Supporting information

Phosphate assisted integrated carbon dioxide capture and conversion to methane

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Contents

1. Experimental

1.1 Materials and Methods

All experiments were carried out under an inert atmosphere (with N_2 or Ar) using standard Schlenk techniques. A commercial 5%Ru/Al_2O_3 catalyst purchased from Alfa Aesar and was used without further activation or purification. Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) (both 99.9% purity) were purchased from Alfa Aesar. Fumed alumina, Al_2O_3 (Aeroxide AluC) was obtained from Evonik. Potassium (Sigma Aldrich, ≥98%), sodium (Alfa, ≥97%), lithium (GFS Chemicals, ≥98%), and calcium (Thermo Scientific, ≥98%) phosphate were used without further purification. D_2O (CIL, D-99.9%), toluene-d_8 (CIL, D-99.9%) and imidazole (Fischer, 99.5%) were used as received. ^{31}P and ^{13}C NMR spectra were recorded on 400, 500 or 600 MHz, Varian NMR spectrometers. ^{13}C NMR chemical shifts were determined relative to the residual solvent signals. ^{31}P NMR were reference to an internal standard, triphenylphosphine oxide (Sigma Aldrich, 98%). The gas mixtures were analyzed using a Thermo Finnigan gas chromatograph (column: Supelco, Carboxen 1010 plot, 30 m X 0.53 mm) equipped with a TCD detector (CO detection limit: 0.099 v/v%). CO_2 (Gilmore, instrument grade), H_2 (Gilmore, ultra-high pure grade 5.0), Methane (Gilmore, instrument grade).

1.2 Catalyst Synthesis

The 25%Ni/Al_2O_3 and the 12%Ni/3%Zn/Al_2O_3 catalysts were synthesized in the following way. A known amount of nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and zinc nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) were dissolved into 100 mL of DI water to either synthesize the 25%Ni/Al_2O_3 or the 12%Ni/3%Zn/Al_2O_3 catalyst. Once the metals were dissolved in the solvent, a known amount of fumed Al_2O_3 was added to the solution, forming a suspension. The solution was stirred for 5 hours. Water was then removed with a rotavapor and the obtained solid dried overnight in an oven at 120°C in air. The dried material was then calcinated at 700°C for 2 hours after heating it from room temperature to 700°C at a rate of 5.8°C/min under an atmosphere of air. The catalyst (prepared and calcinated Ni/Al_2O_3 or Ni/Zn/Al_2O_3) was crushed and sieved to a size of 250 micrometers or less. The sieved material was then activated in a tubular quartz reactor placed in a tubular furnace (Lindberg Blue). Nitrogen was flown through the catalyst at a rate of 75mL/min for 30 minutes at room temperature. After that a mixture of hydrogen/nitrogen (35mL/min and 75 mL/min, respectively) was flown through the catalyst while it was heated to 700°C (5.8°C/min) and held at that temperature for 2 hours. The catalyst was then allowed to cool down and was stored in an inert atmosphere for later use.

1.3 Capture Conditions from Pure CO_2

10 mmol of alkali phosphate, for example sodium phosphate (Na_3PO_4) was dissolved in DI water (10 mL) in a vial with a magnetic stir bar, resulting in a one molar solution. The gases inside the vial were then removed under vacuum. CO_2 was subsequently added while stirring the solution at 800 rpm for 3 h and maintaining the CO_2 pressure inside the vessel at 1 psi. The amount of CO_2 captured was calculated both through the volume of CO_2 added and through gravimetric analysis of the solutions before and after the CO_2 capture.

1.4 Hydrogenation Conditions

The catalyst was weighed in an atmosphere of argon and then transported to a nitrogen chamber. There, the capture solution was added to the catalyst. The catalyst and aqueous solution containing the captured CO_2 were placed in a borosilicate vial. This vial was then placed in a 125 mL Hastelloy Parr reactor that was sealed in a nitrogen chamber. The Parr reactor was pressurized with hydrogen (UHP). After that, the reactor was placed in an aluminum block pre-heated to the desired temperature and held at that temperature for the duration of the reaction. At the end of the reaction,

the reactor was cooled to room temperature, the pressure was released, and the solvent was separated from the catalyst via decanting. A portion of the gas mixture was released into a gas collection bag for gas chromatography (GC) analysis.

1.5 Recycling Experiments

Once the hydrogenation reaction according to the method described in 1.4 was complete the reactor was cooled down to room temperature and the pressure released. Part of the pressure was released into a collection bag for gas chromatography analysis. The reactor was then transferred to a nitrogen chamber and opened. The liquid in the reactor was separated from the catalyst by decantation and placed in a 100 mL round bottom flask. This liquid was then subjected to CO_2 capture following the procedure described in 1.3. The amount of CO_2 captured was measured by both the volume of CO_2 added and gravimetrically. The liquid after capture was then placed back in the reactor with the same catalyst that was utilized in the previous cycle. The hydrogenation reaction was then were performed again with the conditions detailed in 1.4.

1.6 Powder X-Ray Diffraction (XRD)

Powder XRD was performed on a sixth generation Rigaku Miniflex powder diffractometer. The catalyst was wet loaded onto a sample plate and then dried of any solvent. The scan was set from 10°-90° at a scan rate of 3°/min. The resulting spectrum were processed on the PDXL software.

1.7 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) images were obtained from a NanoSEM 450 with an accelerating voltage of 10 kV and a spot size of 3 nm.

1.8 X-Ray Fluorescence (XRF)

X-Ray Fluorescence (XRF) was conducted on a Bruker Tiger S8 instrument. The X-Ray source is rhodium leading to residual rhodium signals, which are labelled in the spectra. The spectra were all collected between 0-60 keV. The weight percentages of the metals were calculated using the Bruker software and all errors of the measurements are reported. The calculations were based on the Kα peak.

2. Data

2.1 Gas Chromatography Analysis

Gas chromatography was used to analyze the gas mixture and determine if methane and any other gases were produced. Figures S1 and S2 show the gas chromatograms for the reaction that produced 7.1 mmol of CH_4 from 7.1 mmol of captured CO_2 under 50 bar of H_2 at room temperature, 200 °C, 300 mg 5%Ru/Al_2O_3, 10 mL H_2O in 6 hours. The peak at 1.7 minutes is H_2 and is labelled in Figure S1. Methane has a retention time of 4.5 minutes and is labelled in Figure S2. If CO or CO_2 appeared in the spectrum, they would have a retention time of 2.5 and 8.6 minutes, respectively. This shows that the reaction did not produce any gas other than methane. Figures S3 and S4 show the GC data for the reaction conducted at 150 °C. Even at lower temperatures, where not all the captured CO_2 was utilized, no other gas was detected in the gas mixture.
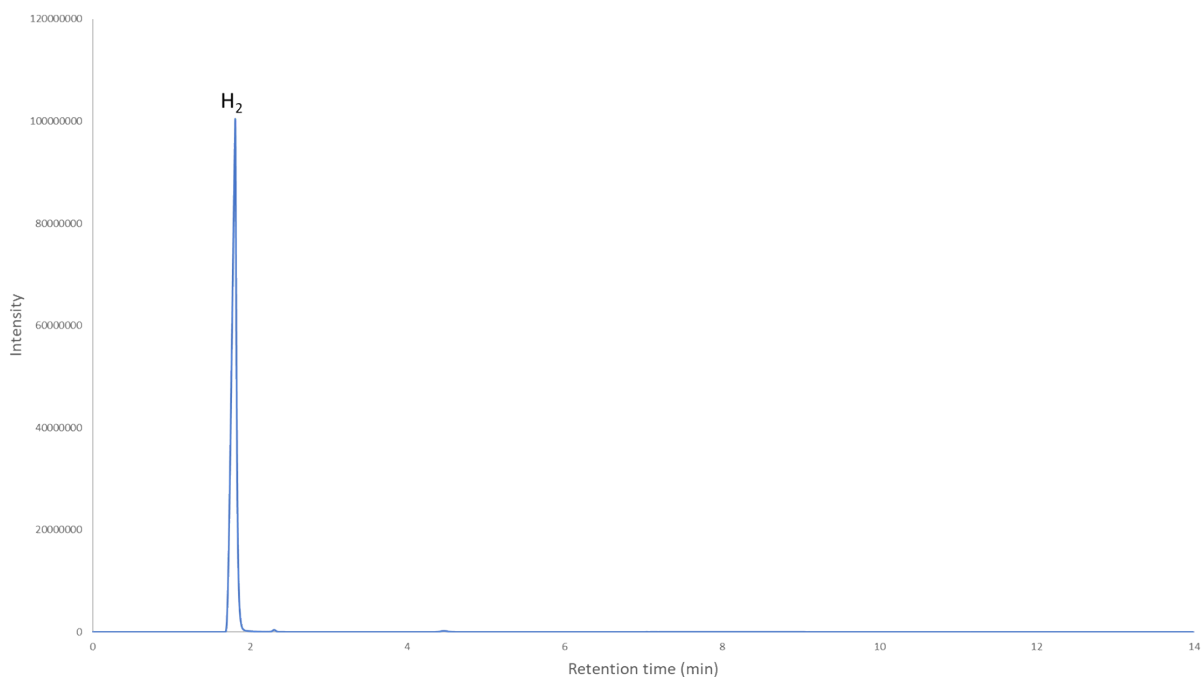
Figure S1. Gas chromatogram of the gas mixture after hydrogenation in a high yielding reaction (conditions: 50 bar H_2 at room temperature, 7.1 mmol of captured CO_2, 6 hour reaction, 200 °C, 300 mg 5%Ru/Al_2O_3, 10 mL H_2O). Peak expansion for methane is shown in Figure S2.
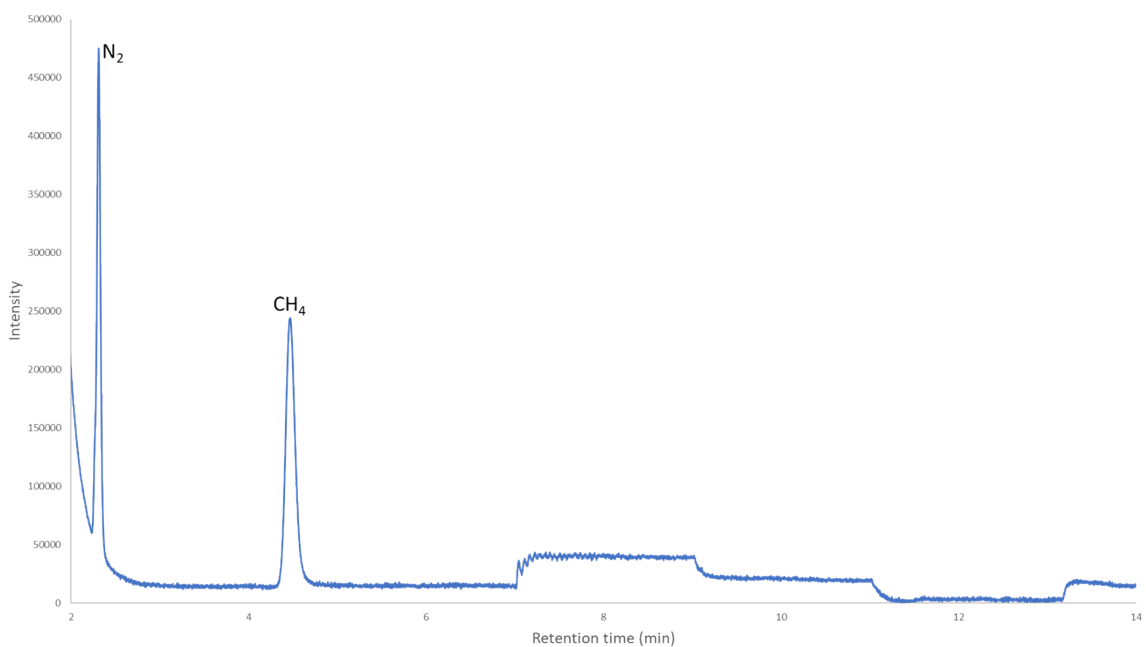
Figure S2. Gas chromatogram of the gas phase after hydrogenation in a high yielding reaction from 2 minutes to 14 minutes (conditions: 50 bar H_2 at room temperature, 7.1 mmol of captured CO_2, 6 hour reaction, 200 °C, 300 mg 5%Ru/Al_2O_3, 10 mL H_2O).
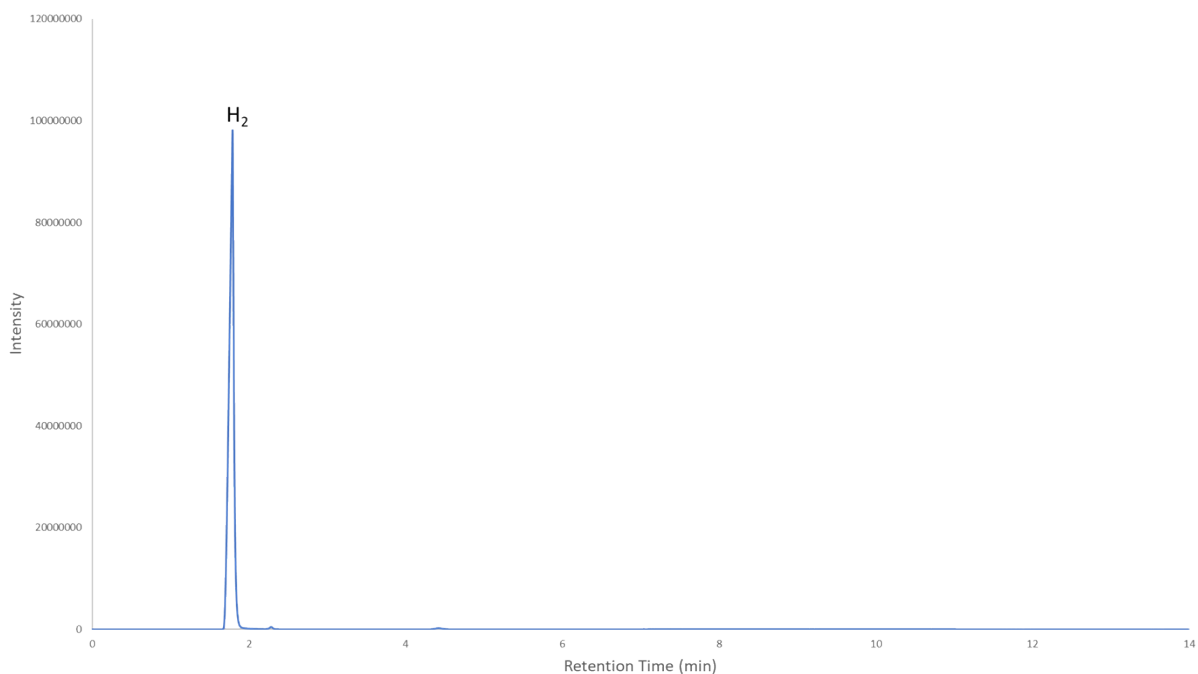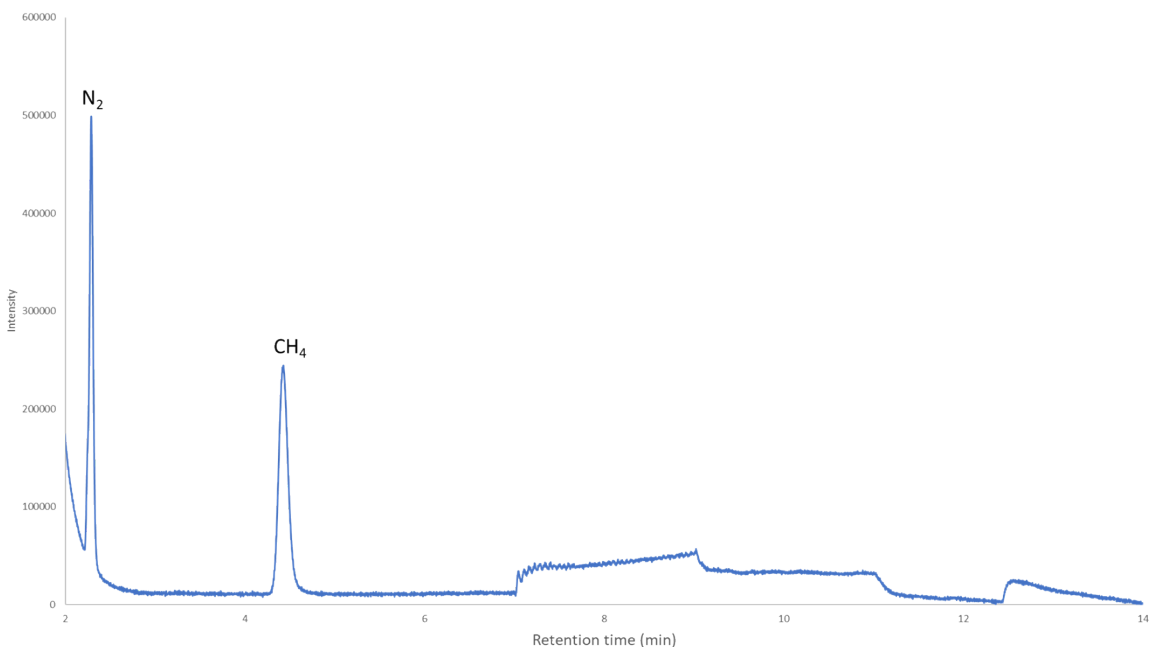

Figure S3. Gas chromatogram of the gas phase after hydrogenation in a reaction at 150 °C (conditions: 50 bar H_2 at room temperature, 7.1 mmol of captured CO_2, 6 hours, 150 °C, 300 mg 5%Ru/Al_2O_3, 10 mL H_2O). Peak expansion for methane is shown in Figure S4.

Figure S4. Gas Chromatogram of the gas phase after hydrogenation in a reaction at 150 °C from 2 minutes to 14 minutes (conditions: 50 bar H_2 at room temperature, 7.1 mmol of captured CO_2, 6 hours, 150 °C, 300 mg 5%Ru/Al_2O_3, 10 mL H_2O).

To calculate the amount of methane that was produced, the integration values were obtained from the gas chromatogram. For example, the chromatograms shown in figures S1 and S2 have 99.26% H_2 and 0.74% CH_4. Nitrogen is excluded from the calculation (it is due to air present during the injection using a gas syringe). These integration values are normalized to account for their response factors. Once the response factors are accounted for the integration values are 97.21% H_2 and 2.79% CH_4. The pressure prior to releasing the gas was recorded and utilized for the next step of the calculation. The pressure of 710 psi at the time of release is multiplied by the percentage of methane. This results in 19.81 psi of methane. This is converted to atm for further computations by dividing the pressure in psi by 14.696 to obtain pressure in atm; in this case 1.347 atm. This pressure is then used in gas law's equation to compute the amount of moles of methane as shown in equation S1. The temperature that is used for the calculation is the temperature at the time of the release of the gas. After using gas law's equation, there was 7.1 mmol of methane in the gas released from the reactor, which corresponds to the 100% yield we observed.

$$mol\ of\ methane = \frac{(1.347\ atm)(0.130\ L)}{(27.0\ ℃ + 273.15)(0.0821\ \frac{atm*L}{mol*K})}$$

Equation S1. 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.

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2.2 NMR Data

Nuclear Magnetic Resonance (NMR) data was also collected to test how the phosphate salt was capturing the carbon dioxide. Figure S5 shows the ^{31}P NMR of sodium phosphate tribasic, Na_3PO_4, referenced to a triphenylphosphine oxide standard, which shows a peak at 5.51 ppm. Figure S6 shows the ^{31}P NMR of sodium phosphate dibasic, Na_2HPO_4, referenced to triphenylphosphine oxide with a peak at 3.28 ppm. Figure S8 shows the ^{31}P NMR (referenced to triphenylphosphine oxide) of the capture solution after being subjected to the carbon dioxide capture conditions described in 1.3 of the SI. The peak in Figure S6, at 4.03 ppm, is further up-field from the peak shown in Figure S5, which is consistent with the phosphate salt becoming protonated. However, it is not fully the sodium phosphate dibasic peak. This indicates that the phosphate salt is deprotonating the water and that the resulting hydroxide anion is assisting in the capture. This is further shown in Figure S9, which is the ^{13}C NMR of the capture solution referenced to the internal imidazole standard (121.9 ppm). This shows a peak at 161, which is similar to sodium bicarbonate, $NaHCO_3$. However, upon increasing the capture time from 3 hours to 12 hours the peak in ^{31}P NMR shifts further up-field and is similar to the sodium phosphate dibasic peak and shows at 3.28 ppm as shown in Figure S8.
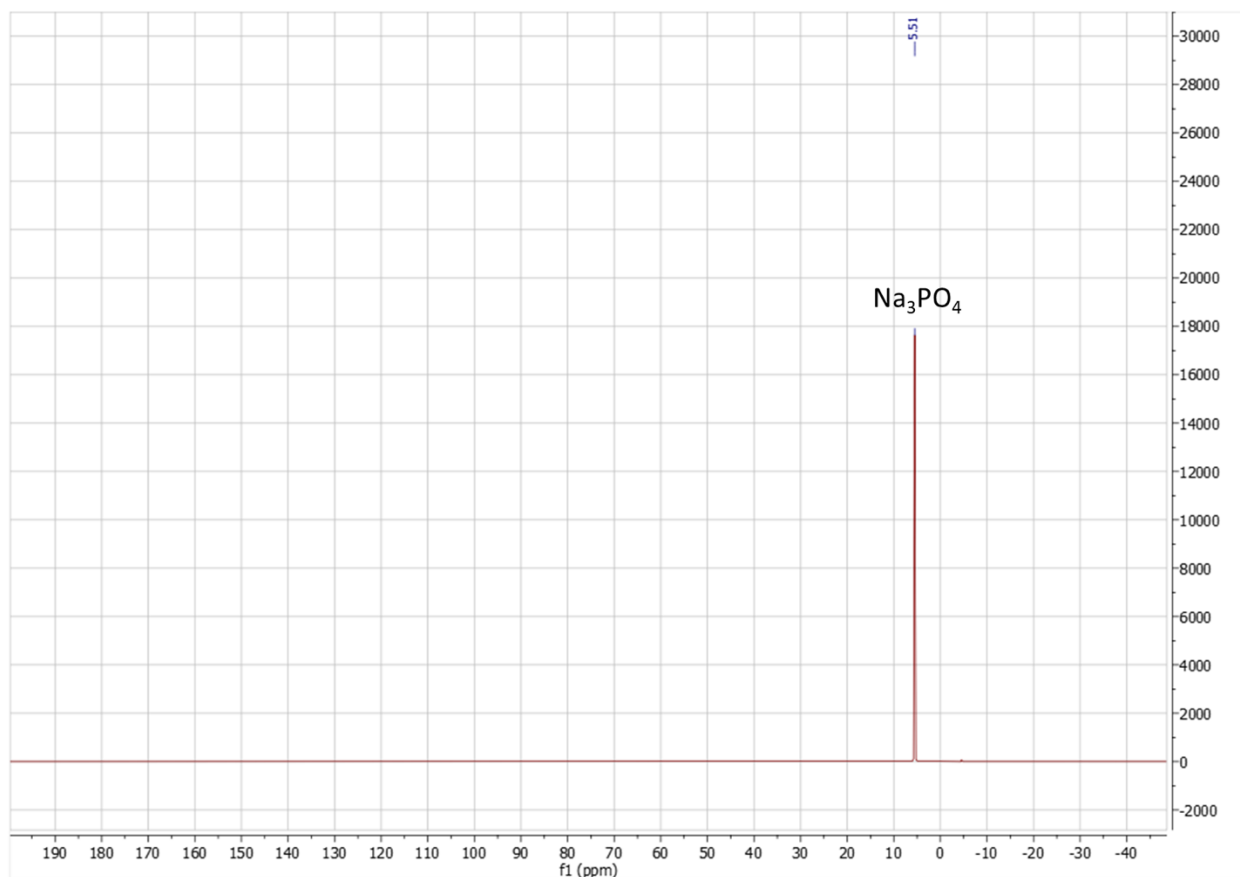
Figure S5. ^{31}P NMR of sodium phosphate tribasic, Na_3PO_4.
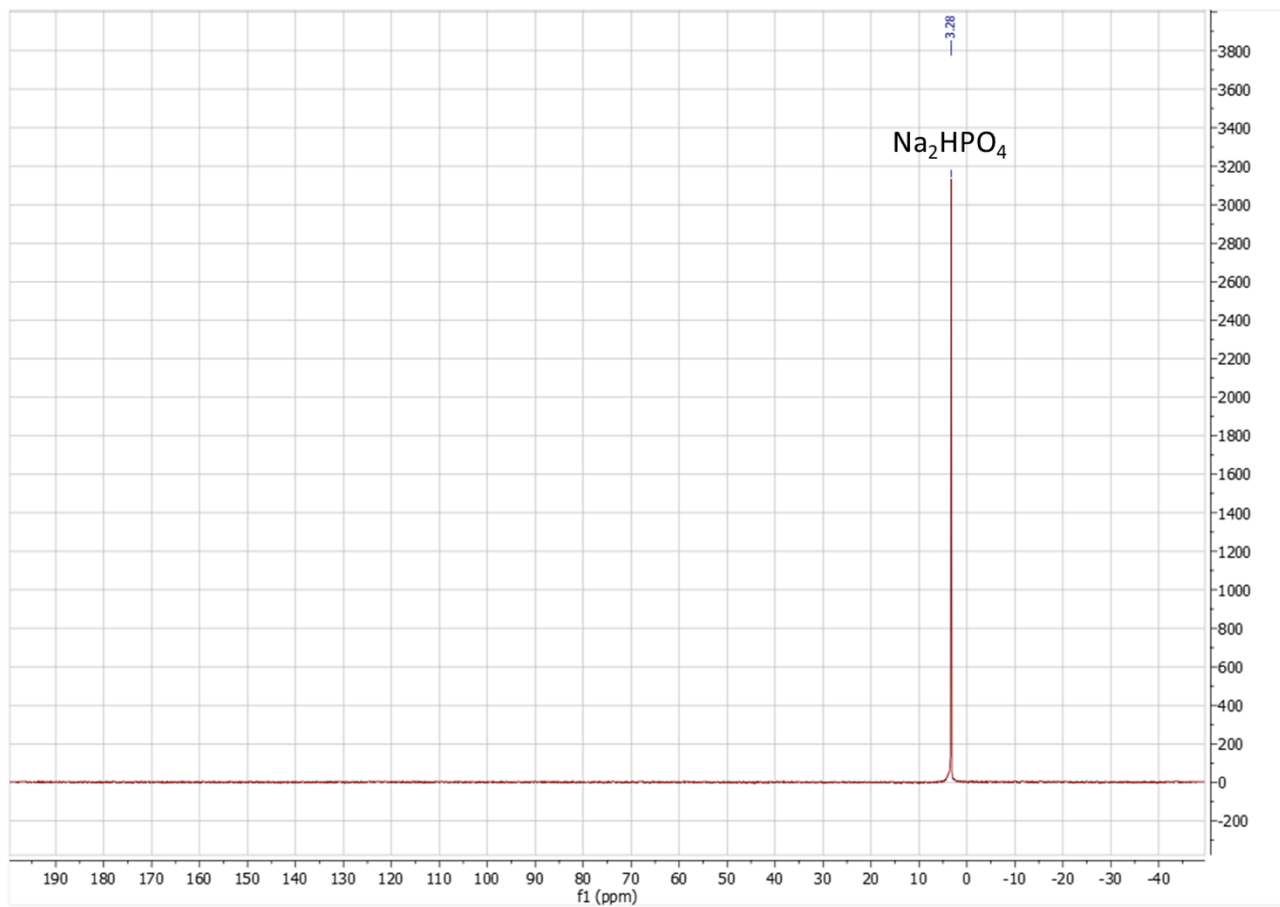
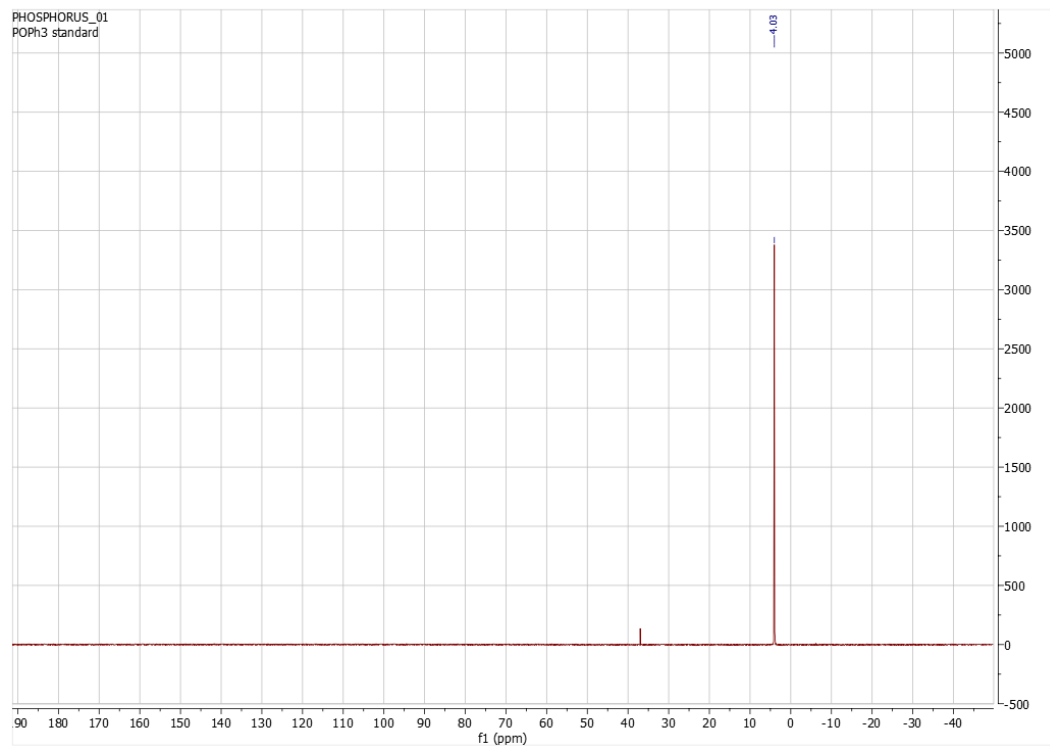Figure S6. ^{31}P NMR of sodium phosphate dibasic, Na_2HPO_4.

Figure S7. ^{31}P NMR of the sodium phosphate tribasic capture solution after 3-hour CO_2 capture.
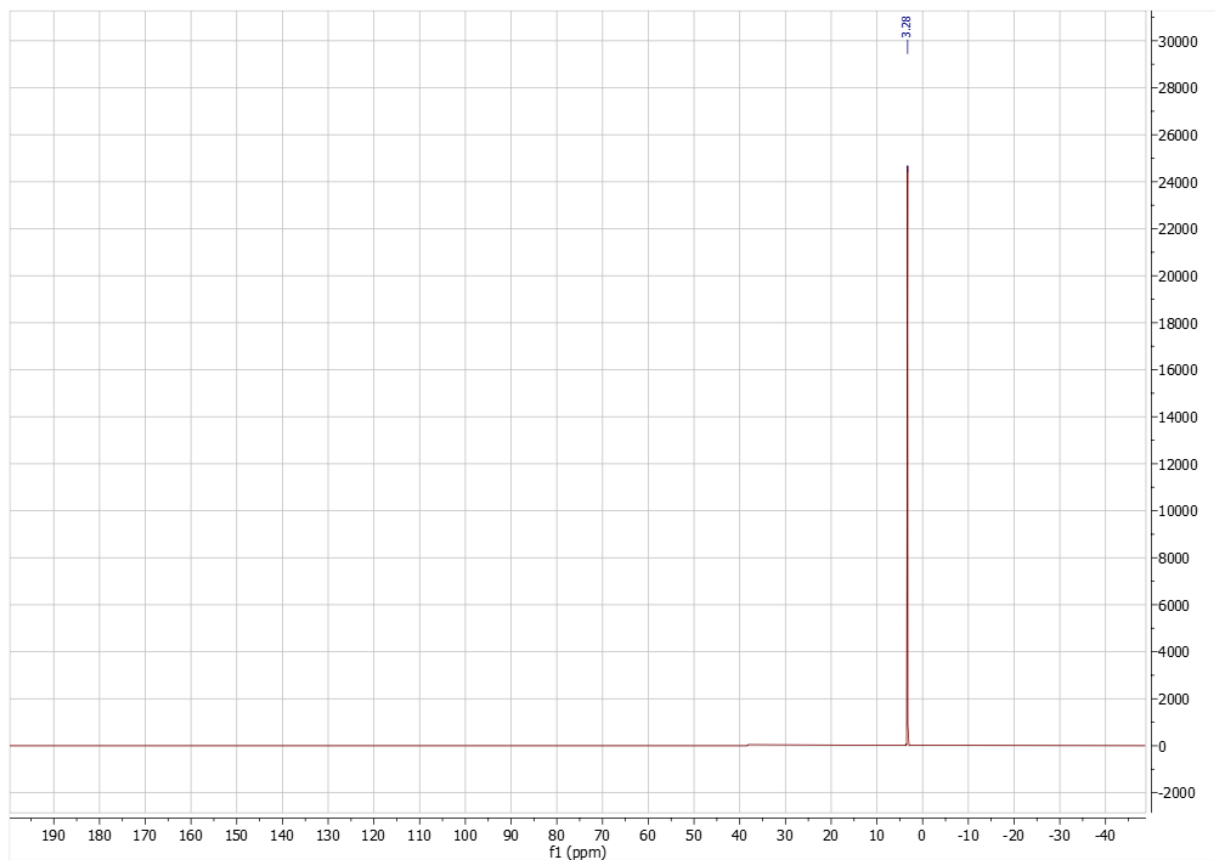
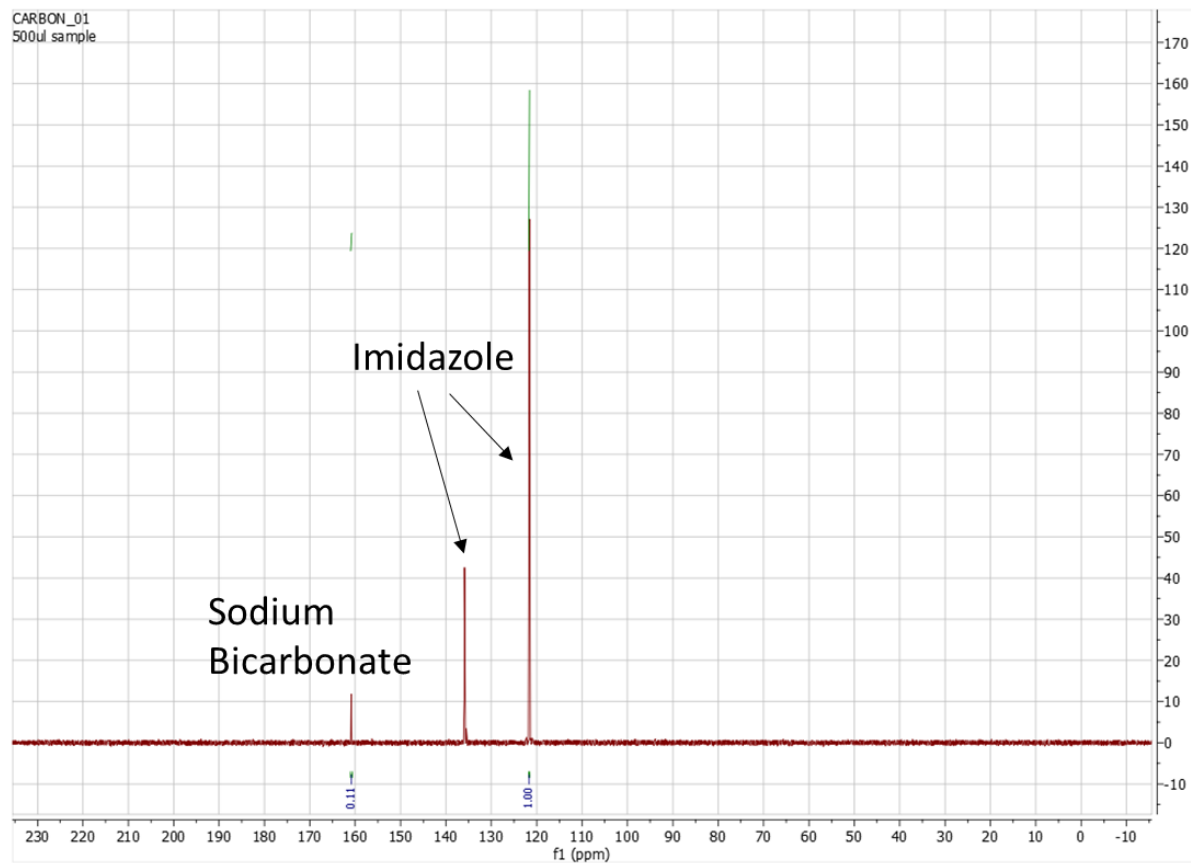Figure S8. ^{31}P NMR of the sodium phosphate tribasic capture solution after 12-hour CO_2 capture.

Figure S9. ^{13}C NMR of the sodium phosphate tribasic capture solution after CO_2 capture.

Figure S10 shows the ^{31}P NMR of the reaction mixture after reaction with 5%Ru/Al$_2$O$_3$. It is evident that we still have a phosphate peak, at 4.27 ppm. This peak is located between the one for sodium phosphate tribasic (5.51 ppm, Figure S5) and sodium phosphate dibasic (3.28 ppm, Figure S6), which could mean that a mixture of these two sodium phosphate is be present after the reaction. This also shows that after the first reaction there is phosphate regeneration. However, upon looking at the ^{31}P NMR of the reaction mixture after five cycles of reaction, the peak is at 2.36 ppm as shown in Figure S11, which is upfield of the peak for sodium phosphate dibasic. This peak is most likely the result of a mixture of sodium phosphate dibasic and monobasic. There are no other peaks besides the peak at 2.36 ppm and the triphenylphosphine oxide reference. This means that the phosphate salt is becoming less basic over consecutive cycles and explains why the recycling experiments are not quantitative over longer lengths of reaction time as the solution is no longer basic enough to efficiently capture CO$_2$.
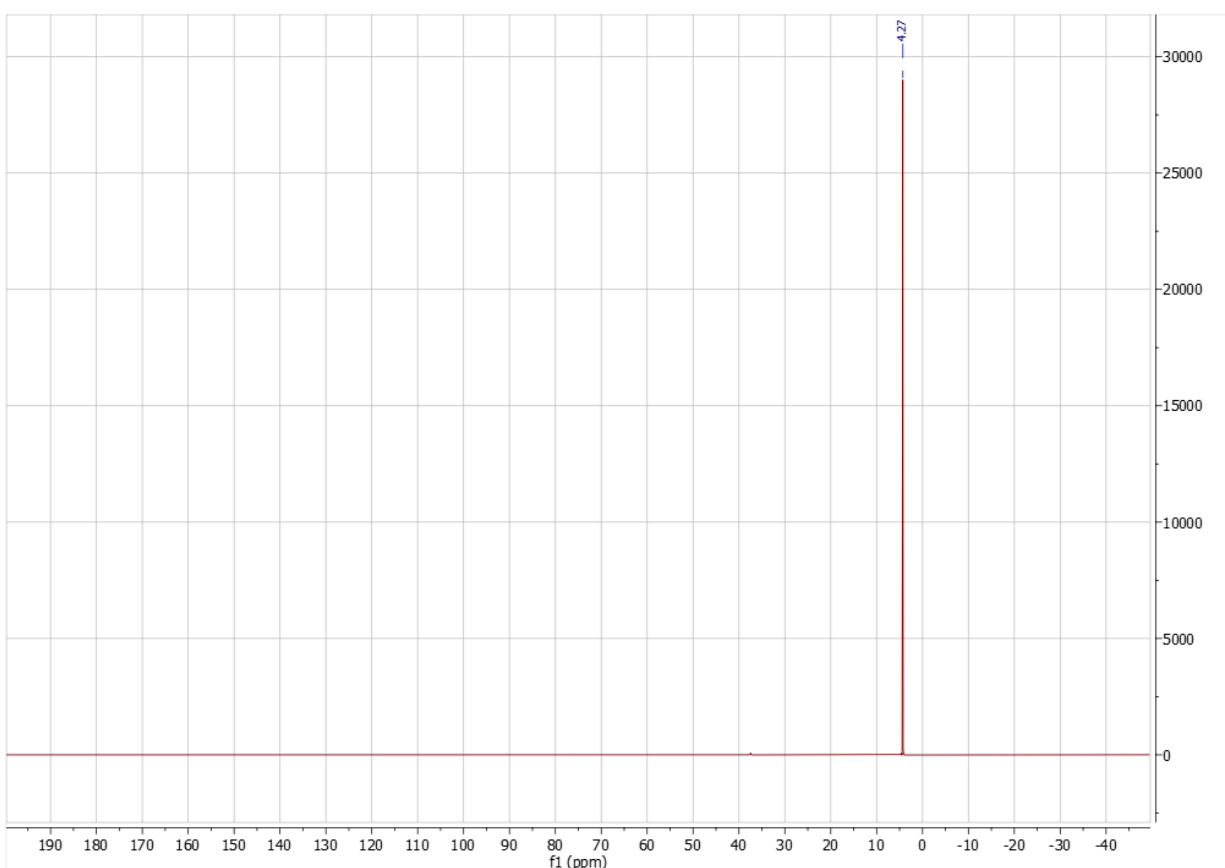
Figure S10. ^{31}PNMR of the solution after the hydrogenation reaction with 5%Ru/Al$_2$O$_3$ (conditions: 300mg 5%Ru/Al$_2$O$_3$, 11.3 mmol captured CO$_2$, 200 °C, 6 hours, 60 bar H$_2$).
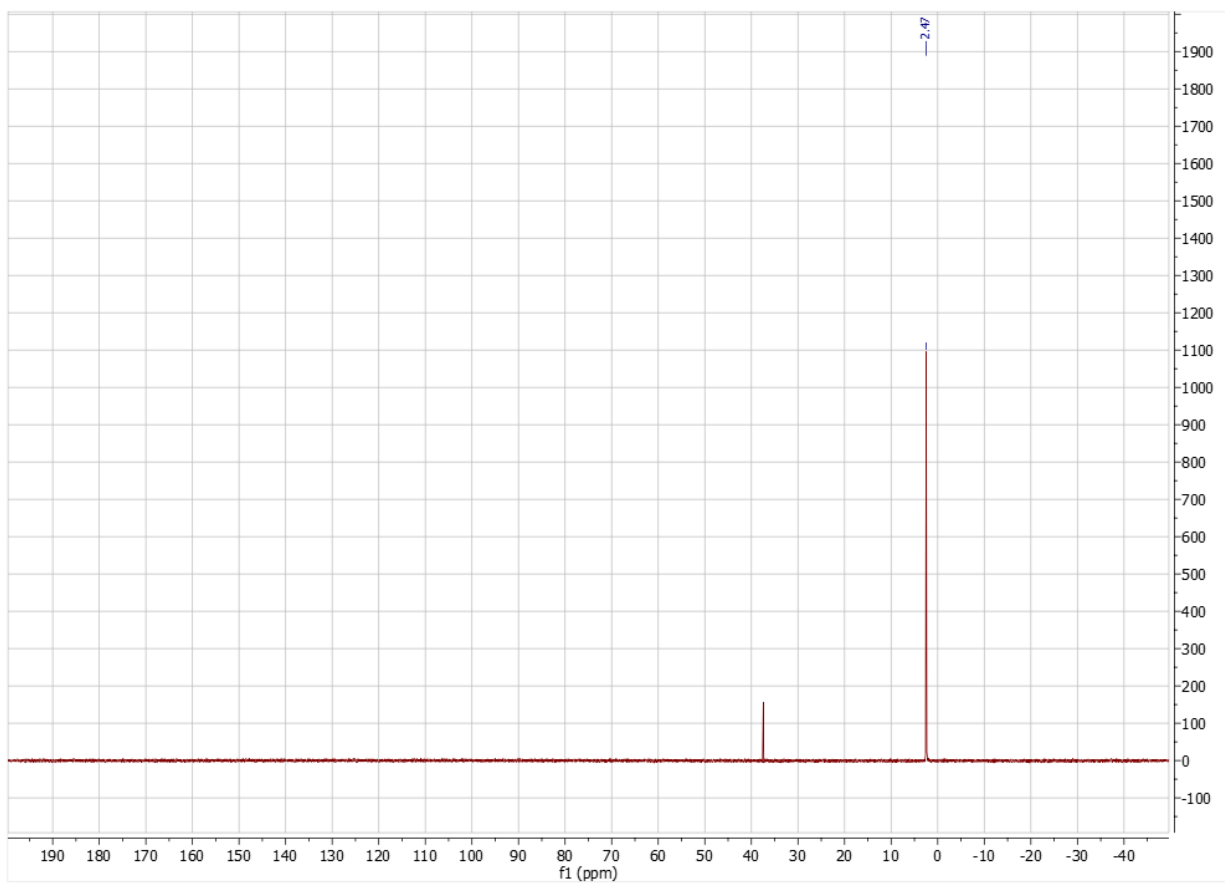
Figure S11. ^{31}P NMR of the solution after 5 cycles of reactivity with the 5%Ru/Al$_2$O$_3$ catalyst.

^{1}H NMR of the gas mixture after the hydrogenation reaction over 5%Ru/Al$_2$O$_3$ was also taken to check if any other gases beside H$_2$ and methane were present at the end of the reaction. Figure S12 displays the ^{1}HNMR of the gas mixture after reaction, which shows that beside hydrogen and methane no other gaseous products were present.
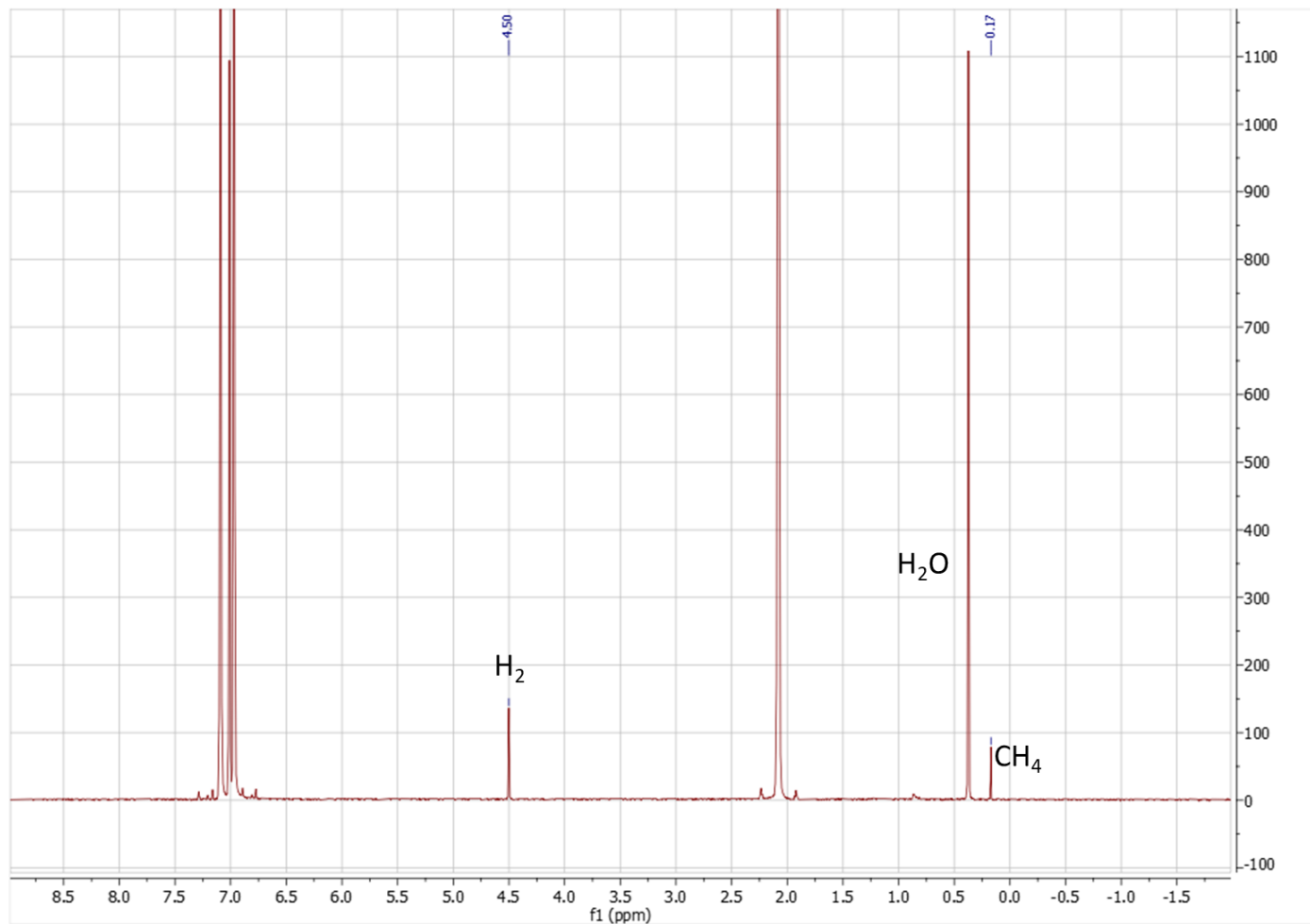

Figure S12. ^{1}H NMR of gas mixture after the hydrogenation reaction with 5%Ru/Al$_2$O$_3$ (conditions: 300mg 5%Ru/Al$_2$O$_3$, 11.3 mmol captured CO$_2$, 200 °C, 6 hours, 60 bar H$_2$).

2.3 X-Ray Diffraction Data

   X-Ray Diffraction (XRD) spectra were taken for each catalyst before and after reaction with the capture solution. D-spacing calculations for each catalyst for the primary metal are shown in table S1 and were calculated with Bragg's law.
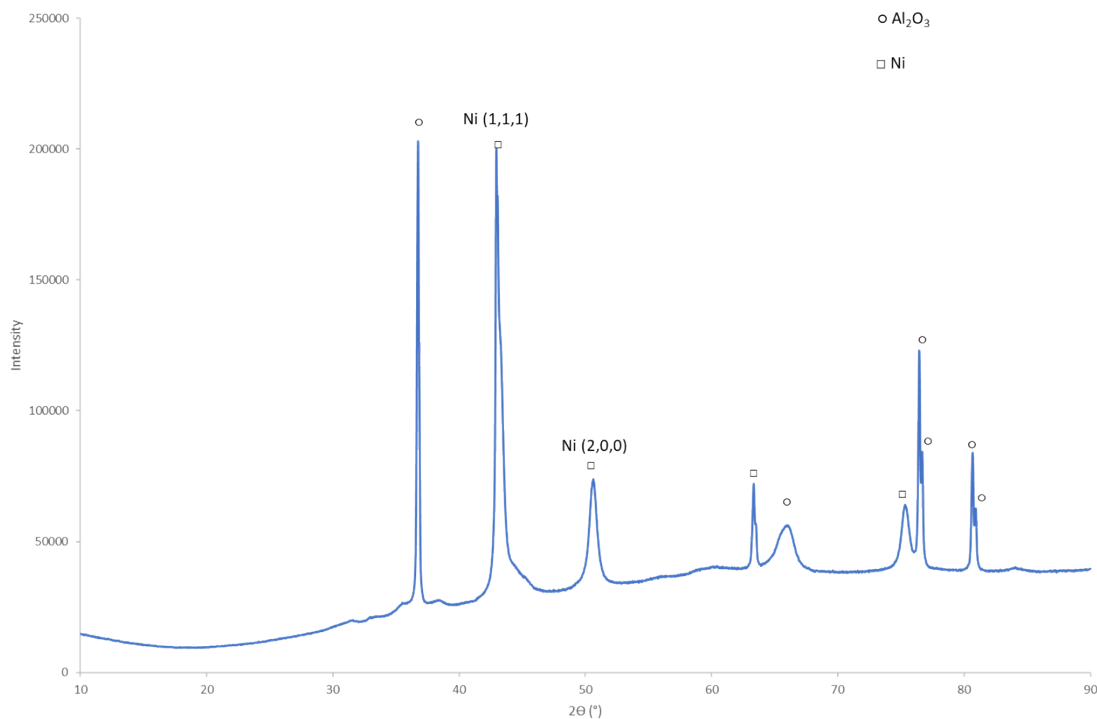
Figure S13. XRD of 25%Ni/Al$_2$O$_3$ before reaction.
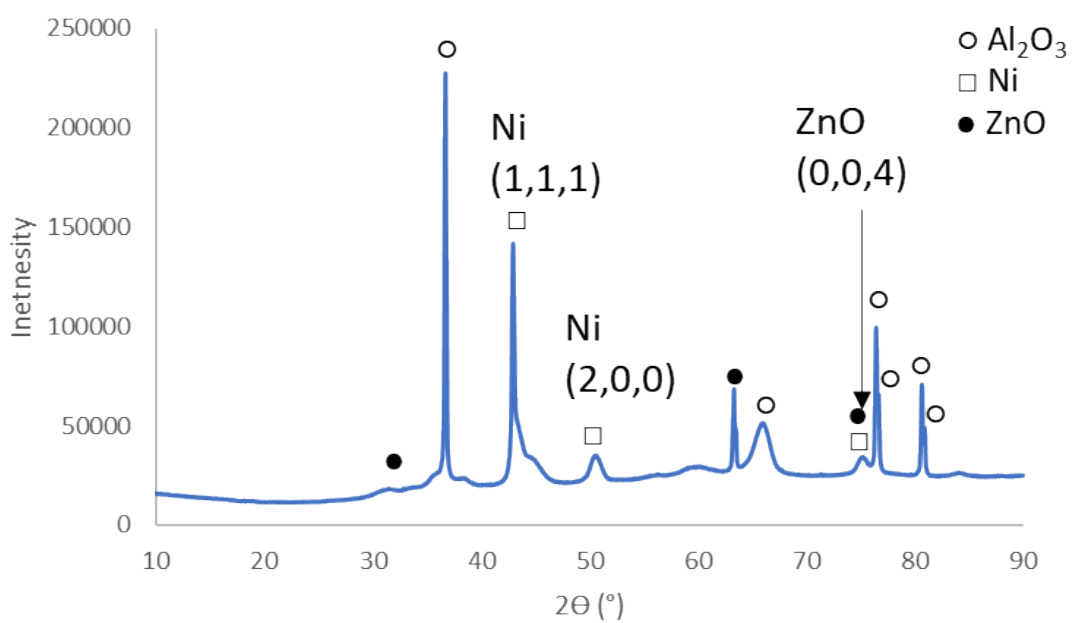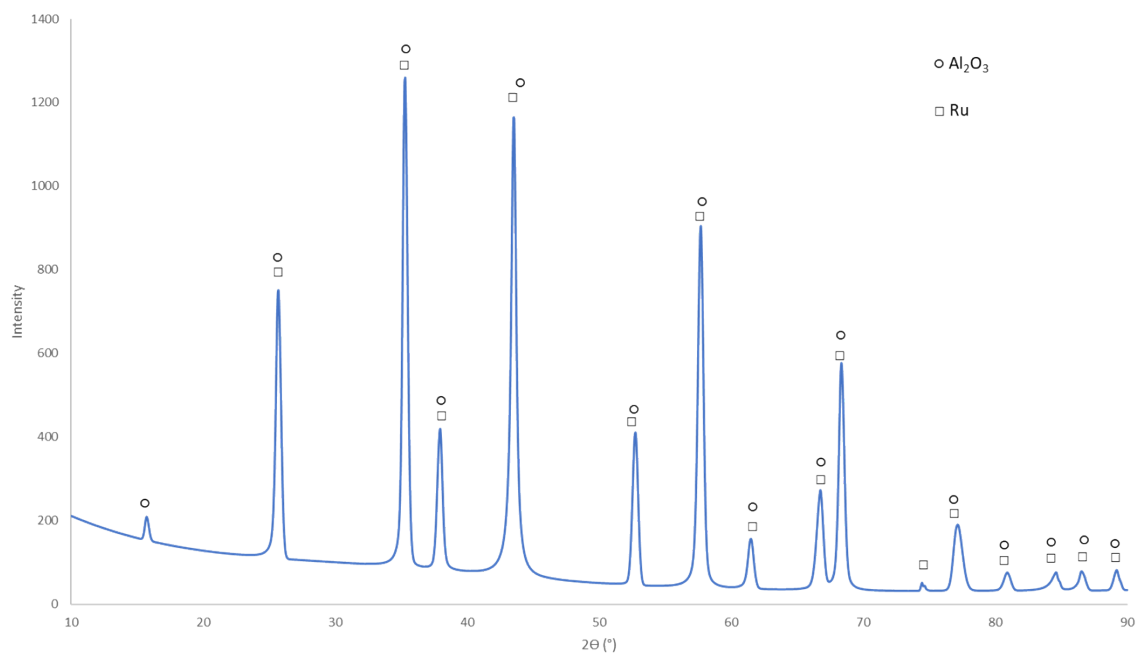

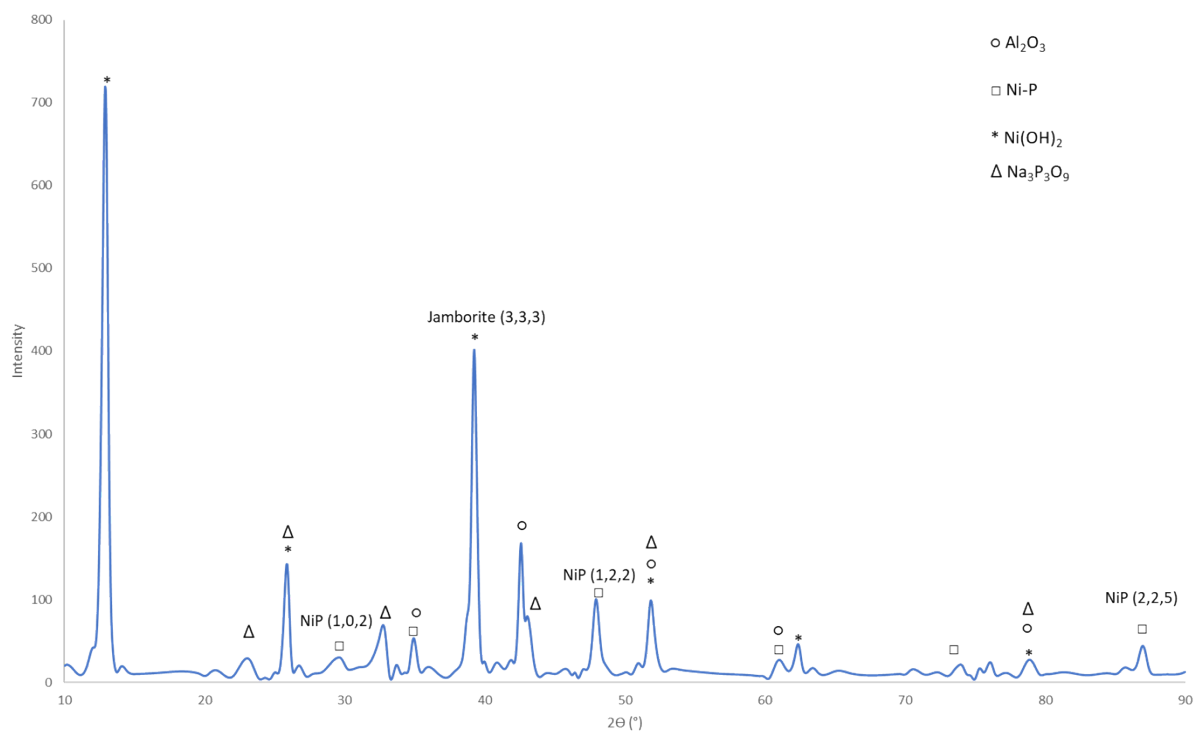Figure S14. XRD of 12%Ni/3%Zn/Al$_2$O$_3$ before reaction.

Figure S15. XRD of 5%Ru /Al$_2$O$_3$ before reaction.

Figure S16. XRD of 25%Ni/Al$_2$O$_3$ after the hydrogenation reaction of the aqueous Na$_3$PO$_4$ capture solution.
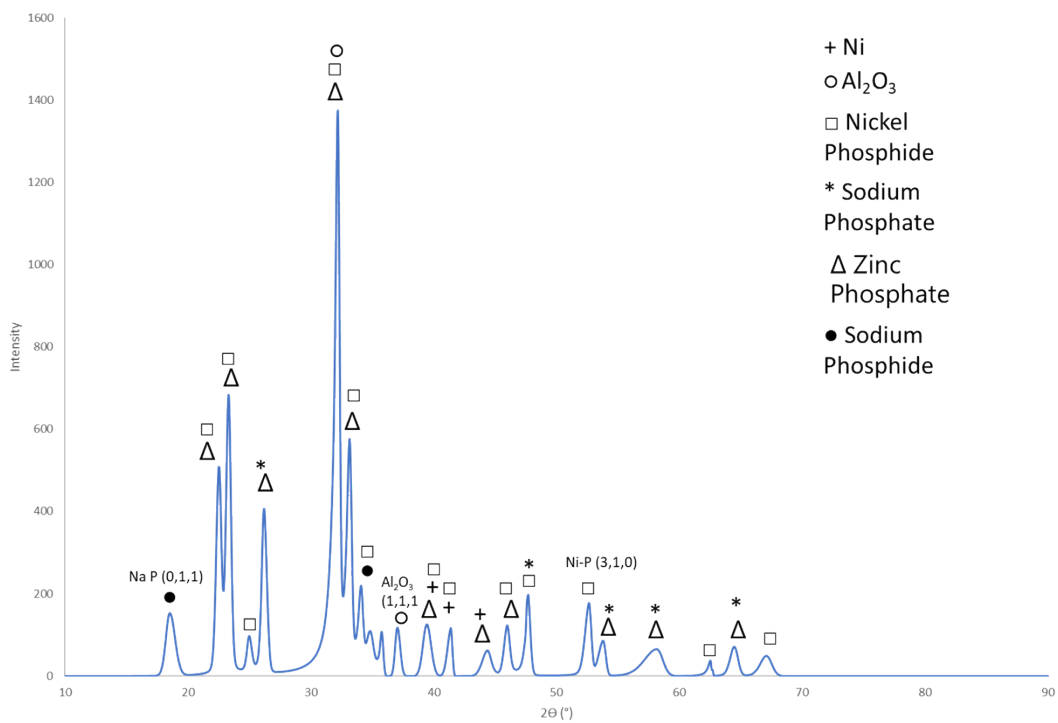
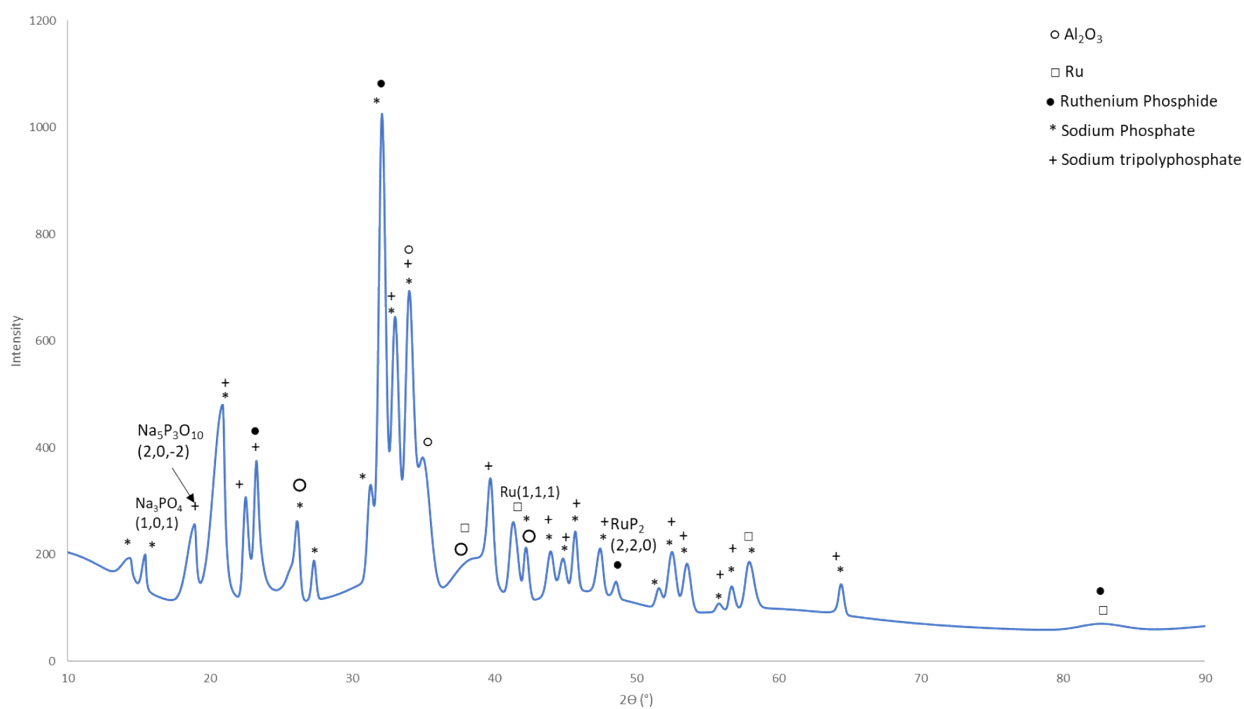Figure S17. XRD of 12%Ni/3%Zn/Al_2O_3 after the hydrogenation reaction with the aqueous Na_3PO_4 capture solution.

Figure S18. XRD of 5%Ru/Al_2O_3 after the hydrogenation reaction with the aqueous Na_3PO_4 capture solution.
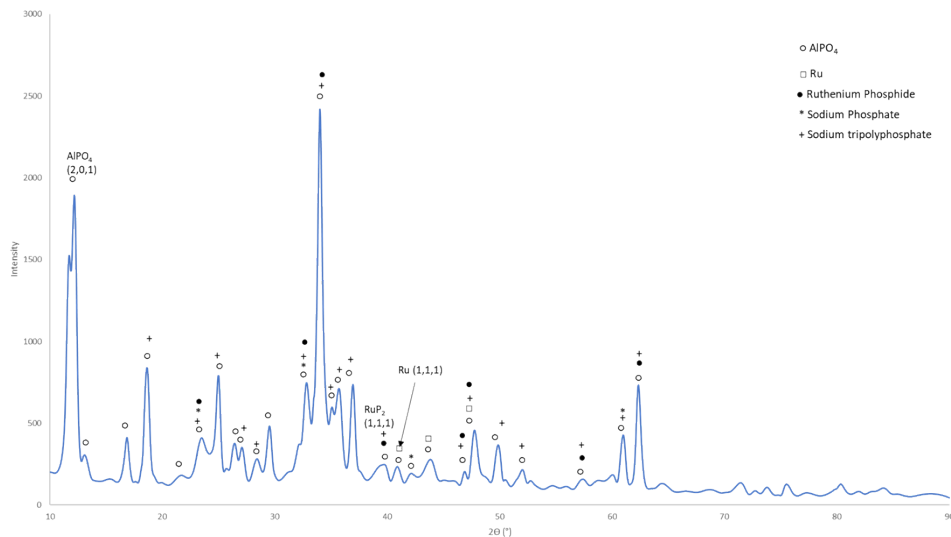
Figure S19. XRD of 5%Ru/Al$_2$O$_3$ and other solid materials after 5 cycles of hydrogenation reaction with the Na$_3$PO$_4$ capture solution.

Table S1. Table of XRD Data

Catalyst	Peak chosen	d-spacing (Å)	Crystallite Size (Å)
25%Ni/Al$_2$O$_3$	Ni (1,1,1)	2.0931 (5)	144 (3)
12%Ni/3%Zn/Al$_2$O$_3$	Ni (1,1,1)	2.0880 (6)	44.2 (5)
5%Ru/Al$_2$O$_3$	Ru (1,1,1)	2.0787 (17)	217 (18)
25%Ni/Al$_2$O$_3$ after reaction	Ni (1,1,1)	2.10248 (9)	225 (41)
12%Ni/3%Zn/Al$_2$O$_3$ after reaction	Ni (1,1,1)	2.12616 (8)	177 (12)
5%Ru/Al$_2$O$_3$ after reaction	Ru (1,1,1)	2.0603 (18)	134 (9)
5%Ru/Al$_2$O$_3$ after 5 cycles of reaction	Ru(1,1,1)	2.2040 (15)	224 (31)

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

Comment [AJG]: How comes this one is only 134 A whereas before and after 5 cycles it is 217 and 224 A, respectively?

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2.4 SEM Images

SEM images were collected of the 5%Ru/Al$_2$O$_3$ catalyst before and after the reaction with conditions 10 mmol Na$_3$PO$_4$ salt after 3 hours under pure CO$_2$ stream, 10 mL DI H$_2$O, 200 °C, 6 hours reaction time, 300 mg 5%Ru/Al$_2$O$_3$, 50 bar H$_2$ and are shown in Figures S14 and S15 respectively.

Figure S20. SEM image of 5%Ru/Al$_2$O$_3$ before the reaction.
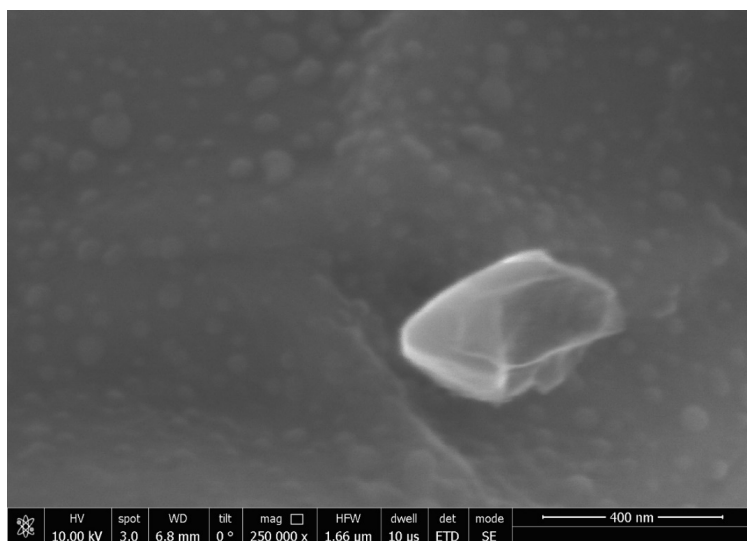
Figure S21. SEM image of 5%Ru/Al$_2$O$_3$ after hydrogenation of the Na$_3$PO$_4$ capture solution.

Comment [AJG]: Which reaction?

2.5 X-Ray Fluorescence Data (XRF)

XRF measurements were obtained to calculate the weight concentrations of each metal on the catalysts. All measurements are shown with errors. The radiation is detected by three types of crystals (LiF200, XS-55, and PET), which required each spectrum to have several runs so that each crystal can be used for detection. This results in what looks like different baselines that can often be seen above 20 KeV.
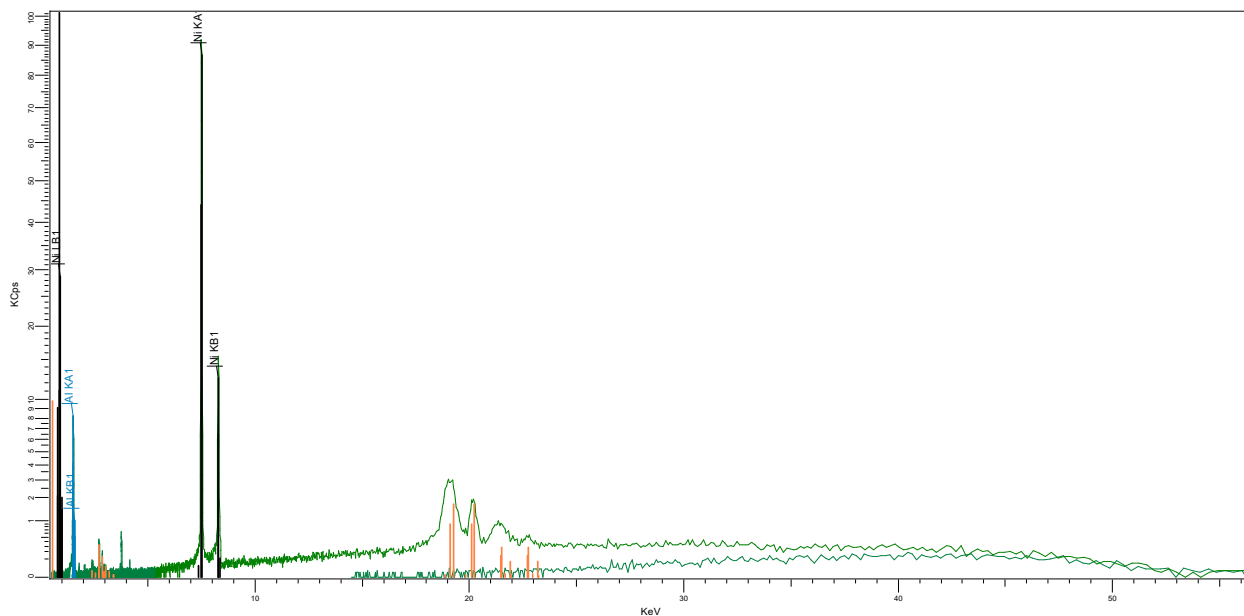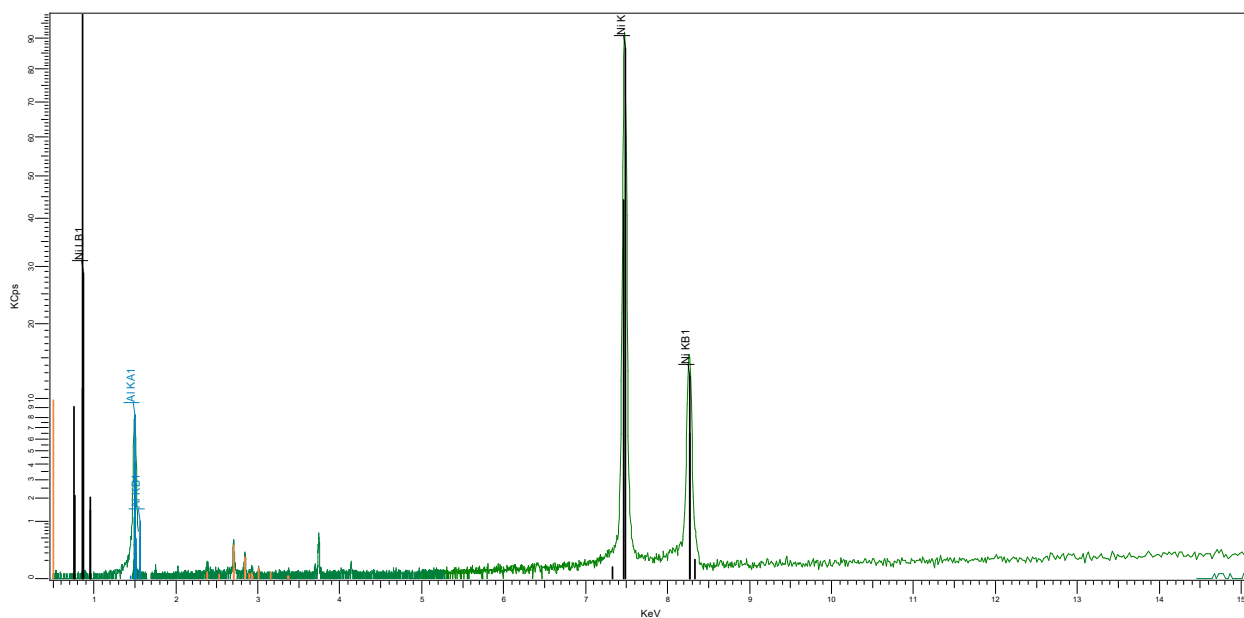

Figure S22. XRF spectra of 25%Ni/Al$_2$O$_3$

Figure S23. XRF spectra of 25%Ni/Al$_2$O$_3$ zoomed into 0-15KeV
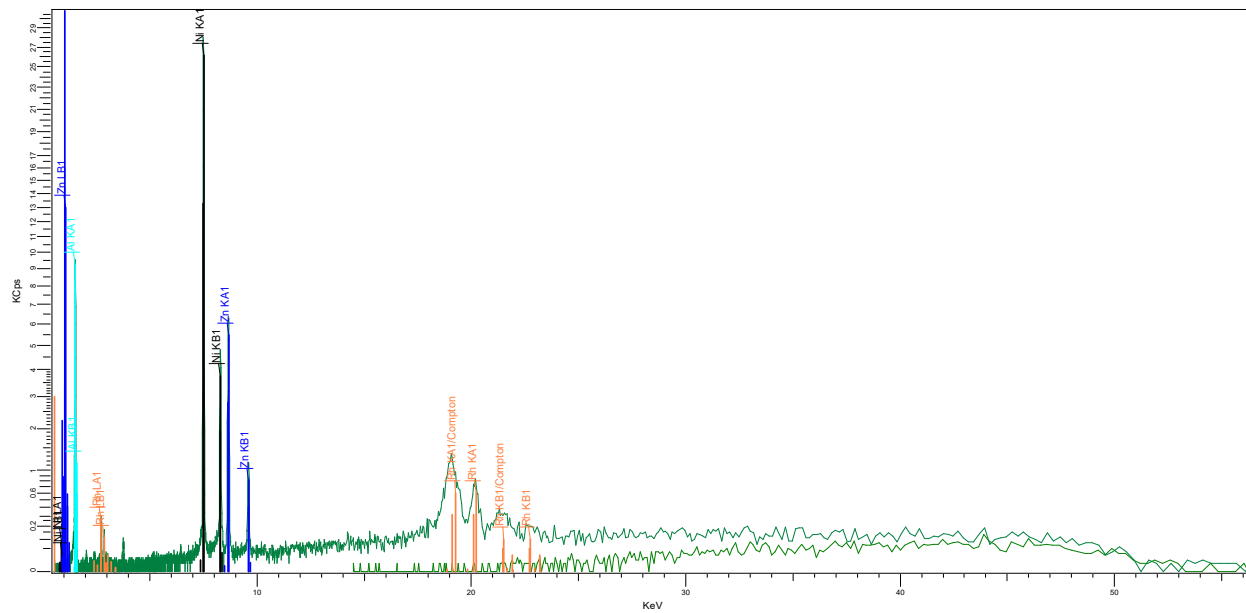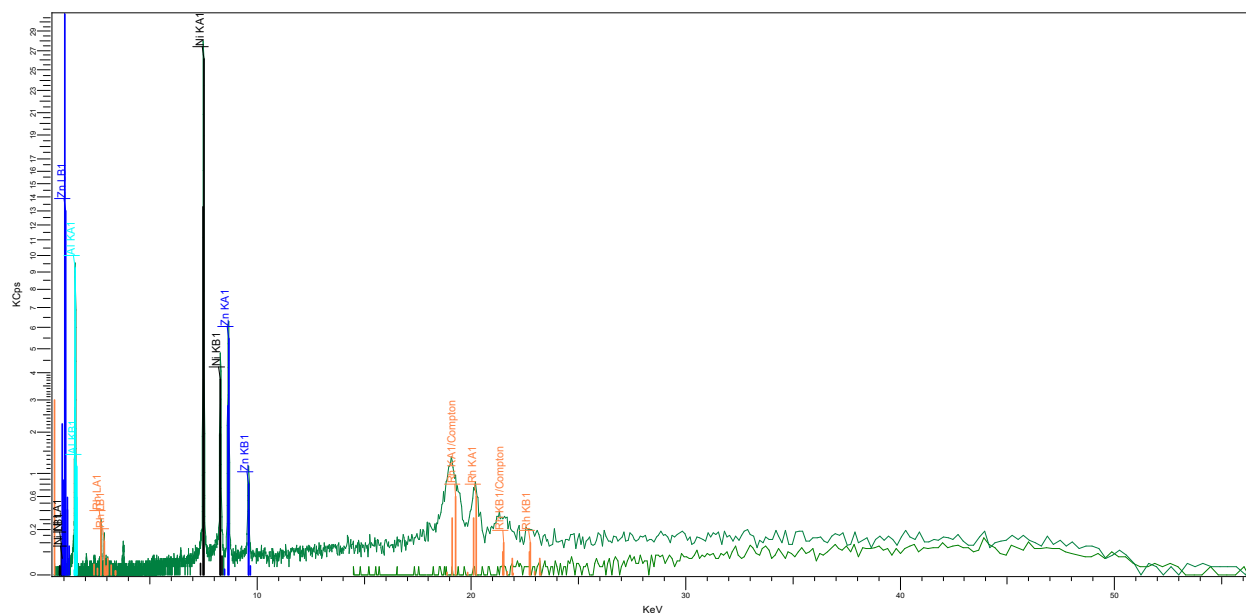
Figure S24. XRF spectra of 12%Ni/3%Zn/Al$_2$O$_3$

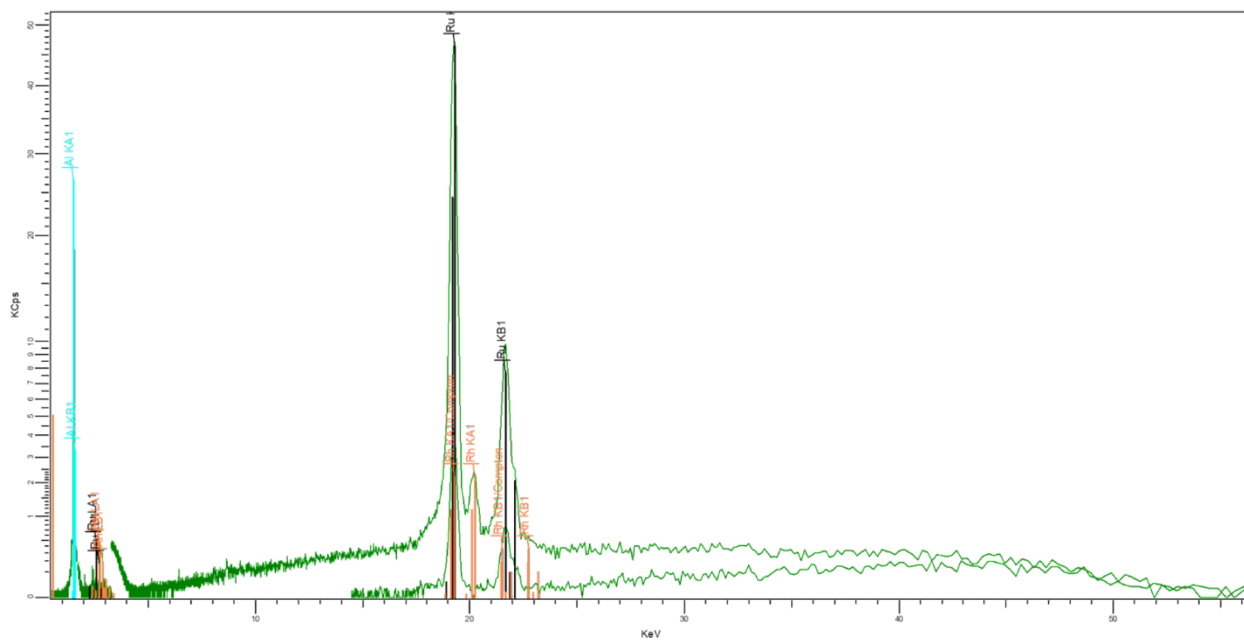Figure S25. XRF spectra of 12%Ni/3%Zn/Al$_2$O$_3$ zoomed between 0-11 KeV

Figure S26. XRF of commercial 5%Ru/Al$_2$O$_3$

Table S2. Weight percentages of synthesized catalysts

Catalyst	Nickel (%w)	Zinc (%w)
25%Ni/Al$_2$O$_3$	25.80±0.35	N/A
12%Ni/3%Zn/Al$_2$O$_3$	11.94±0.62	2.28±1.33
5%Ru/Al$_2$O$_3$	6.27±1.62	N/A