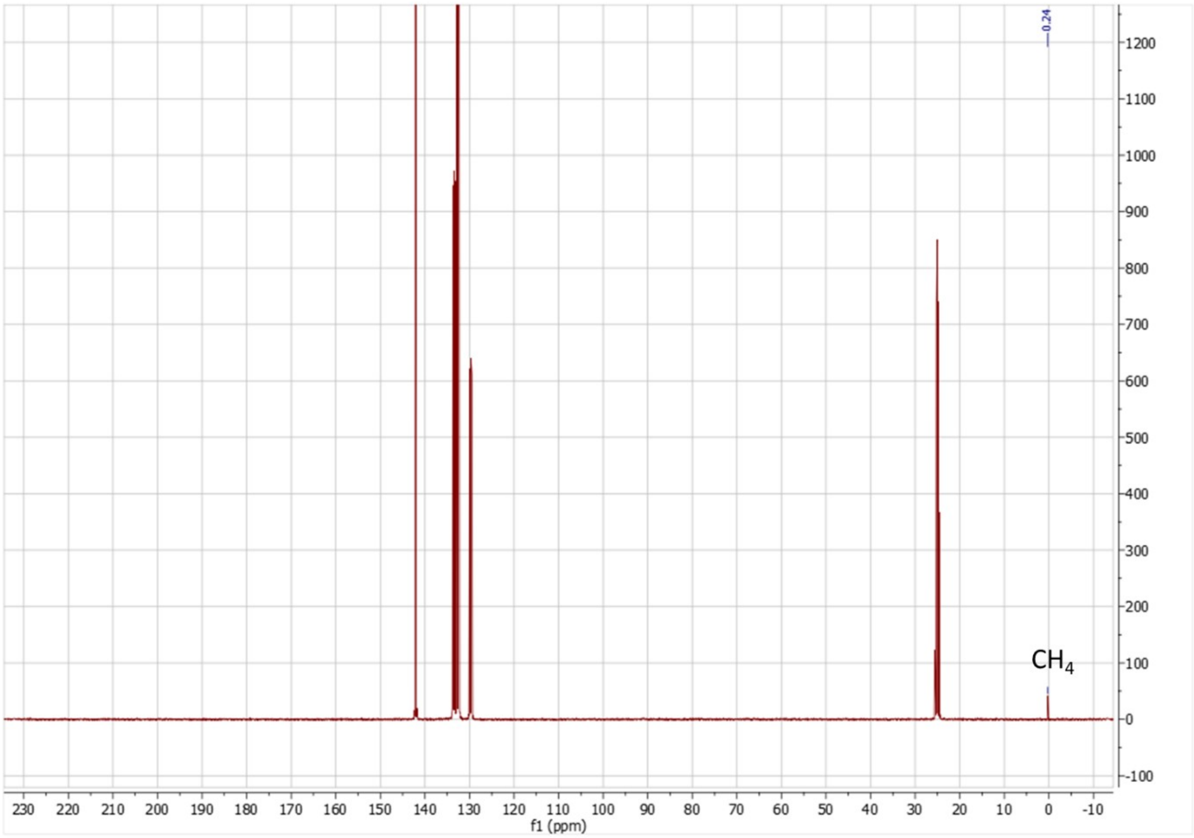


Figure S5. ^{13}CNMR of the gas mixture after reaction with $K_2{}^{13}CO_3$ (conditions: 300 mg 50% Ni/12.5% Yb/Al_2O_3, 225°C, 50 bar H_2, 24 hours, 10 mL DI H_2O, 10 mmol $K_2{}^{13}CO_3$).

Figure S6 shows the ^{13}C NMR of the solution of the direct air capture experiment from which the amount of CO_2 captured was quantified. The captured CO_2 is in the form of potassium carbonate and appears at 167.2 ppm. An internal standard of imidazole was added to reference the ^{13}C NMR in D_2O to quantify the amount of CO_2 captured in the form of carbonate.

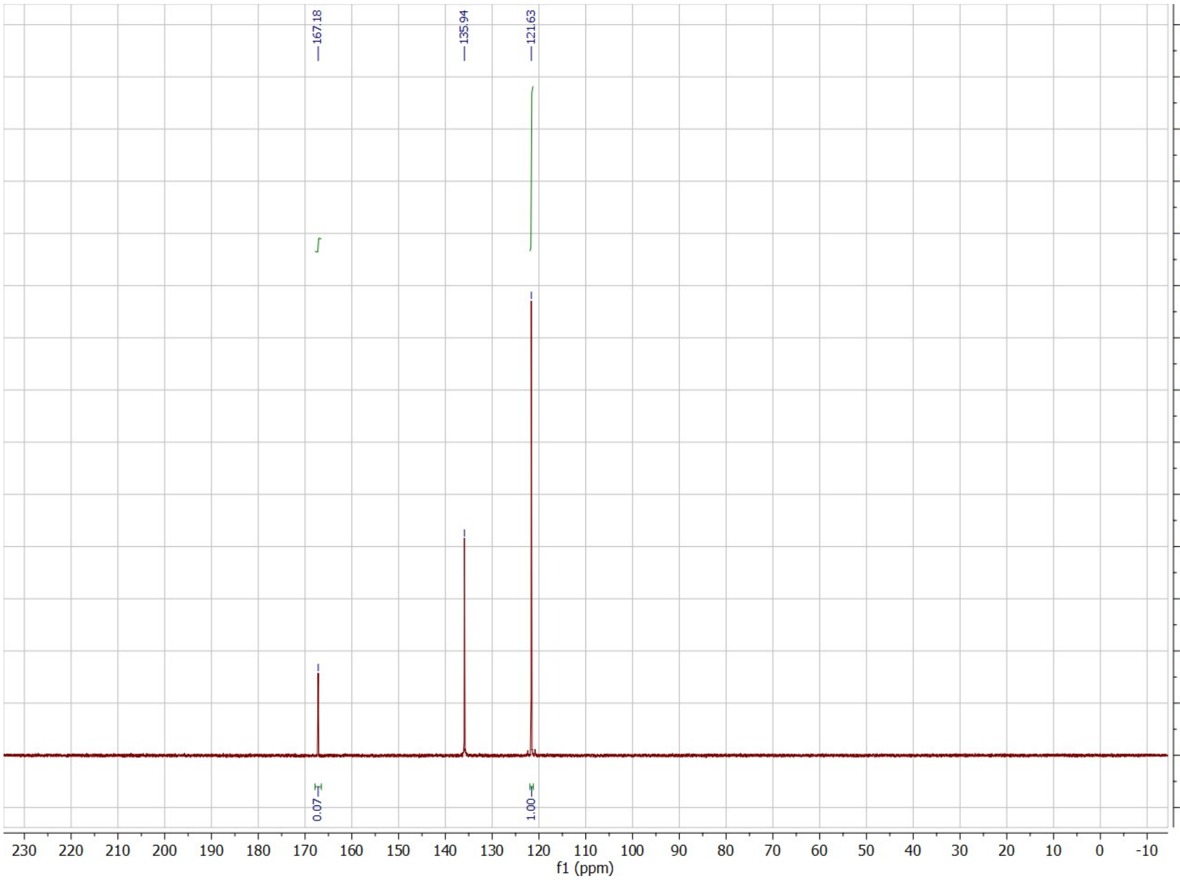


Figure S6. ^{13}C NMR of direct air capture media (capture conditions: 300 mL/min air, 72 hours).

XRD Data

X-ray diffraction (XRD) spectra were collected of the following unreacted and reacted catalysts. Figure S7 shows 50% Ni/12.5% Yb/Al_2O_3 before the reaction. Figure S8 shows the catalyst after one reaction cycle. The presence of boehmite peaks occurs from interactions between hydroxide and alumina. However, the catalyst from the recycling experiments in Figure S9 does not show significant boehmite peaks because less carbonate was utilized for this set of experiments. There was less hydroxide to interact with the alumina. In Figure S10 and Figure S11, 12% Ni/3% Ce/Al_2O_3 catalyst did not have a significant presence of boehmite because less carbonate was hydrogenated to form hydroxide.

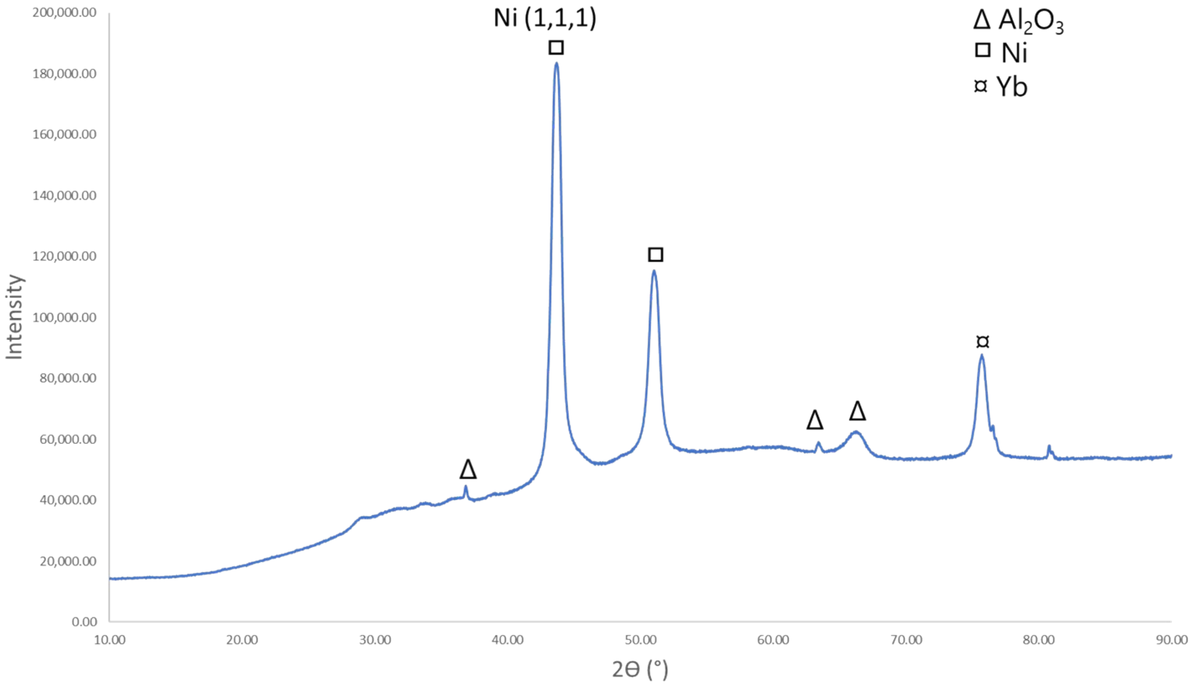


Figure S7. XRD of 50% Ni/12.5% Yb/Al_2O_3 before reaction.

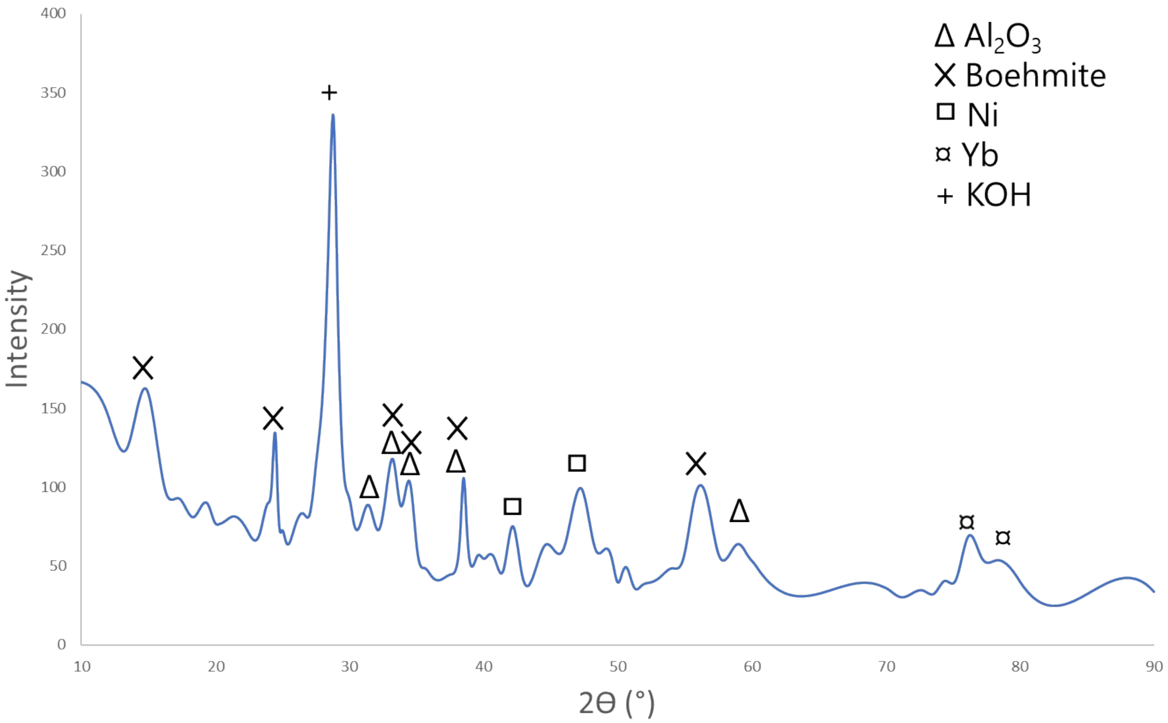


Figure S8. XRD of 50% Ni/12.5% Yb/Al_2O_3 after reaction (conditions: 300 mg 50% Ni/12.5% Yb/Al_2O_3, 225°C, 50 bar H_2, 24 hours, 10 mL DI H_2O, 10 mmol K_2CO_3).

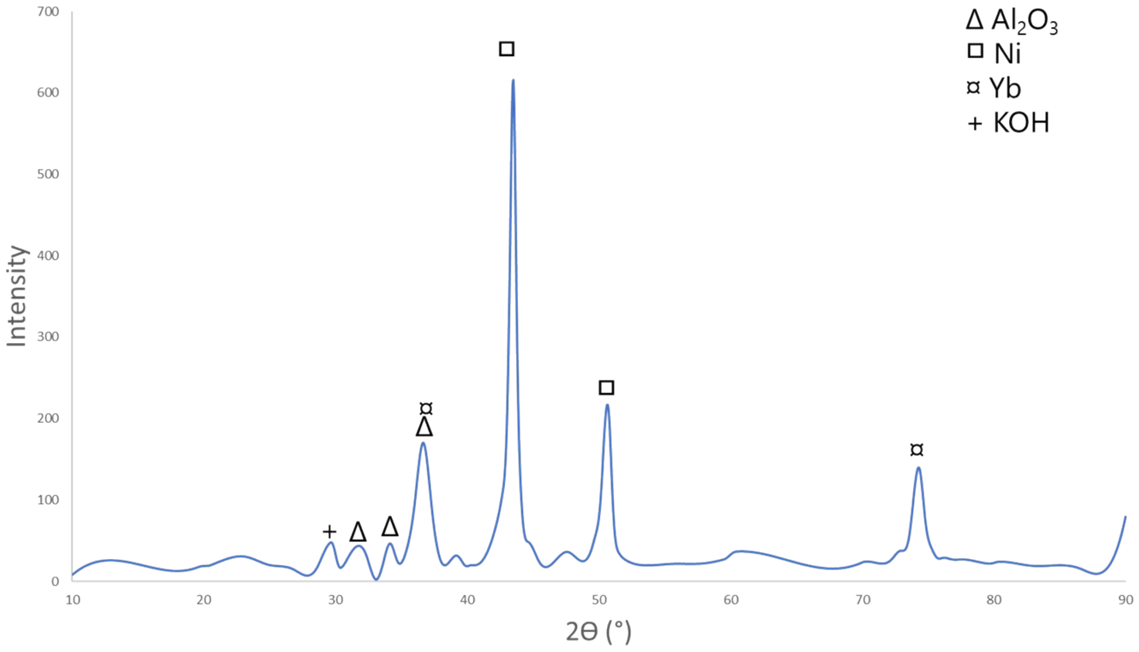


Figure S9. XRD after 5 cycles of reactivity with 50% Ni/12.5% Yb/Al_2O_3 (conditions: 300 mg 50% Ni/12.5% Yb/Al_2O_3, 225°C, 50 bar H_2, 24 hours, 10 mL DI H_2O, 4 mmol K_2CO_3 used in the first cycle).

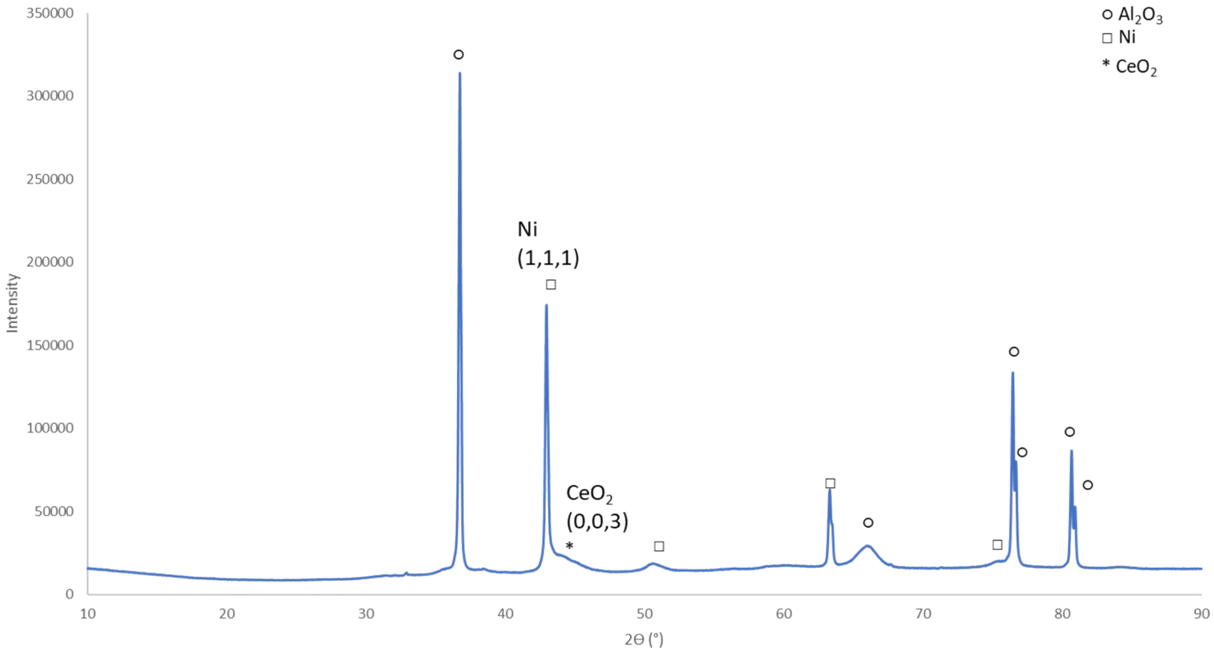


Figure S10. XRD of 12% Ni/3% Ce/Al_2O_3 before reaction.

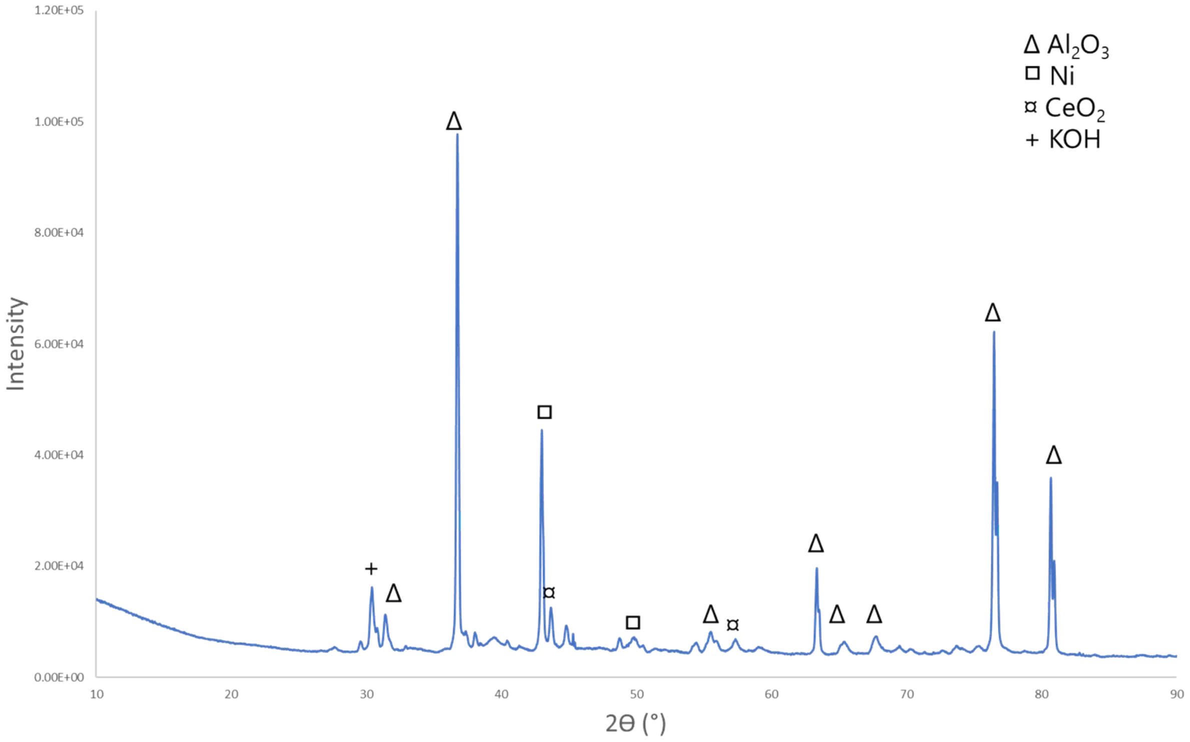


Figure S11. XRD of 12% Ni/3% Ce/Al_2O_3 after reaction. (conditions: 300 mg catalyst, 225°C, 50 bar H_2, 24 hours, 10 mL DI H_2O, 10 mmol K_2CO_3)

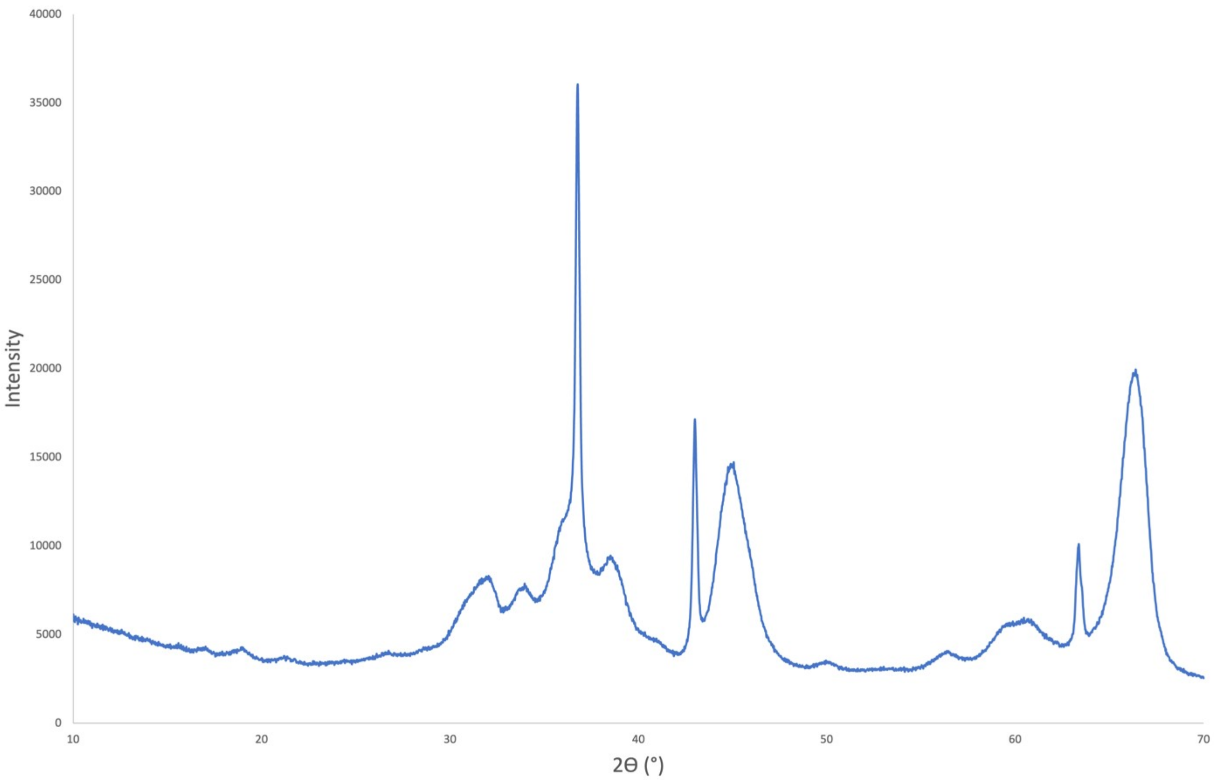


Figure S12. XRD of alumina.

Table S2. Table of D-spacing and crystallite size for the spectra shown if Figures S6-S11.

Sample	Ni (1,1,1) D spacing (Å)	Ni (1,1,1) Crystallite Size (Å)
50% Ni/12.5% Yb/Al_2O_3 before reaction	2.0716 (4)	108.4 (10)
50% Ni/12.5% Yb/Al_2O_3 after reaction	2.030 (4)	100 (36)
50% Ni/12.5% Yb/Al_2O_3 after 5 cycles of reaction	2.08093 (2)	154 (6)
12% Ni/3% Ce/Al_2O_3 before reaction	2.0747 (3)	35.7 (2)
12% Ni/3% Ce/Al_2O_3 after reaction	2.07256 (32)	447.4 (2)

d-space is calculated with Bragg's law, all calculation errors are shown in parentheses, error is ± the number in parentheses referenced to the last digit.

Scanning Electron Microscopy (SEM) Images

SEM images were collected for the 50% Ni/12.5% Yb/Al_2O_3 catalyst to identify possible morphology changes in the catalyst during the reactions. Looking at Figure S13 and Figure S14, no obvious or major morphology changes in the catalyst could be observed after the reaction when compared to before the reaction. The morphology of the catalyst is further changed over more cycles of reactivity as shown in Figure S15. All samples experienced charging, which decreased the resolution of the image. The charging was worse for the sample after the reaction due to other components, like hydroxide salts, being in the sample.

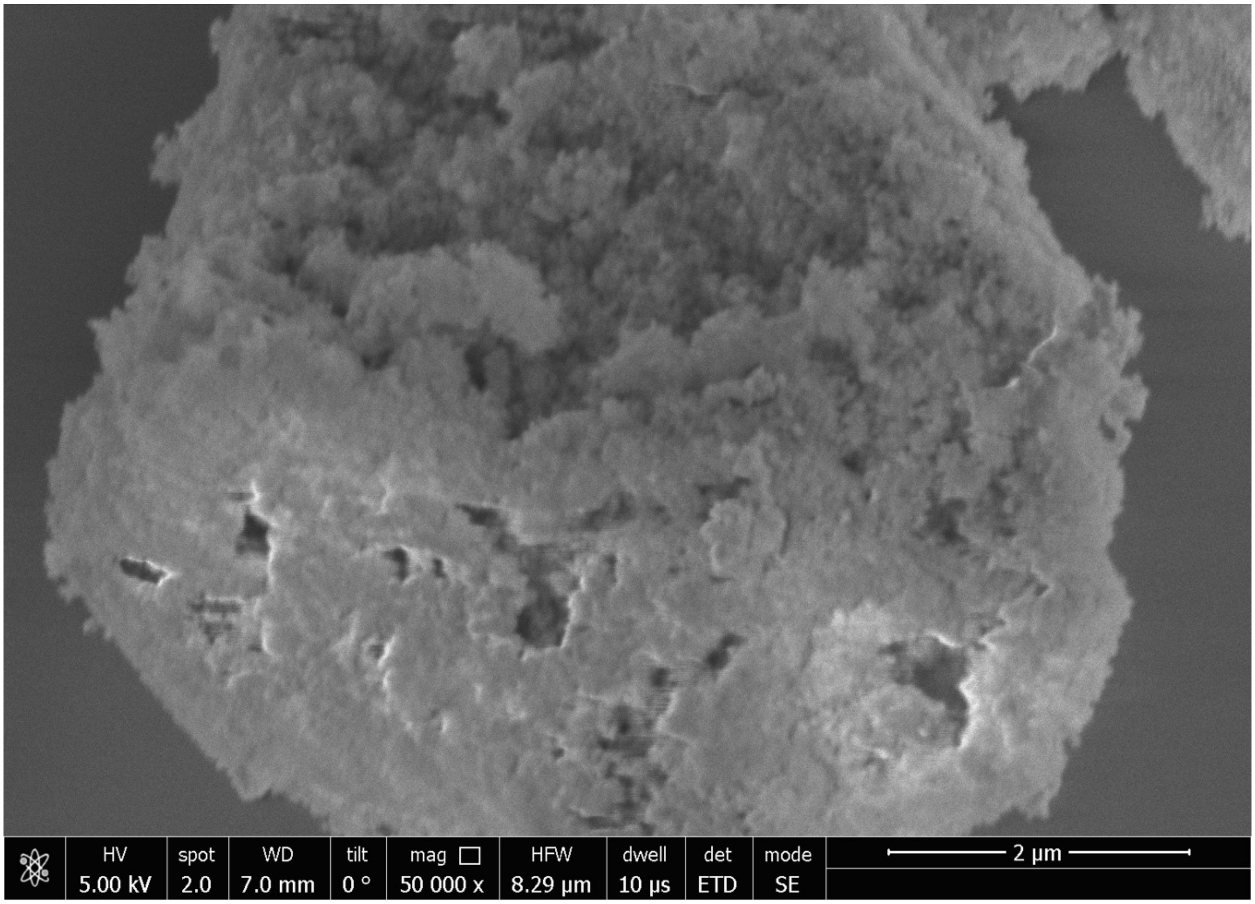


Figure S13. SEM Image of the 50% Ni/12.5% Yb/Al_2O_3 catalyst before reaction.

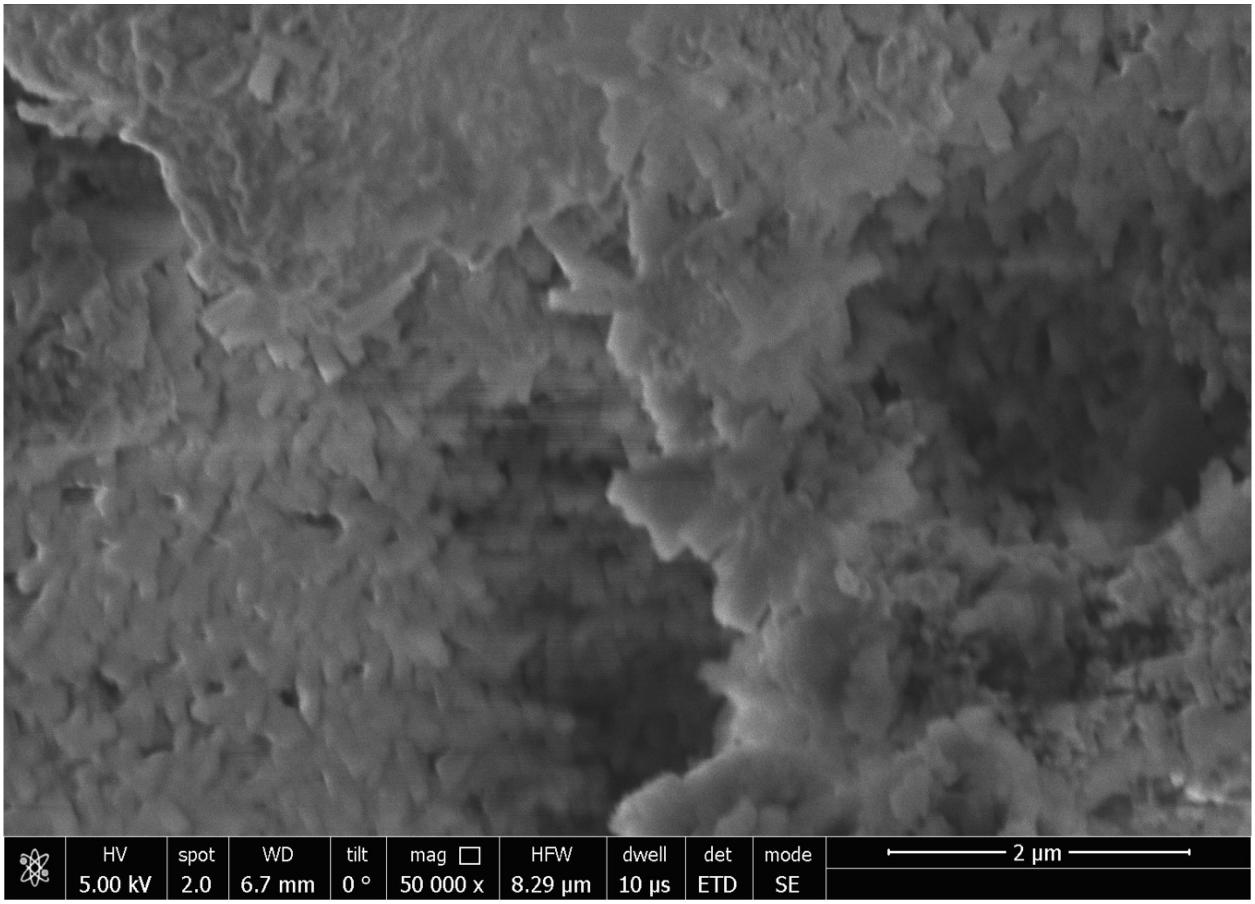


Figure S14. SEM Image of the 50% Ni/12.5% Yb/Al_2O_3 catalyst after reaction (conditions: 300 mg 50% Ni/12.5% Yb/Al_2O_3, 225°C, 50 bar H_2,24 hours, 10 mL DI H_2O, 10 mmol K_2CO_3).

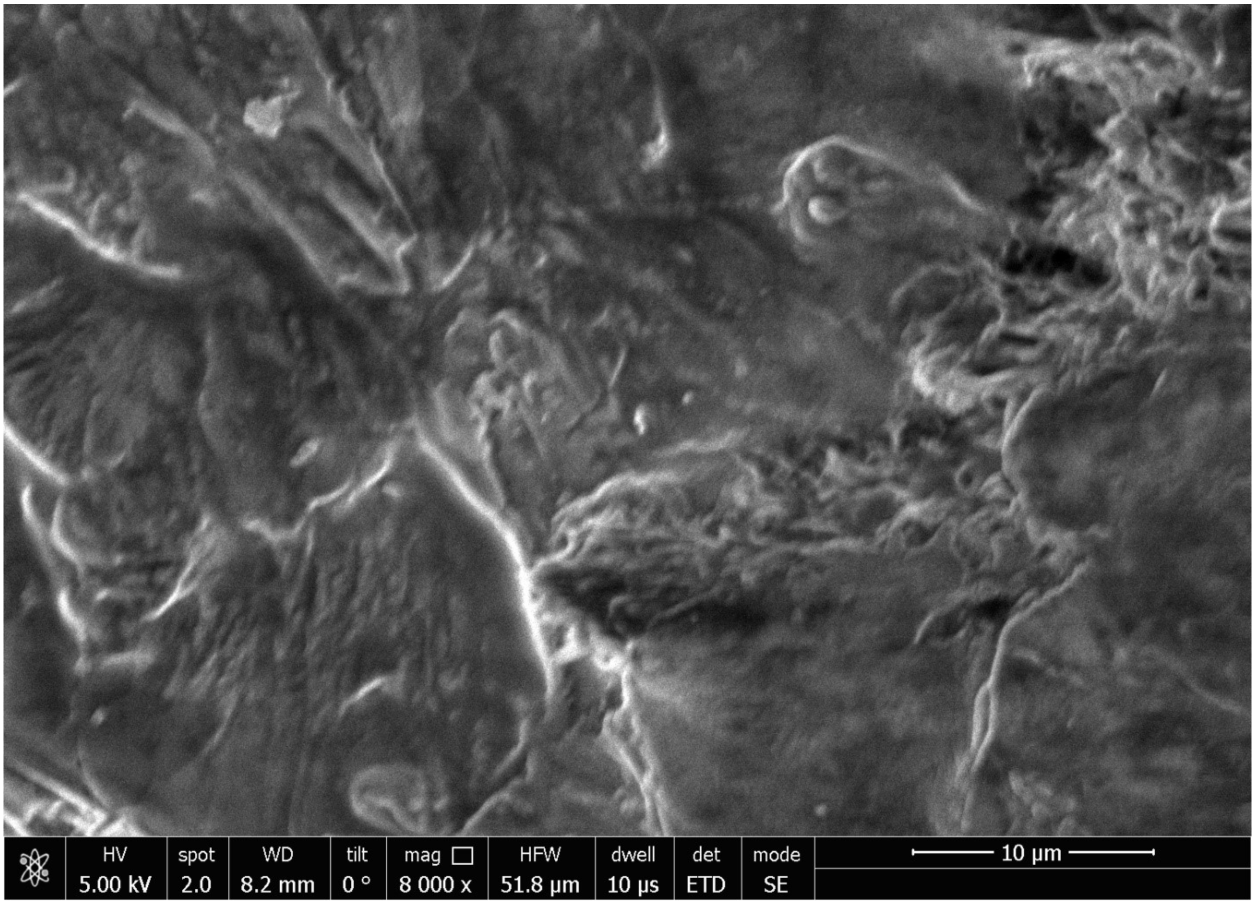


Figure S15. SEM Image of the 50% Ni/12.5% Yb/Al_2O_3 catalyst after 5 cycles of reactivity (conditions: 10 mL DI H_2O, 225°C, 300 mg 50% Ni/12.5% Yb/Al_2O_3, 50 bar H_2 at room temperature, 24 hours. 4 mmol KOH used in first cycle).

BET Data

Brunauer-Emmett-Teller (BET) surface area measurements of select catalysts were collected using Quantachrome Nova 2200E BET instrument. An example Multi BET plot is shown in Figure S16. Summary of surface areas for catalysts and supports are listed in Table S3. Notably, the 12% Ni/SiO_2 catalyst has a much greater surface area than any of the nickel catalysts.

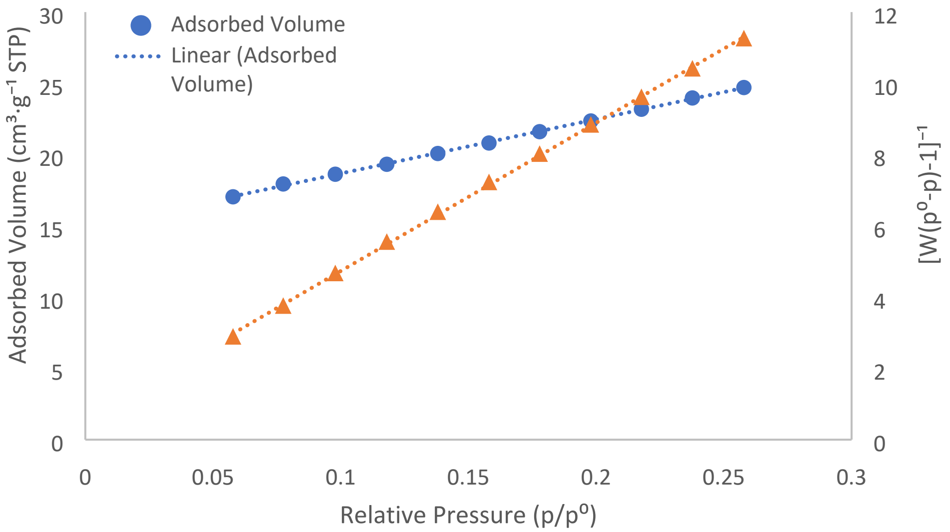


Figure S16. BET surface area graph for 12% Ni/3% Yb/Al_2O_3.

Table S3. Summary of surface area measurements using BET for select catalysts and supports.

Compound	**Surface Area ($m^2 \cdot g^{-1}$)**
Al_2O_3	91.0
SiO_2	255.6
25% Ni/Al_2O_3	61.5
12% Ni/Al_2O_3	68.7
12% Ni/SiO_2	236.4
12% Ni/3% Yb/Al_2O_3	76.9
12% Ni/3% Ce/Al_2O_3	78.2
50% Ni/12.5% Yb/Al_2O_3	47.6

XRF Data

X-Ray Fluorescence was collected for each catalyst in the study to determine if the weight percentages of the elements in the catalysts were correct. Each catalyst's XRF spectrum is shown between 0–60 KeV. The X-Ray source is rhodium, which creates residual rhodium peaks in the spectra. Additional spectra are shown for the Ni/Yb catalysts as the K_α peaks overlap, but the K_β are resolved. The weight percentages of the elements (Ni, Co, Ru, rare earth elements, etc.) were calculated using a Bruker software, Quantexpress, and the results are shown in Table S4.

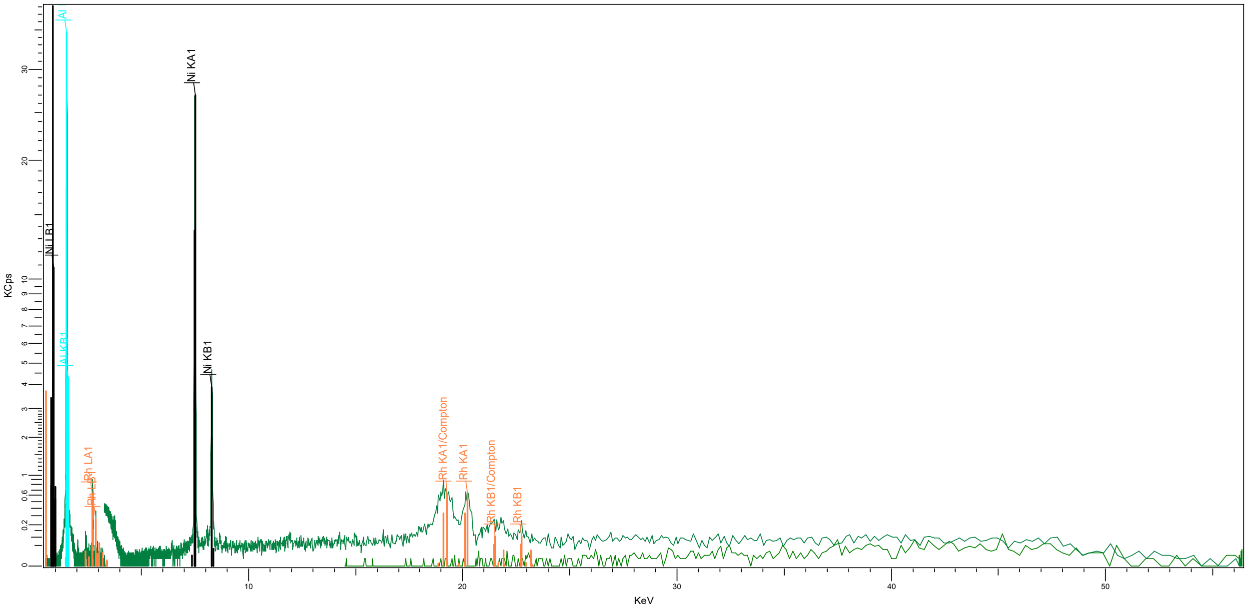


Figure S17. XRF spectra of 12% Ni/Al_2O_3

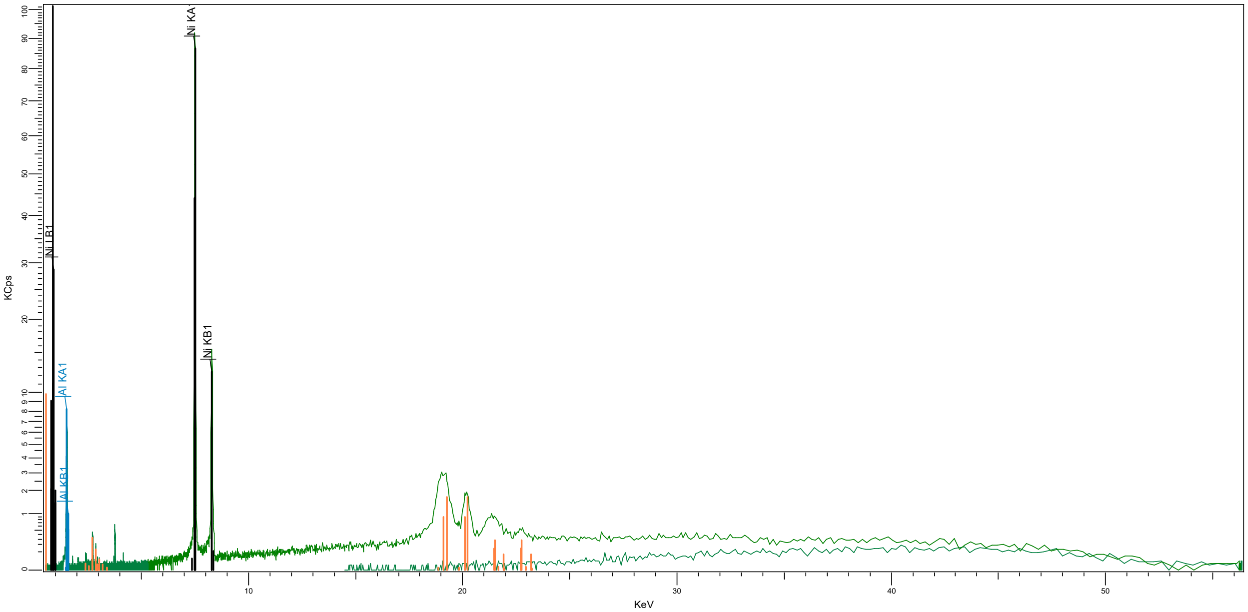


Figure S18. XRF of 25% Ni/Al_2O_3 from 0 to 60 KeV.

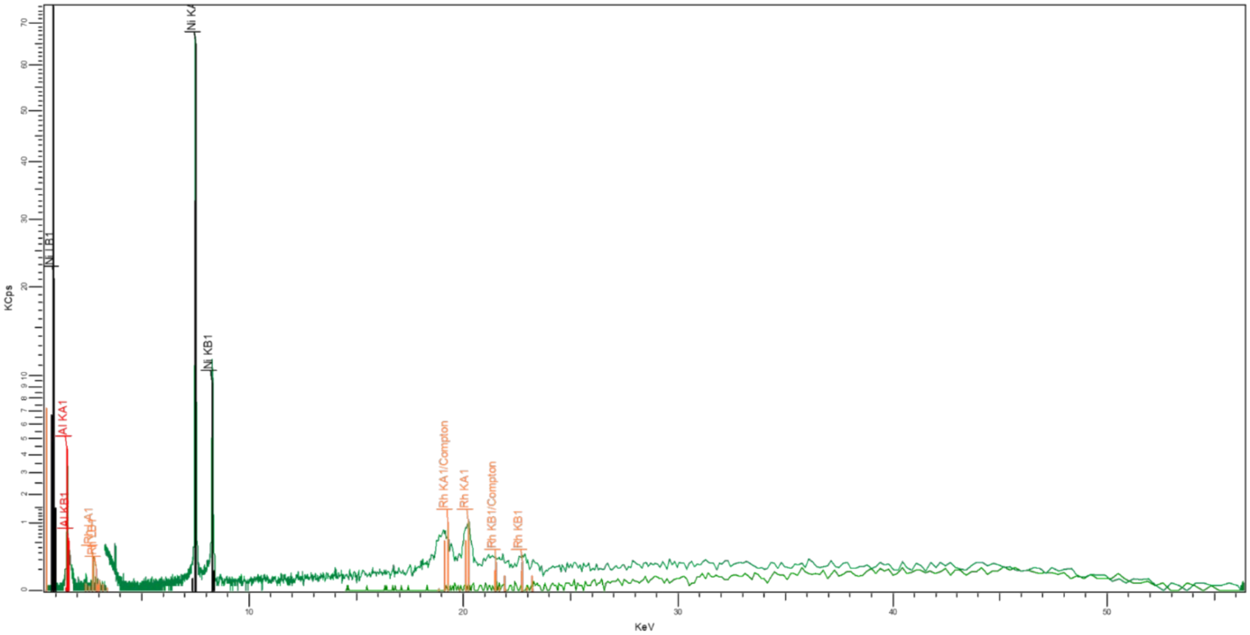


Figure S19. XRF of 33% Ni/Al_2O_3 from 0 to 60 KeV.

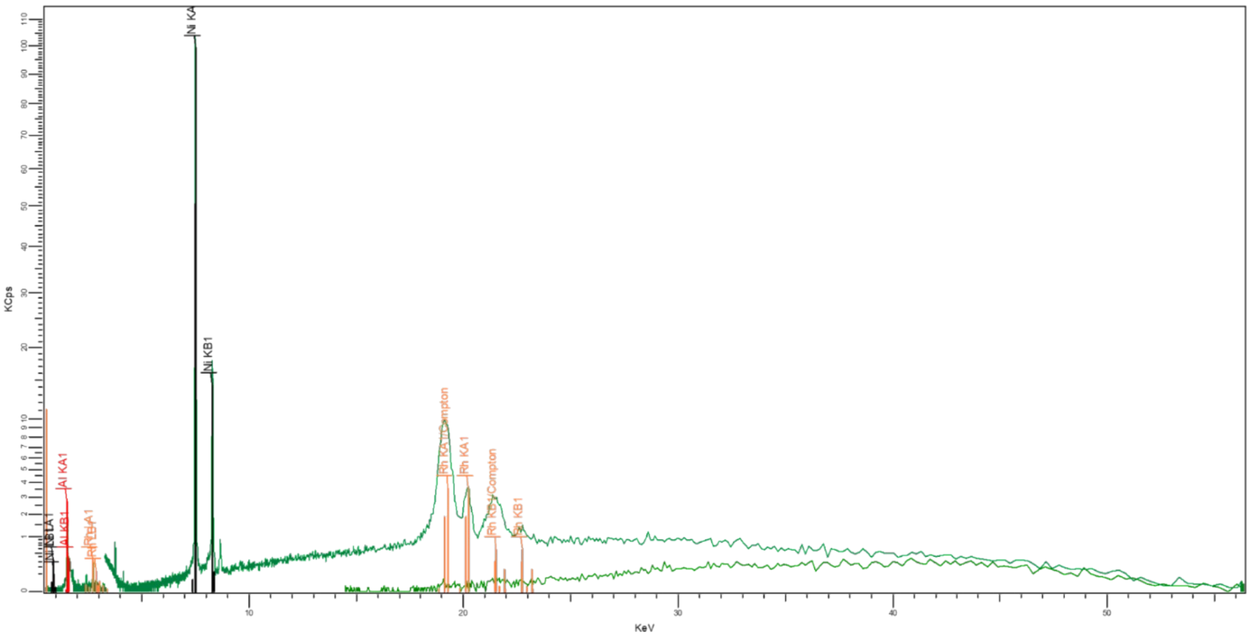


Figure 20. XRF of 50% Ni/Al$_2$O$_3$ from 0 to 60 KeV.

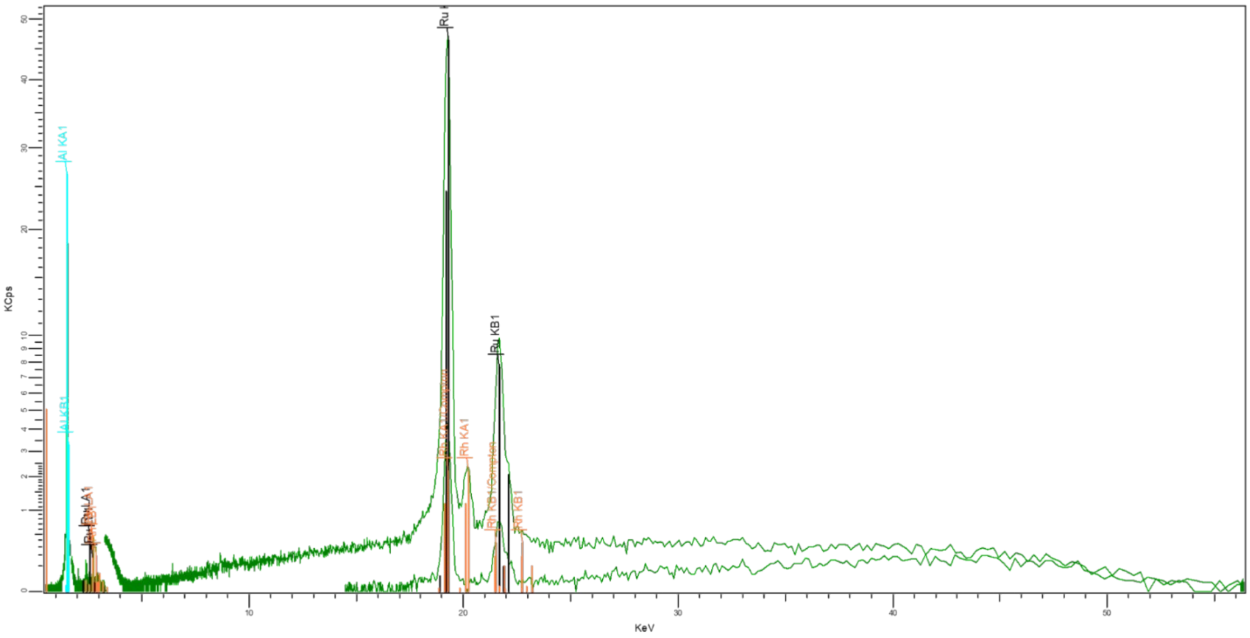
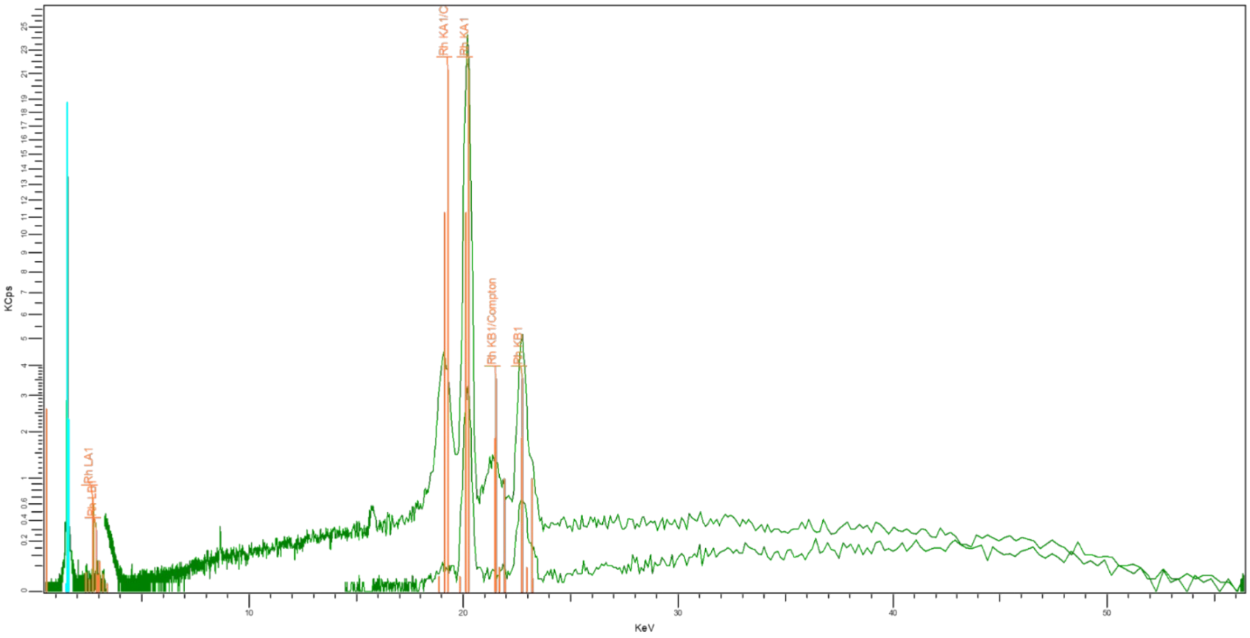


Figure S21. XRF of 5% Ru/Al$_2$O$_3$ from 0 to 60 KeV.



Fiugre S22. XRF of 5% Rh/Al_2O_3 from 0 to 60 KeV.

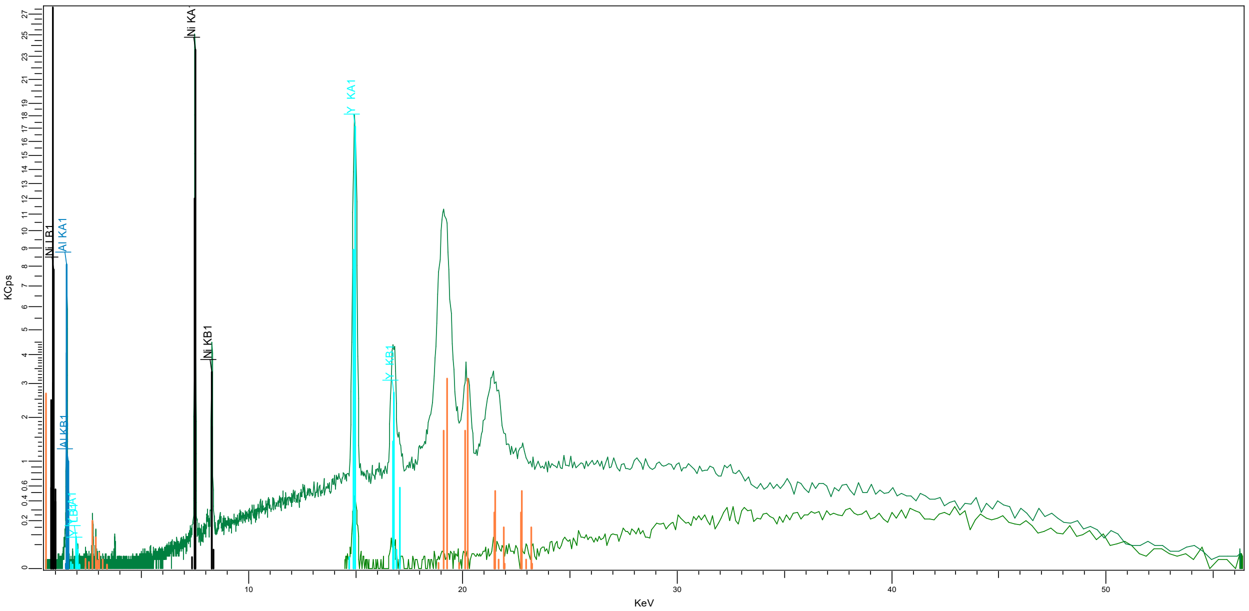


Figure S23. XRF of 12% Ni/3% Y/Al_2O_3 from 0 to 60 KeV.

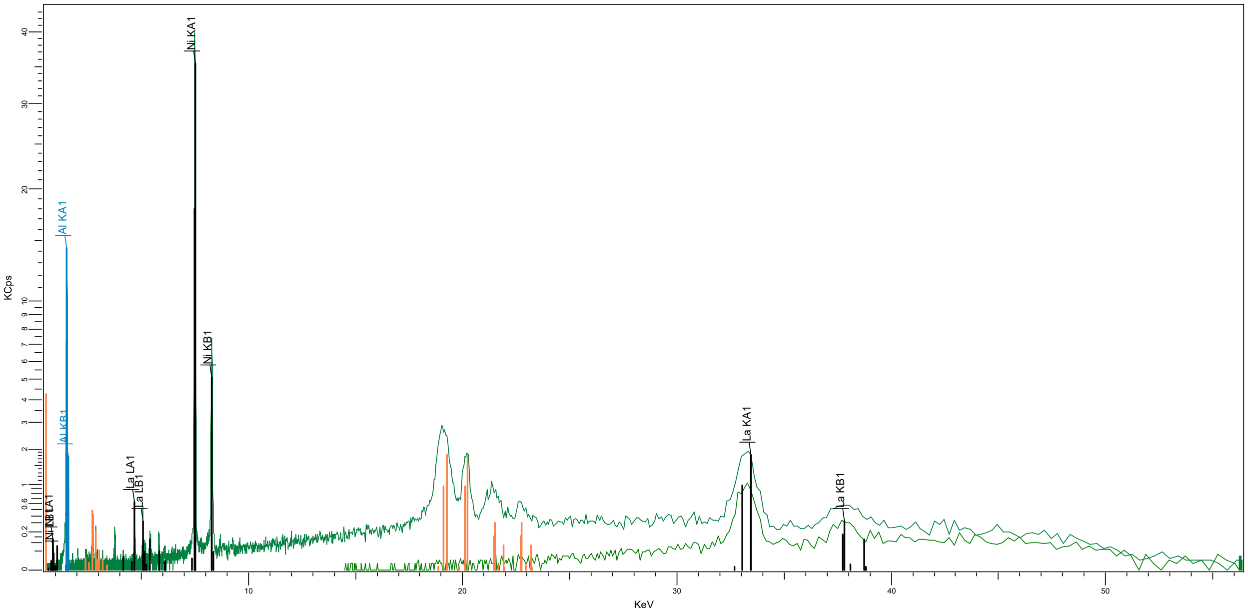


Figure S24. XRF of 12% Ni/3% La/Al_2O_3 from 0 to 60 KeV.

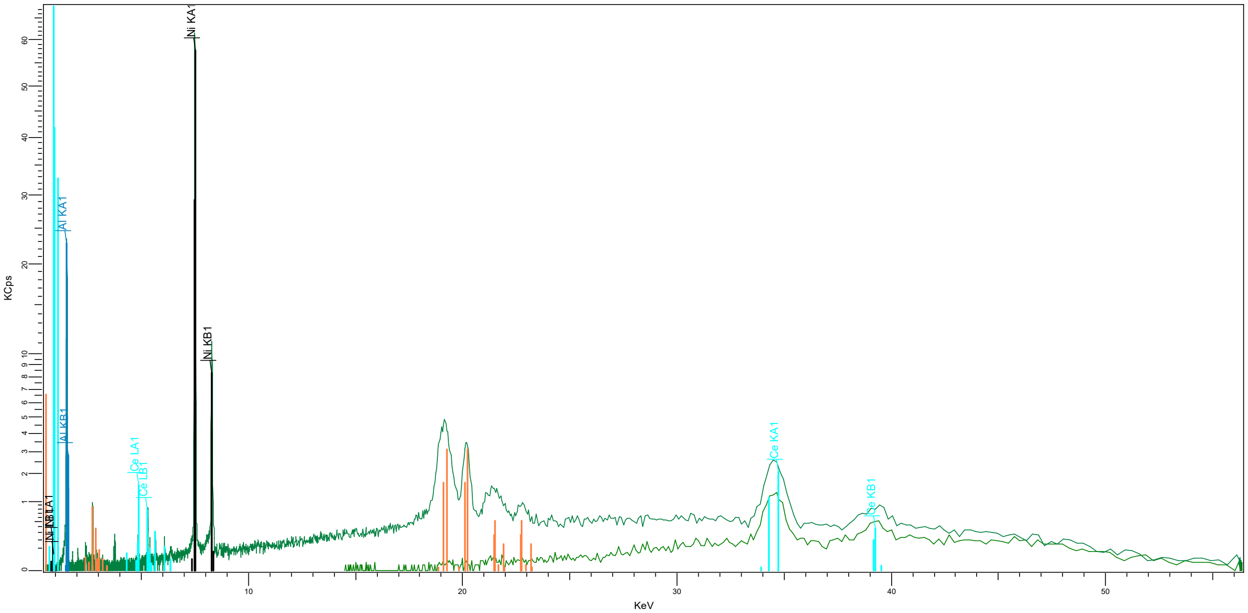


Figure S25. XRF of 12% Ni/3% Ce/Al_2O_3 from 0 to 60 KeV.

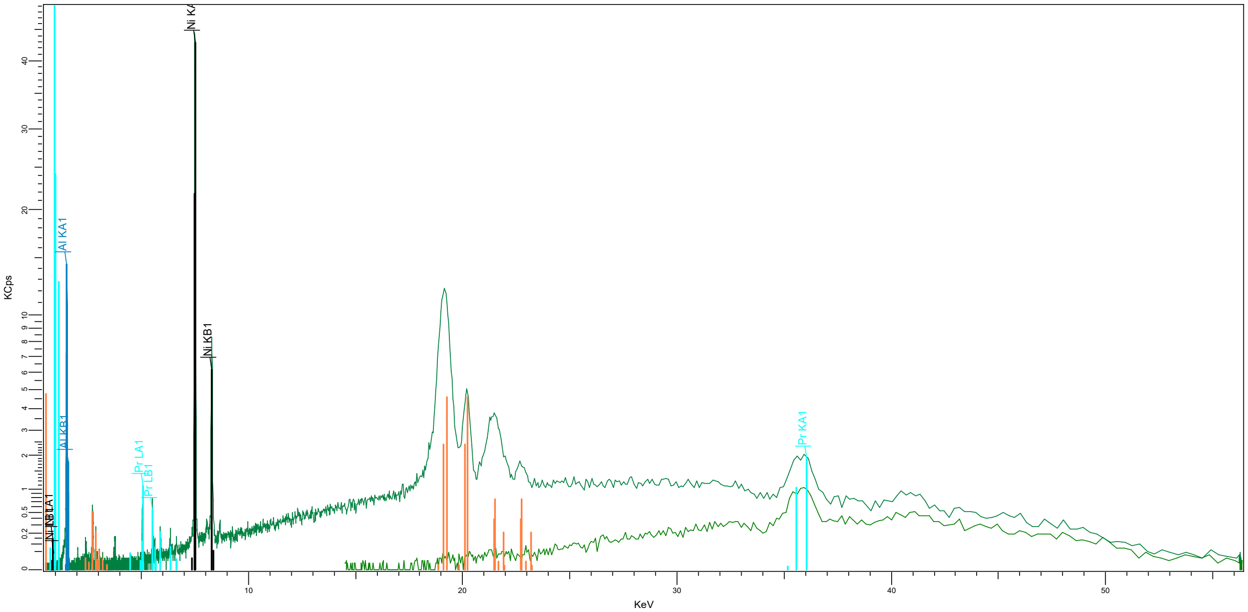


Figure S26. XRF of 12% Ni/3% Pr/Al_2O_3 from 0 to 60 KeV.

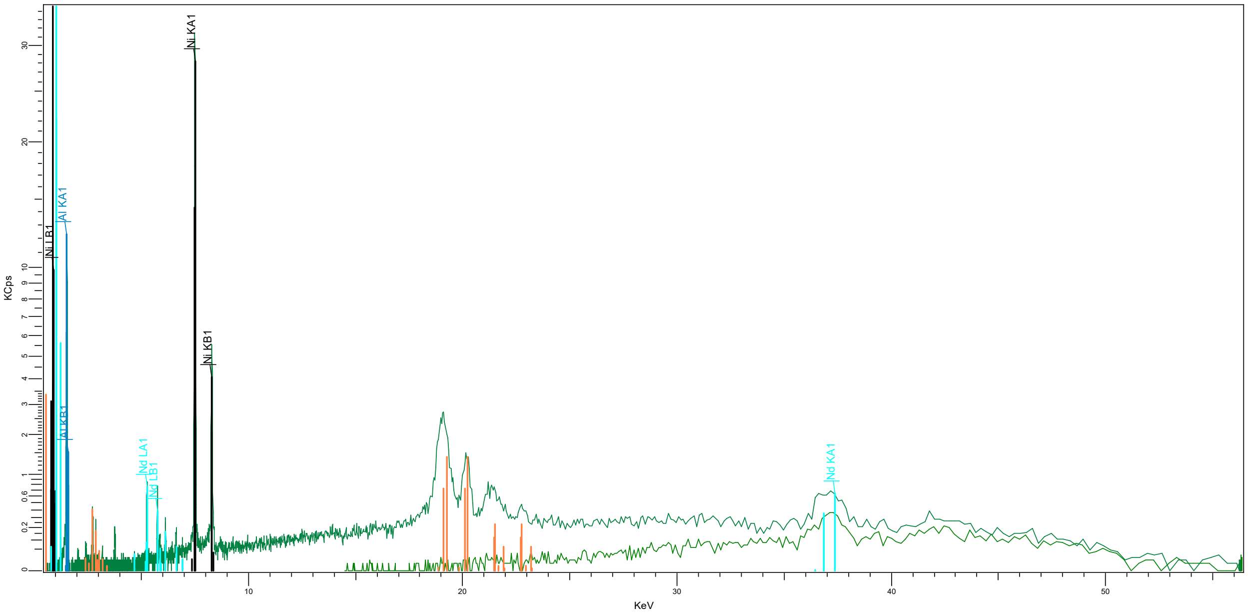


Figure S27. XRF of 12% Ni/3% Nd/Al_2O_3 from 0 to 60 KeV.

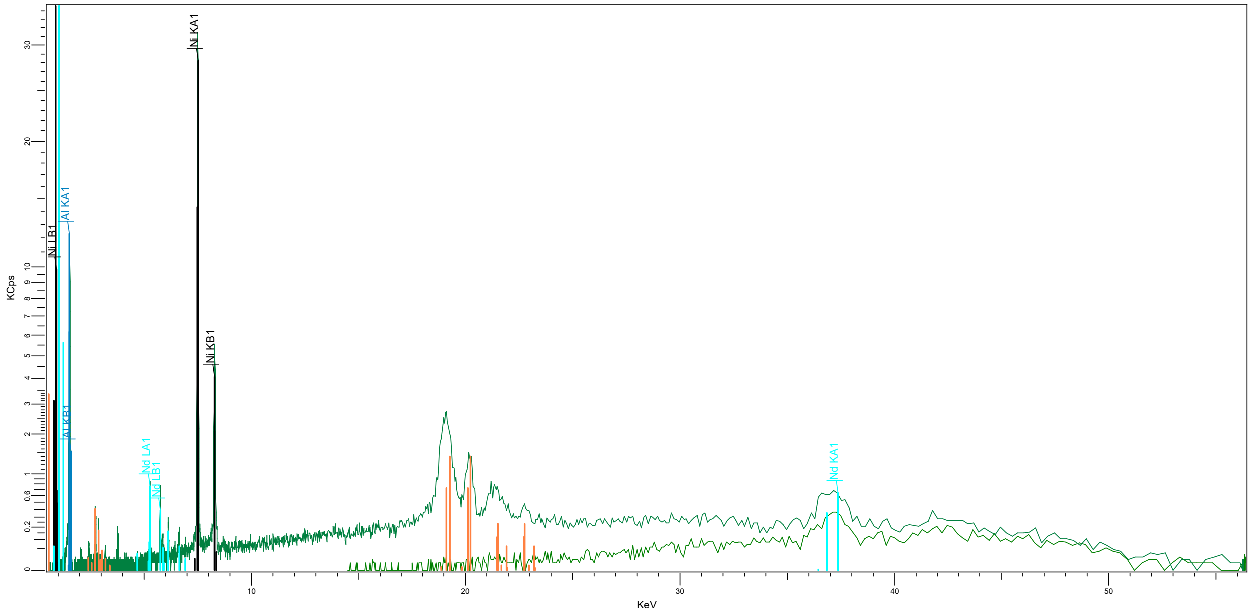


Figure S28. XRF of 12% Ni/3% Sm/Al_2O_3 from 0 to 60 KeV.

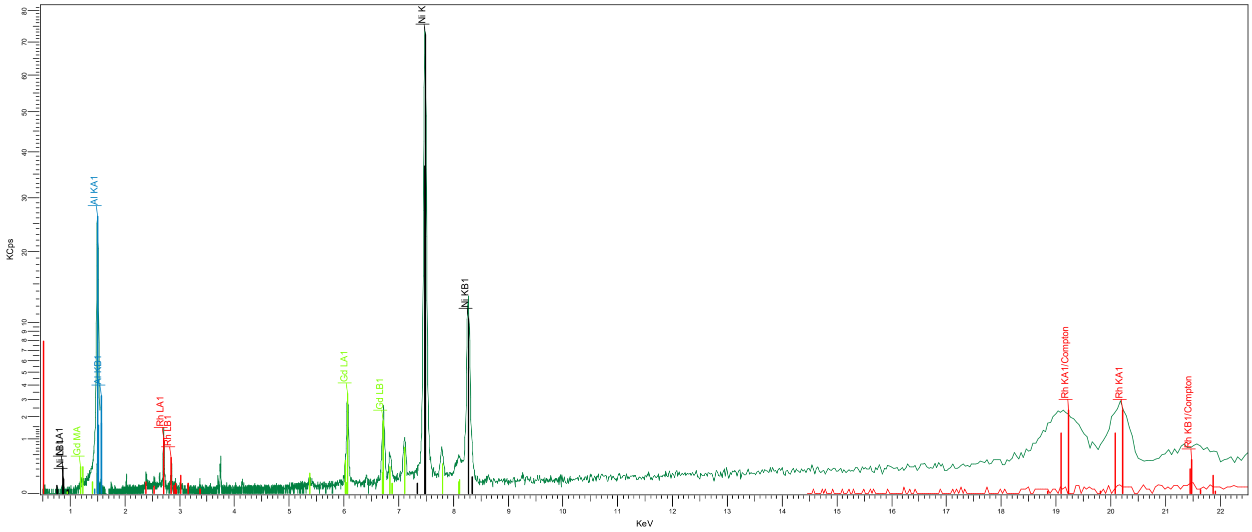
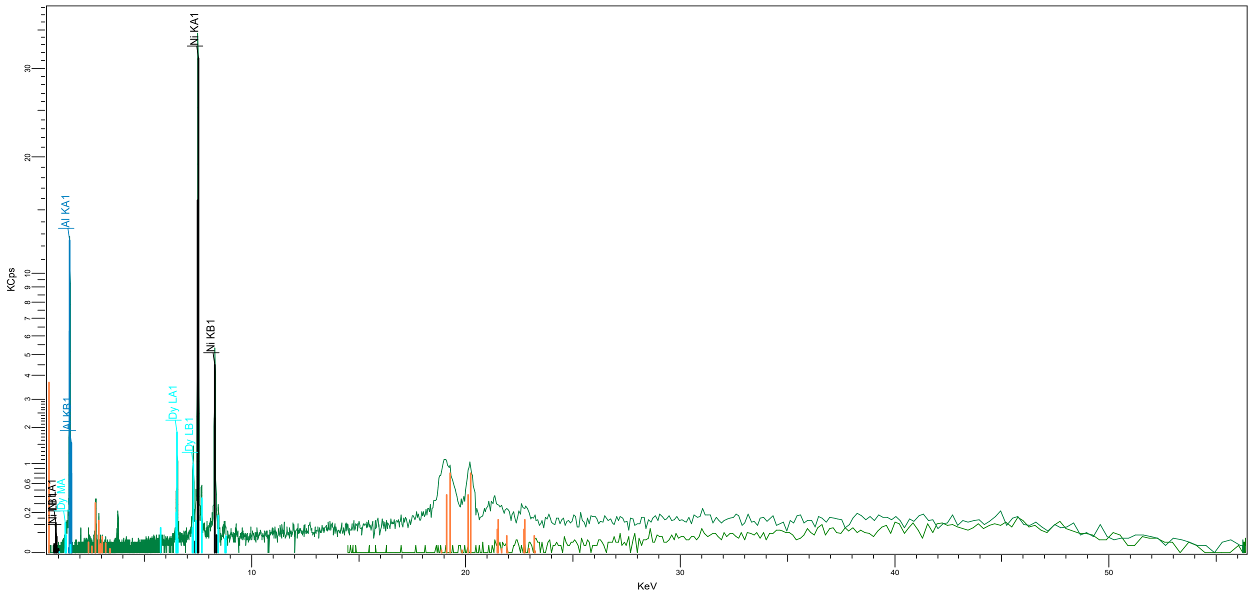


Figure S29. XRF of 12% Ni/3% Gd/Al_2O_3 from 0 to 22 KeV.



Fiugre S30. XRF of 12% Ni/3% Dy/Al_2O_3 from 0 to 60 KeV.

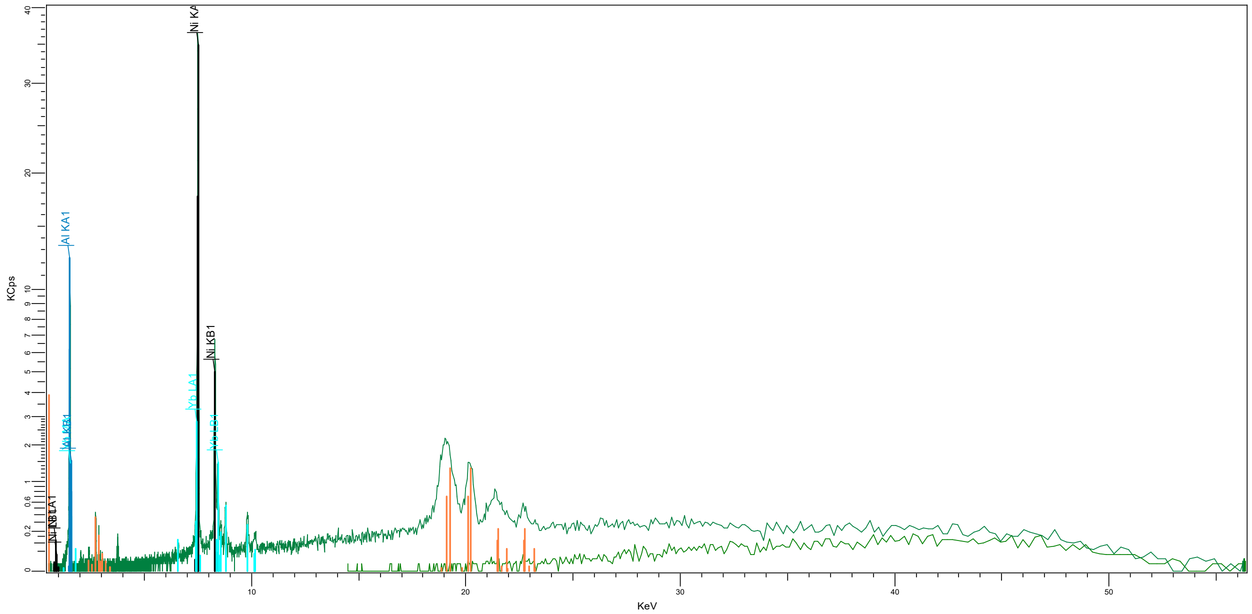


Figure S31. 12% Ni/3% Yb/Al_2O_3 from 0 to 60 KeV.

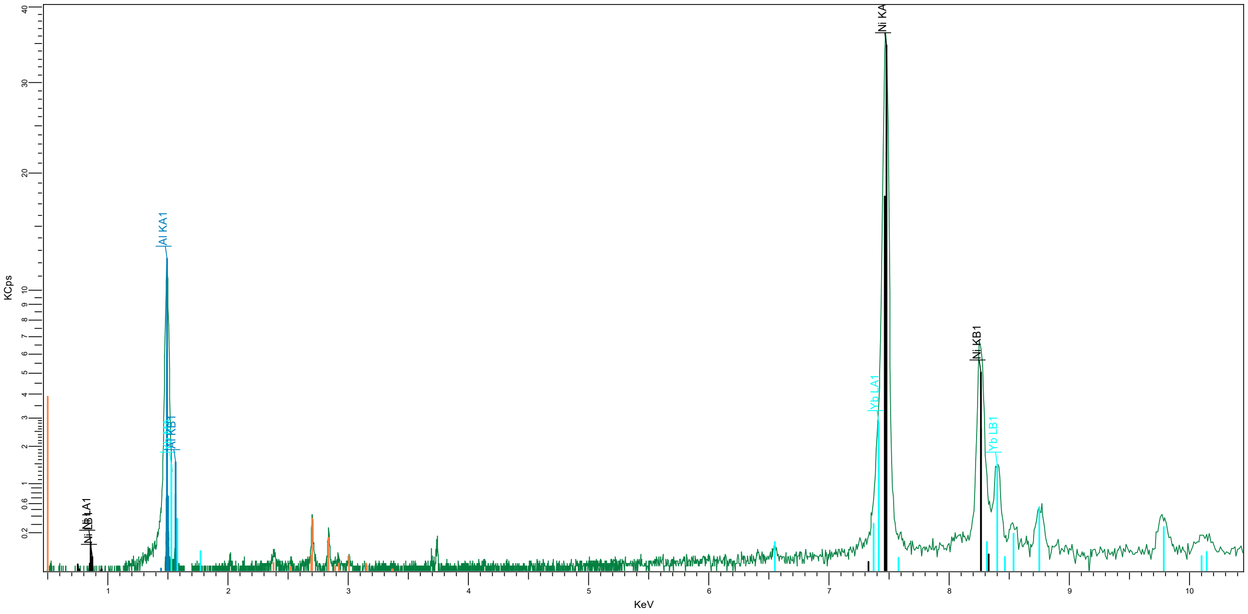


Figure S32. 12% Ni/3% Yb/Al_2O_3 from 0 to 11 KeV.

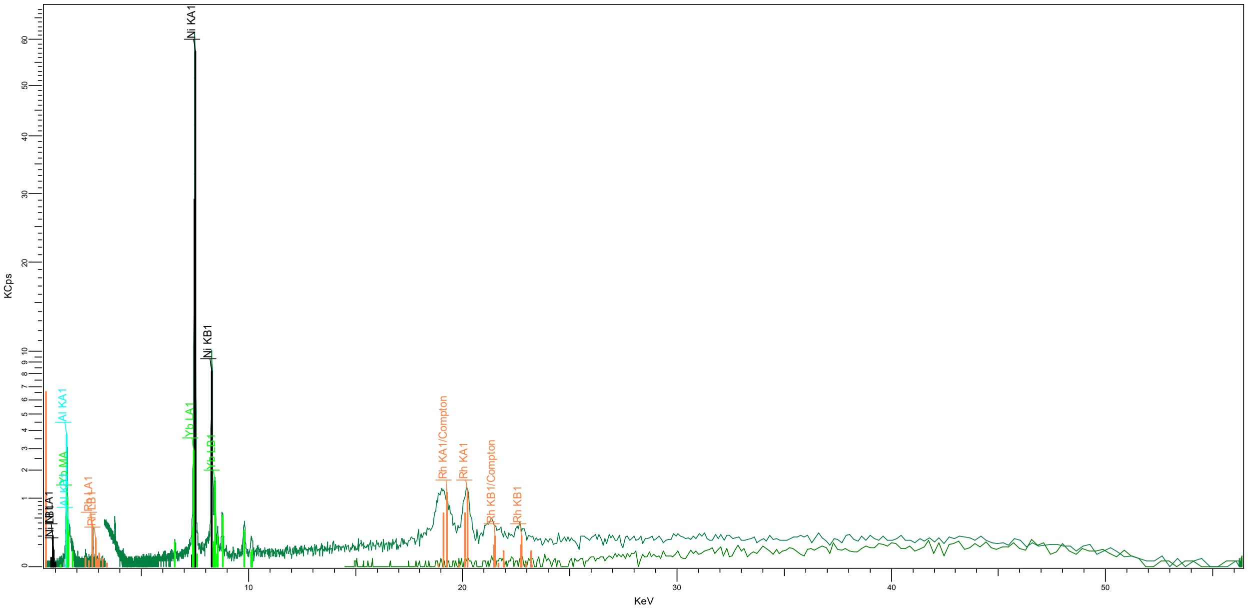


Figure S33. 33% Ni/8% Yb/Al_2O_3 from 0 to 60 KeV.

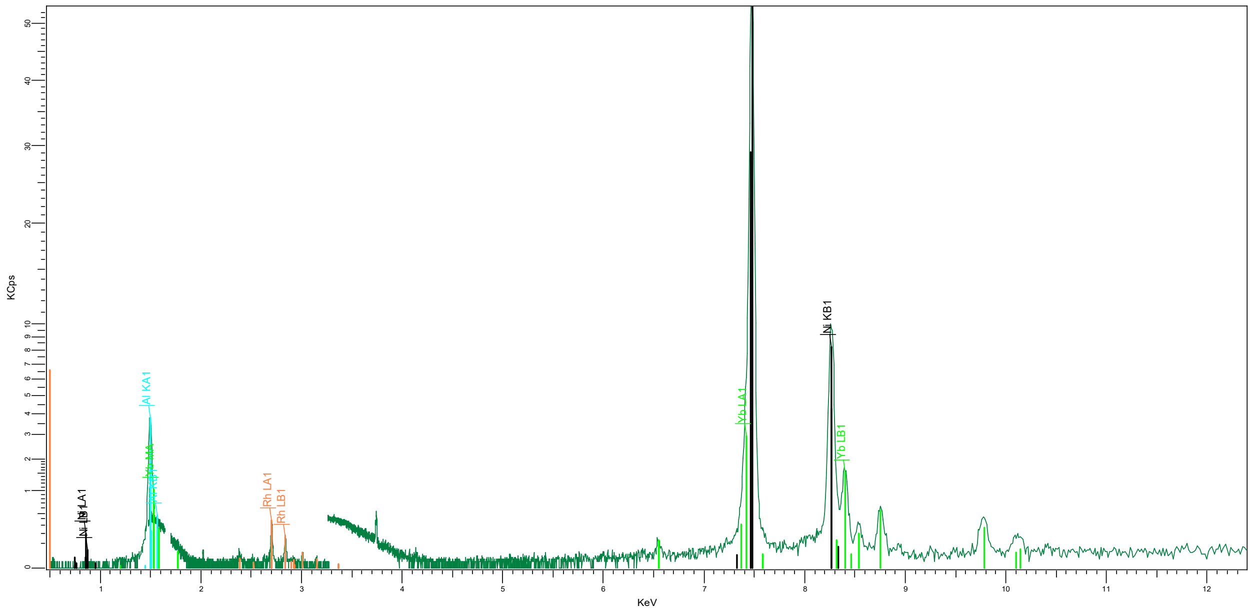


Figure S34. 33% Ni/8% Yb/Al_2O_3 from 0 to 11 KeV.

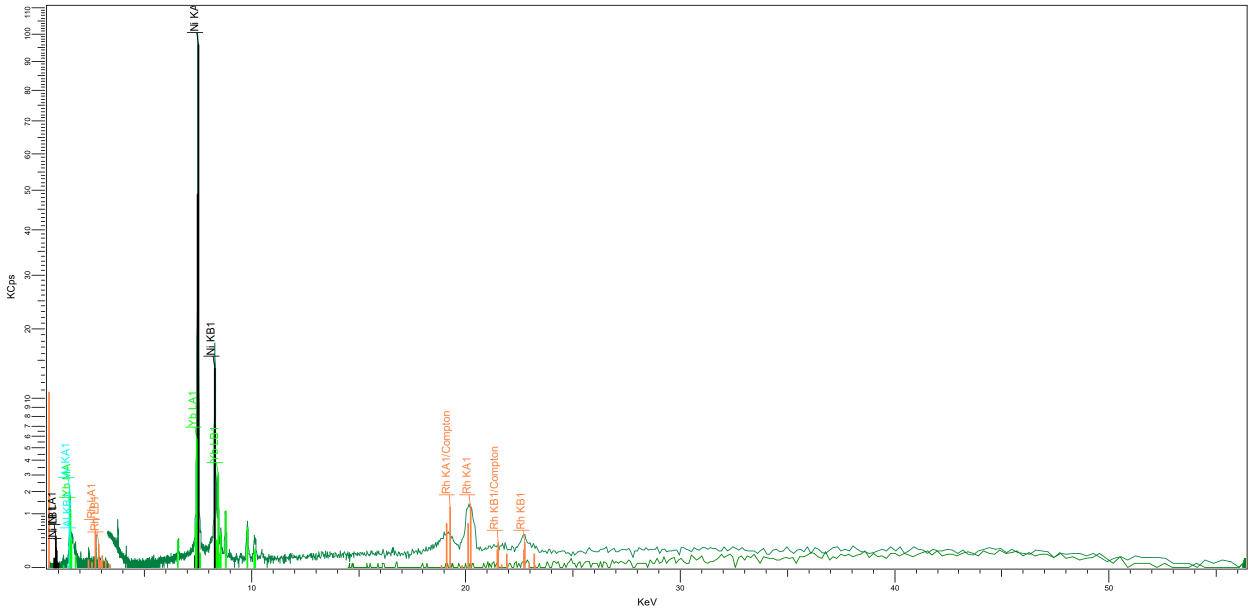


Figure S35. XRF of 50% Ni/12.5% Yb/Al_2O_3 from 0 to 60 KeV.

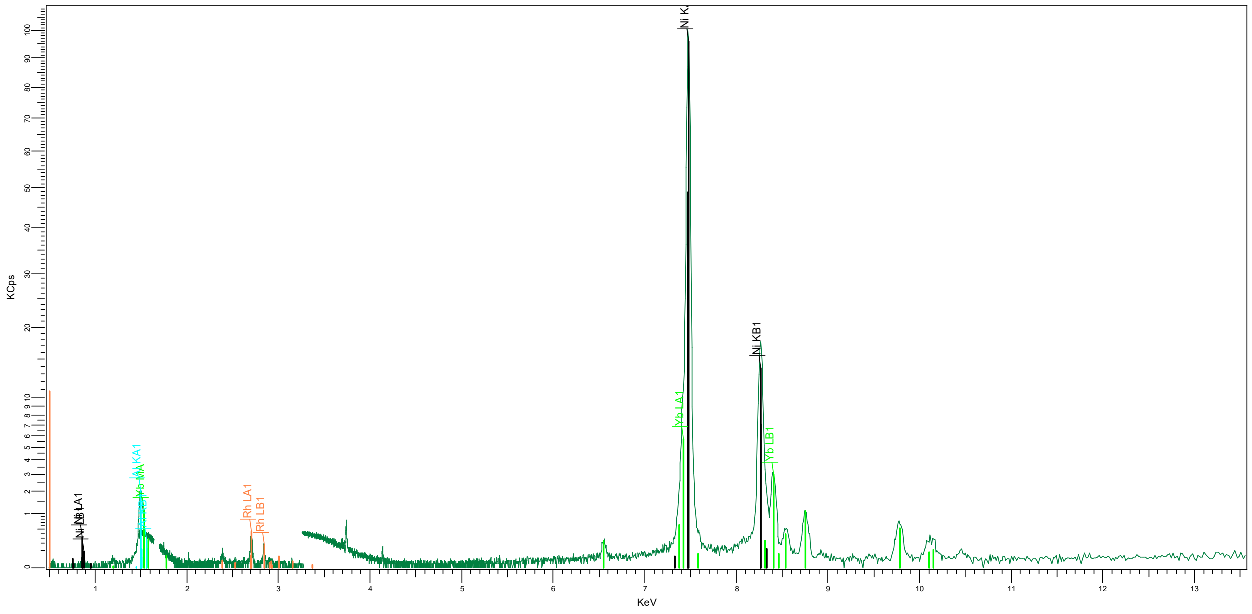


Figure S36. XRF of 50% Ni/12.5% Yb/Al_2O_3 from 0 to 11 KeV.

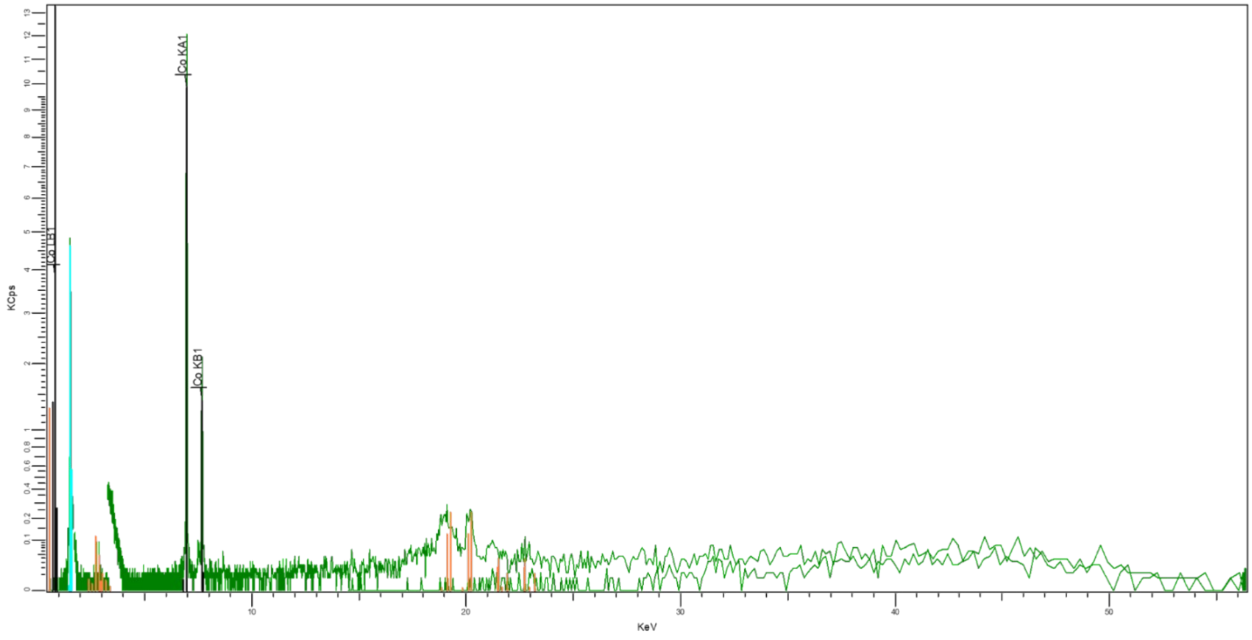


Figure S37. XRF of 12% Co/Al_2O_3 from 0 to 60 KeV.

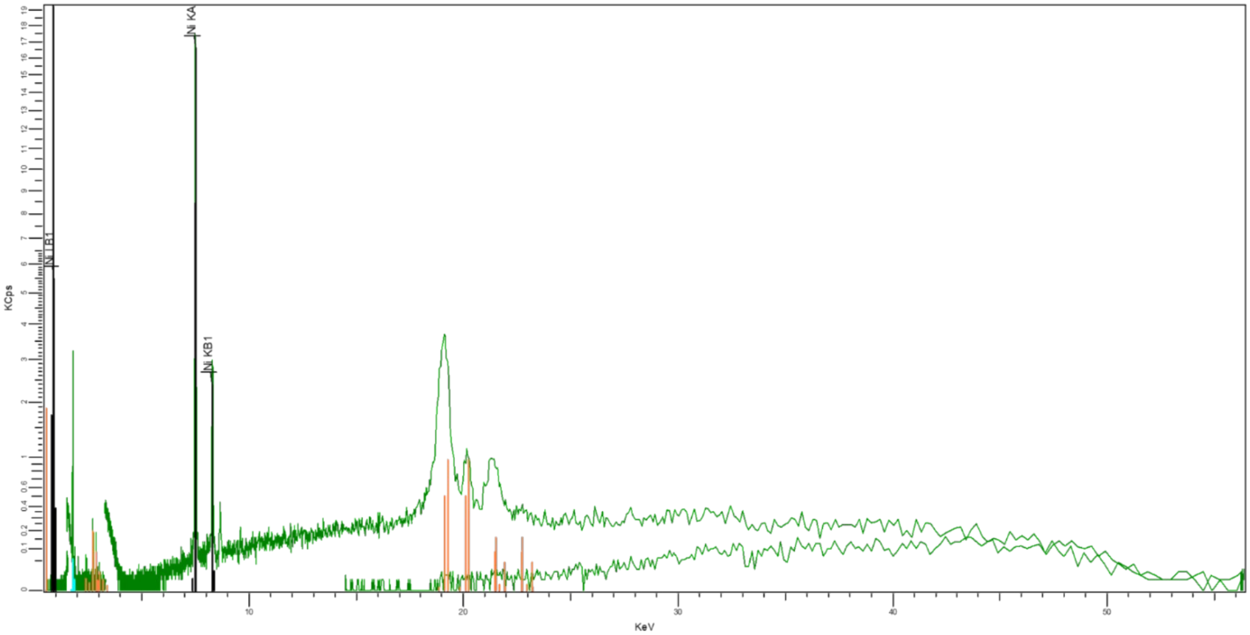


Figure S38. XRF of 12% Ni/SiO$_2$ from 0 to 60 KeV.

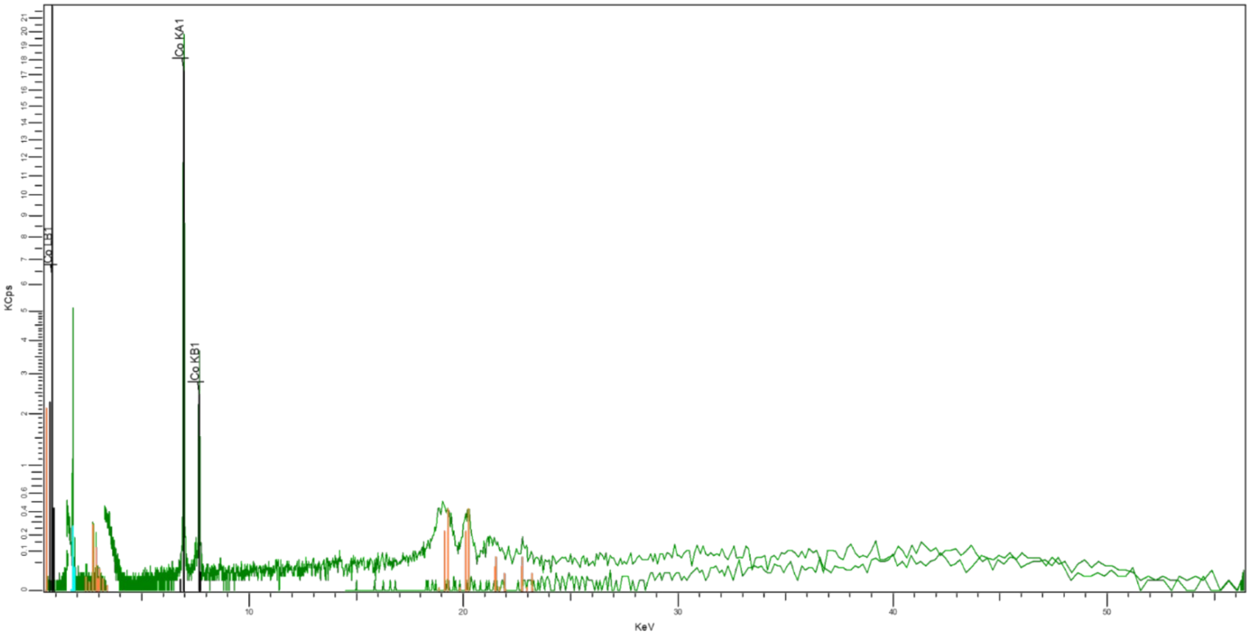


Figure S39. XRF of 12% Co/SiO$_2$ from 0 to 60 KeV.

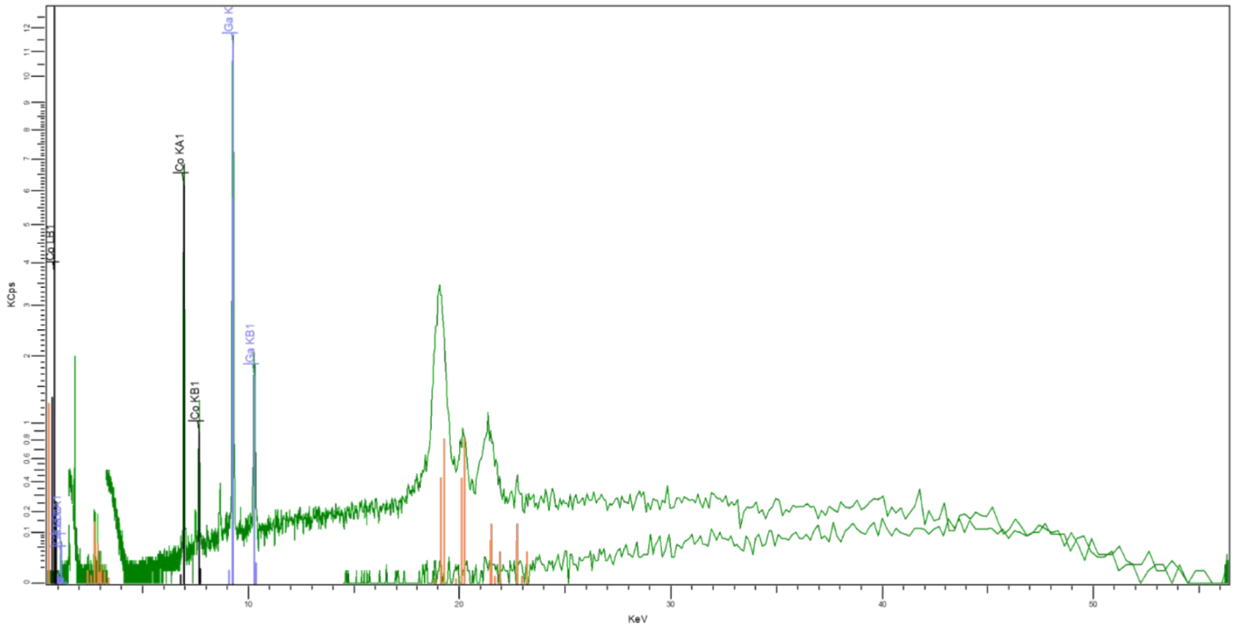


Figure S40. XRF of 17% CoGa/SiO_2 from 0 to 60 KeV.

Table S4. Weight percentages of metals in all the catalysts utilized.

Catalyst	main metal (%)	Promoter (%)
12% Ni/Al_2O_3	10.23±0.63	N/A
25% Ni/Al_2O_3	25.80±0.35	N/A
33% Ni/Al_2O_3	32.78±0.40	N/A
50% Ni/Al_2O_3	50.29±0.26	N/A
5% Ru/Al_2O_3	6.27±1.62	N/A
5% Rh/Al_2O_3	5.15±1.87	N/A
12% Ni/3% Y/Al_2O_3	9.63±0.66	2.09±0.82
12% Ni/3% La/Al_2O_3	12.20±0.53	3.89±4.10
12% Ni/3% Ce/Al_2O_3	15.10±0.43	5.55±3.23
12% Ni/3% Pr/Al_2O_3	10.00±0.50	5.04±3.24
12% Ni/3% Nd/Al_2O_3	9.53±0.6	3.92±4.05
12% Ni/3% Sm/Al_2O_3	9.65±0.67	3.83±3.45
12% Ni/3% Gd/Al_2O_3	12.95±0.38	4.17±1.86
12% Ni/3% Dy/Al_2O_3	10.00±0.57	3.96±2.60
12% Ni/3% Yb/Al_2O_3	10.60±0.55	4.12±4.21
33% Ni/8% Yb/Al_2O_3	34.98±0.86	8.12±4.26
50% Ni/12.5% Yb/ Al_2O_3	51.19±1.33	10.5±2.49
12% Ni/3% Cu/Al_2O_3	13.10±0.37	3.14±0.67

12% Co/Al_2O_3	11.64±0.97	N/A
12% Ni/SiO_2	10.02±1.60	N/A
12% Co/SiO_2	13.00±1.48	N/A
7% Co/11% Ga/SiO_2	6.76±2.27	11.24±2.31

Carbonate Thermogravimetric Analysis and Solubility Data

TGA data that showcases the temperature of decomposition of various carbonates used in this study is depicted in Figure S41. The data for Cs_2CO_3 was measured by heating the sample from 25°C to 1000°C at a rate of 10°C/min in an air atmosphere. The data for the other carbonates was adapted from the literature. The lowest of these thermal decomposition temperatures is for calcium carbonate, starting at about 600°C. The decomposition temperature of all carbonates was significantly higher than the 200-250 °C used in the hydrogenation reaction presented in this paper. This could indicate that the carbonate salts themselves are being directly converting into methane rather than CO_2 desorbing from the carbonate and that resulting CO_2 being converted to methane. Table S5 displays the solubility in water of the carbonates used in this study.

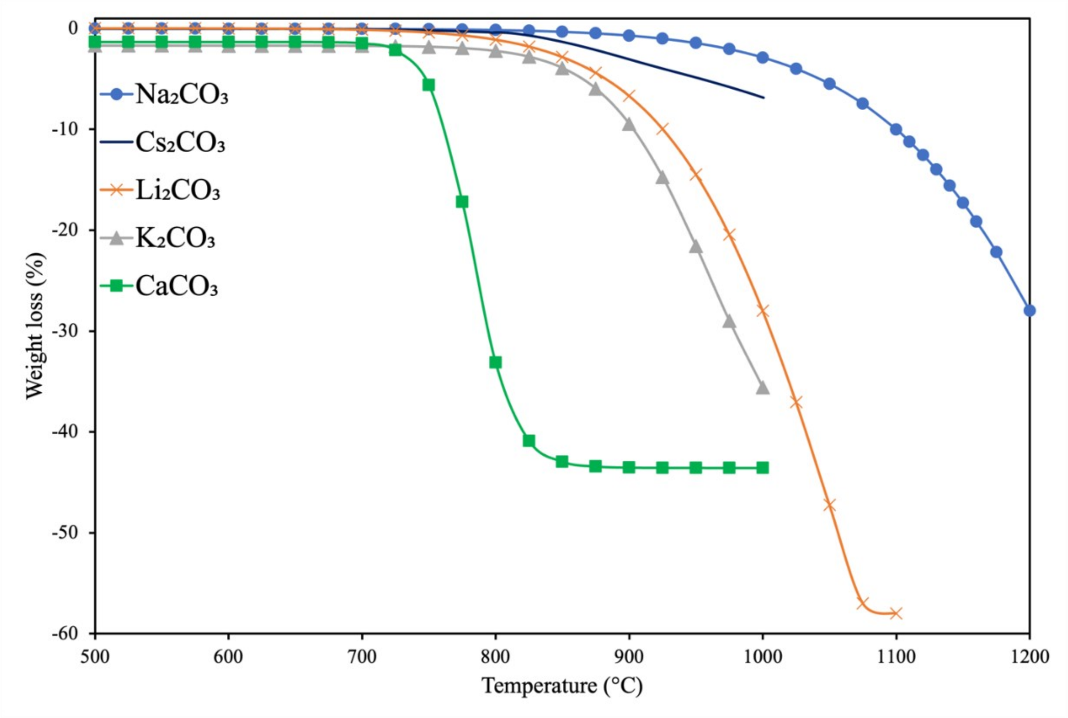


Figure S41. Thermogravimetric analysis of the carbonates used in this study. Data for Li_2CO_3 and Na_2CO_3 obtained from [1]. Data for K_2CO_3 obtained from [2]. Data for $CaCO_3$ obtained from [3]. Decomposition of $CsCO_3$ measured by TGA on a TA instrument SDT650 using a 10°C·min^{-1} heating rate.

Table S5. Solubility of carbonates in water.

Carbonate Salt	Solubility (g/L)	Temperature (°C)
Li_2CO_3	12.9	25
Na_2CO_3	340	28
K_2CO_3	1103	20
Cs_2CO_3	2605	15
$MgCO_3$	0.139	25
$CaCO_3$	0.013	25

Catalyst Cost Assessment

The bulk prices for commercially available 5% Ru/Al_2O_3 and 5% Rh/Al_2O, and nickel metal precursors were extrapolated from lab-scale pricing. First, lab-scale prices at different pack sizes for the compound of interest were found using reputable vendors and fitted to a power function (Equation S3). A log-log regression of the fitted data was used to extrapolate the bulk cost for a large commercial substance purchase of 1100 kg and compared to Alibaba. The price of the nickel-ytterbium, ruthenium, and rhodium catalysts were estimated using CatCost, a program developed by the Energy Material Network from the U. S. Department of Energy.[4-5] The assumptions for all cost analyses using a process template of “Metal on Metal Oxide – Incipient Wetness” are shown in Table S6. The step method was chosen as “Metal (Earth Abundant) on Metal Oxide”. The assumptions for the bulk cost of all raw materials are listed in Table S7 These costs were then converted to the price of catalyst per kilogram of methane produced using 300 mg of catalyst and the methane generated from the reaction (Equation S4). The price of each catalyst in USD dollar per kilogram of methane produced ($\$_{cat} \cdot kg_{methane}^{-1}$) using the step, CapEx/OpEx, and combined methods from CatCost are listed in Table S8. The net cost of each catalyst was calculated for a three-year catalyst lifetime at a rate of one cycle per day. The ytterbium promoted nickel catalysts were shown to be more cost effective than unpromoted nickel, ruthenium, and rhodium counterparts. These numbers represent the input cost of the catalyst to produce methane.

Equation S3. Power function where unit price p is the quote price P divided by quote quantity Q. The scaling parameter b and discount factor γ is used to calculate p.

$$p\,(Q) = b \times Q^{\gamma}$$

Table S6. Assumptions for the economics for the catalyst preparation .

Basis Year	**2022**
Currency	USD ($)
Step Method Inputs	
Synthesis Campaign Size	30 ton
Synthesis Time	3.0 days
Cleaning Time	1.0 days
G&A Overhead	5%
SARD Overhead	5%
Selling Margin	23%
CapEx and OpEx Factors Inputs	
Annual Production	1.2×10^6 kg
Capacity Factor	100%
Operating Hours (Labor)	8760 hrs
On-Stream Factor	90%
Operating Hours (Production)	7884 hours
Design Production Rate	1.52×10^2 kg/hr
Plant Life	20 years
Return on Capital Invested ROI (pre-tax)	25%

Table S7. Assumptions for the raw materials for the catalyst preparation.

General			
Losses Due to Waste/Spoilage	3%		
Material Prices[6-10]	**Calculated**	**Alibaba**[11-14]	
$Ni(NO_3)_2$ $6H_2O$	\$10.08/kg	\$10-15/kg	
$Yb(NO_3)_3$ $5H_2O$[a]	\$4.52/kg	\$3-15/kg	
$RuCl_3$ xH_2O	\$36,400/kg	\$40,000-50,000/kg	
$RhCl_3$ xH_2O	\$351,900/kg	\$280,000-350,000/kg	
Alumina	\$3.12/kg	-	
Ammonium Nitrate	\$0.35/kg	-	
Water	\$0.001/kg	-	
Hydrogen	\$1.01/kg	-	
Nitrogen	\$0.22 /kg	-	
Compressed Air	\$0.02/kg	-	
Utilities	**Cost**		
Cooling Water	\$0.14/gal		
Process Water	\$1.3/gal		
Steam, 150 psig	\$5/ton		
Steam, 600 psig	\$5.7/ton		
Electricity	\$0.06/kWh		
Natural gas	\$3/MMBtu		
Equipment	**Quantity**	**Material**	**Size**
Carbon steel bin	1	Carbon steel	53.3 ft^3
Carbon steel feeder, belt	1	Carbon steel	35.7 ft^3/hr
Reactor, jacketed, agitated	1	Carbon steel	2.4 m^3
Reactor, jacketed, agitated	1	Carbon steel	3.0 m^3
Heat exchanger, U-tube shell and tube	1	Carbon steel	0.5 m^2
Compressor, rotary twin-screw, electric motor	2	Cast iron	85.8 hp
Fan, centrifugal backward-curved, 0–4 in H2O head	1	Carbon steel	16.9 ACFM
Tank, cone roof (Seider)	1	Carbon steel	200 gal
Tank, cone roof (Seider)	1	Carbon steel	20,000 gal
Tank, cone roof (Seider)	1	Carbon steel	22,000 gal
Water ion exchange plant	1	Carbon steel	1.2 m^3/hr

[a]estimated from two vendors since not enough data points were found from a single vendor.

Equation S4. Formula to calculate the cost of the catalyst in dollars of catalyst per kilogram of methane produced.

$$\frac{\$_{cat}}{kg_{cat}} \times \frac{3 \times 10^{-4}\, kg_{cat}}{kmol_{methane}} \times \frac{1000\, kmol_{methane}}{16040\, kg_{methane}} = \frac{\$_{cat}}{kg_{methane}}$$

Table S8. Summary of cost and value-added of each catalyst for a three-year lifetime. The number of cycles taken were relative to reaction duration. For example, 24 h is 1095 cycles and 6 h is 4380 cycles.

Catalyst	Time	Step Method	CapEx/OpEx	Combined
5% Rh/Al_2O_3				
Cost ($\$_{cat} \cdot kg_{cat}^{-1}$)		50,190	42,630	42,630
Cost ($\$_{cat} \cdot kg_{methane}^{-1}$)	24 h	612	520	520
5% Ru/Al_2O_3				
Cost ($\$_{cat} \cdot kg_{cat}^{-1}$)		5,090	4,390	4,400
Cost ($\$_{cat} \cdot kg_{methane}^{-1}$)	24 h	8.69	7.50	7.52
	12 h	4.57	3.95	3.95
	6 h	2.82	2.44	2.44
12% Ni/3% Yb/Al_2O_3				
Cost ($\$_{cat} \cdot kg_{cat}^{-1}$)		20.17	15.95	21.69
Cost ($\$_{cat} \cdot kg_{methane}^{-1}$)	24 h	0.05	0.04	0.05
	12 h	0.07	0.05	0.07
	6 h	0.08	0.06	0.08
12% Ni/Al_2O_3				
Cost ($\$_{cat} \cdot kg_{cat}^{-1}$)		19.81	15.64	21.38
Cost ($\$_{cat} \cdot kg_{methane}^{-1}$)	24 h	0.28	0.22	0.30
33% Ni/8% Yb/Al_2O_3				
Cost ($\$_{cat} \cdot kg_{cat}^{-1}$)		34.50	28.10	33.84
Cost ($\$_{cat} \cdot kg_{methane}^{-1}$)	24 h	0.07	0.06	0.07
	12 h	0.07	0.06	0.07
	6 h	0.06	0.05	0.06
33% Ni/Al_2O_3				
Cost ($\$_{cat} \cdot kg_{cat}^{-1}$)		33.53	27.27	33.01
Cost ($\$_{cat} \cdot kg_{methane}^{-1}$)	24 h	0.09	0.07	0.09
50% Ni/12.5% Yb/Al_2O_3				
Cost ($\$_{cat} \cdot kg_{cat}^{-1}$)		46.17	38.00	43.74
Value ($\$_{cat} \cdot kg_{methane}^{-1}$)	24 h	0.08	0.06	0.07
	12 h	0.07	0.06	0.06
	6 h	0.06	0.05	0.06
50% Ni/Al_2O_3				
Cost ($\$_{cat} \cdot kg_{cat}^{-1}$)		44.64	36.70	42.45
Value ($\$_{cat} \cdot kg_{methane}^{-1}$)	24 h	0.10	0.08	0.09

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