

Metal Hydroxide Assisted Integrated Direct Air Capture and Conversion to Methane with Ni/Al₂O₃ catalysts

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1. Experimental part

1.1 Materials and Methods

All experiments were carried out under an inert atmosphere (with N₂ or Ar) using standard Schlenk techniques with the exclusion of moisture unless otherwise stated. Commercial Ni/CaAl₂O₄ catalyst was purchased from Alfa Aesar (HiFUEL R110). Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) (99.9% purity) was purchased from Alfa Aesar. Fumed alumina, Al₂O₃, Aeroxide AluC, was obtained from Evonik. Potassium carbonate, potassium bicarbonate, sodium carbonate, lithium carbonate, cesium carbonate and calcium carbonate were purchased from Sigma Aldrich, had all a purity of 99.9% or higher, and were used without further purification. Potassium hydroxide was purchased from Sigma Aldrich and had a purity of 97%. ¹³C-labelled potassium carbonate was purchased from Stable Isotopes with a purity of 98.7%, D₂O (CIL, D-99.9%), toluene-d₈ (CIL, 99.5%) and imidazole (Fischer, 99.5%) were used as received. ¹H and ¹³C NMR spectra were recorded on 400, 500 or 600 MHz, Varian NMR spectrometers. ¹H and ¹³C NMR chemical shifts were determined relative to the residual solvent signals. 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%). CO₂ (Gilmore, instrument grade), H₂ (Gilmore, ultra-high pure grade 5.0), Methane (Gilmore, instrument grade), and ¹³C-Methane (Monsanto Research Corporation, 99%) were used without further purification.

Caution: Reactions are associated with H₂ gas. They should be carefully handled inside proper fume hoods without any flame, spark or static electricity sources nearby.

1.2 Catalyst synthesis

3.3 g of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) was dissolved into 100 mL of DI water. 6.7g of fumed Al₂O₃ was then 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. 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.

1.3 Catalyst activation

The catalyst (prepared and calcinated Ni/Al₂O₃ or commercial Ni/CaAl₂O₄) 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.

1.4 Hydrogenation of carbonates to methane

All carbonate and bicarbonate salts were purchased with a purity of 99.9% or higher from Sigma Aldrich. The activated catalyst was weighed in an atmosphere of argon and then transported to a nitrogen chamber. There, 10 mmol of carbonate was mixed with DI water as the solvent. The catalyst, solvent (water), and carbonate salt were placed in a borosilicate vial. This vial was then placed in a 125 mL Hastelloy Parr reactor that was sealed in the nitrogen chamber. The Parr reactor was pressurized with hydrogen (UHP). Then, the reactor was placed in a pre-heated aluminum block, 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. The yield was then computed by integration of the gas peaks from the GC analysis. A sample calculation is provided in section 2.2.

1.5 Air capture of CO₂ with potassium hydroxide

To capture CO₂ from air (~420 ppm CO₂) potassium hydroxide (Sigma Aldrich, 97%) was dissolved in 10 mL of DI H₂O in a vial. The vial was sealed and air from the lab was then flown through the vial at the rate of 300 mL/min. The air capture was run for 48 hours. Afterwards, tert-butanol (tBuOH) was added as an internal standard to a 0.1 mL aliquot of the capture solution. This aliquot was analyzed by ¹³C NMR with D₂O as the deuterated solvent. The amount of CO₂ was quantified through ¹³C NMR analysis. The remaining solution was used for hydrogenation.

1.6 CO₂ from pure CO₂ capture

A known amount of alkali hydroxide (KOH) was dissolved in DI water (10 mL) in a vial with a magnetic stir bar. The gases inside the vial were then removed under vacuum. CO₂ was subsequently added while stirring the solution at 800 rpm for 3 h and maintaining the CO₂ pressure inside the reactor at 1 psi above atmospheric pressure. The amount of CO₂ captured was calculated both through the volume of CO₂ added and through gravimetric analysis of the solutions before and after the capture.

1.7 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. After evacuation, the subsequent capture conditions follow the same parameters as detailed in 1.6. The amount of CO₂ captured was measured by both the volume of CO₂ added and gravimetrically. The liquid was then placed back in the reactor with the catalyst that was utilized in the previous cycle. The hydrogenation reaction was then performed again with the conditions detailed in 1.4.

1.8 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° - 80° at a scan rate of $3^{\circ}/\text{min}$. The resulting spectrum were processed on the PDXL software.

1.9 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) images were obtained from a JEOL JSM-7001F electron microscope with an acceleration voltage of 18 keV.

1.10 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 spectrum. 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 $K\alpha$ peak.

2 Data

2.1 XRD data

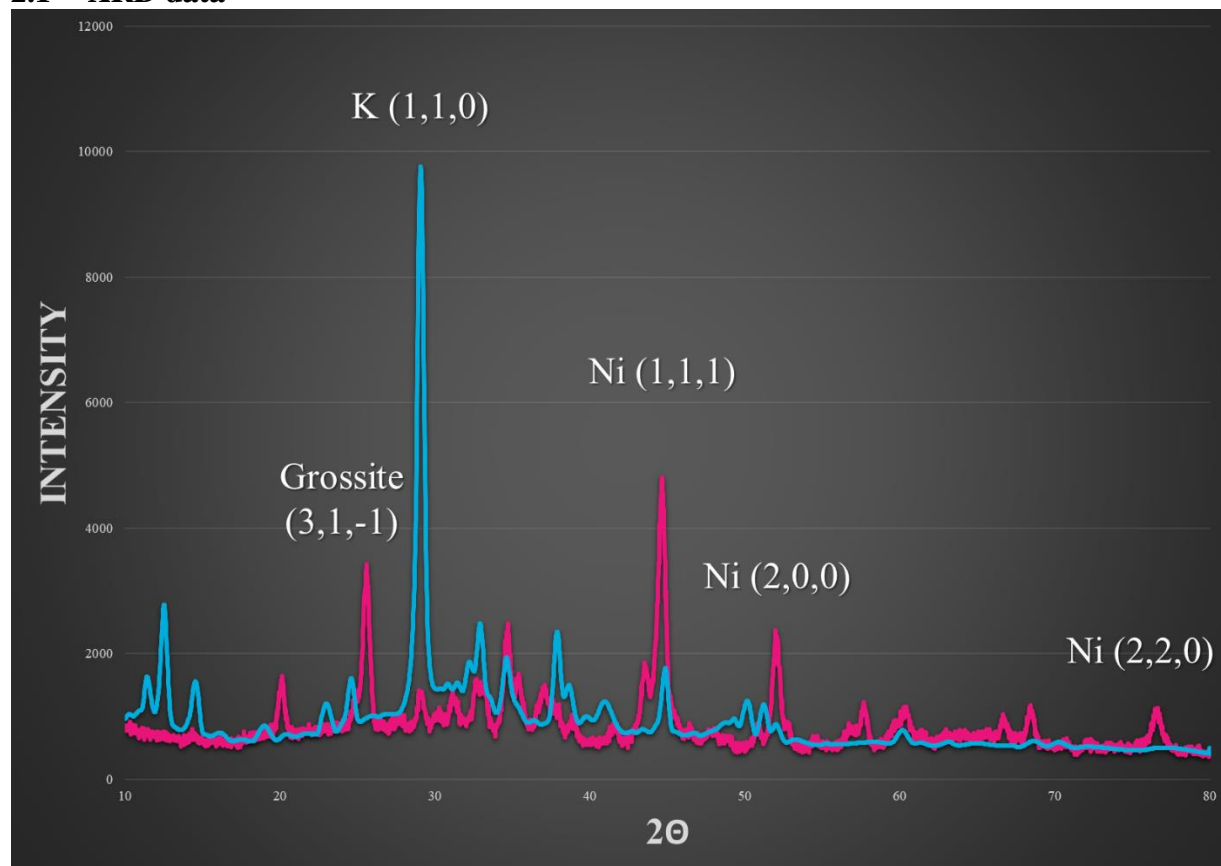


Figure S1. Powder XRD of Ni/CaAl₂O₄ before the reaction (shown in red) and after the reaction with potassium bicarbonate (shown in blue).

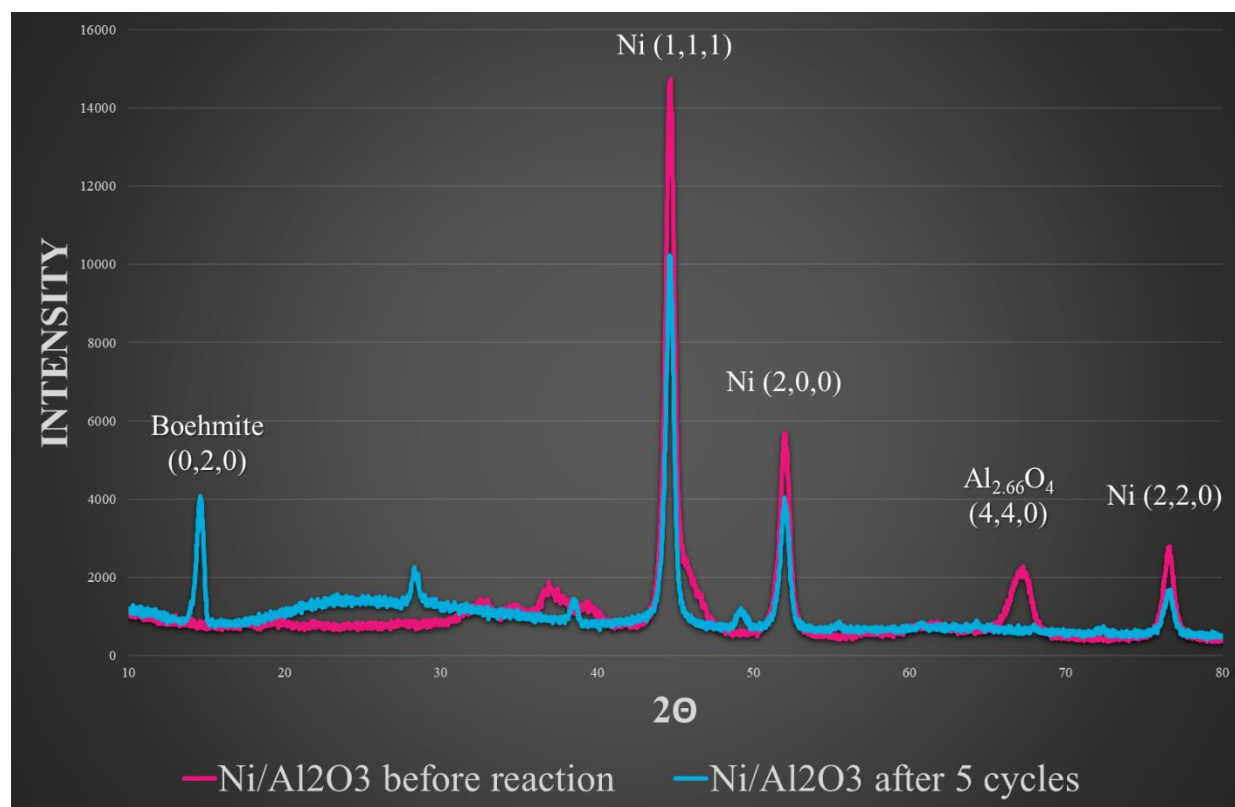


Figure S2. Powder XRD of Ni/Al₂O₃ before the reaction (shown in red) and after five cycles of the reaction (shown in blue).

Table S1. D-spacing and crystallite size of the catalyst before and after reaction

Sample	D-spacing (Å) ^[a]	Crystallite Size (Å) ^[b]
Ni/CaAl ₂ O ₄ (HiFuel 110)	2.03	156
Ni/CaAl ₂ O ₄ after reaction with KHCO ₃	2.02	189
Ni/CaAl ₂ O ₄ after reaction with K ₂ CO ₃	2.03	87
Ni/CaAl ₂ O ₄ after 5cycles	2.03	123
Ni/Al ₂ O ₃	2.03	139
Ni/Al ₂ O ₃ after reaction with KHCO ₃	2.08	138
Ni/Al ₂ O ₃ after reaction with K ₂ CO ₃	2.03	166
Ni/Al ₂ O ₃ after reaction with Na ₂ CO ₃	2.03	147
Ni/Al ₂ O ₃ after 5 cycles	2.03	154

[a] D-spacing was calculated by Bragg's law and all measurements are within 0.1 Å [b] crystallite size measurements are all within 1 Å.

2.2 Gas Chromatography data

Figures S3 and S4 show the standard gas chromatography, which was used for the analysis of the products. The gas chromatography shows a peak at 1.8 minutes which corresponds to hydrogen. The peak 2.2 minutes relates to nitrogen/air and the peak at 4.5 minutes corresponds to methane, the reaction product. If carbon monoxide or carbon dioxide were present a peak would appear in the gas chromatography at 2.8 minutes and 8.5 minutes, respectively.

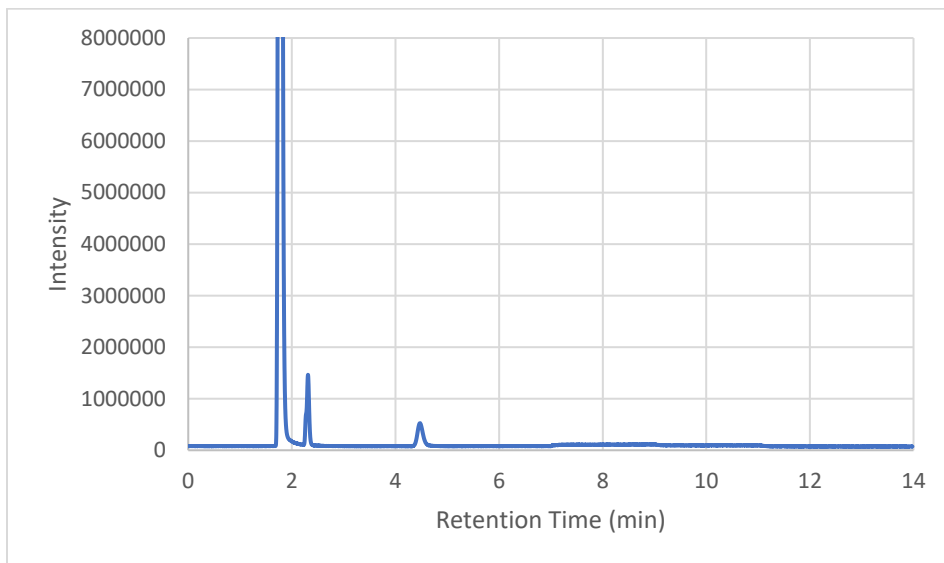


Figure S3. A representative GC spectrum of the reaction with the conditions of 48 hours, 300mg Ni/Al₂O₃, 225° C, 10 mL H₂O, 50 bar H₂, 10 mmol K₂CO₃. 1.8 min: H₂, 2.2 min N₂/air, 4.5 min CH₄.

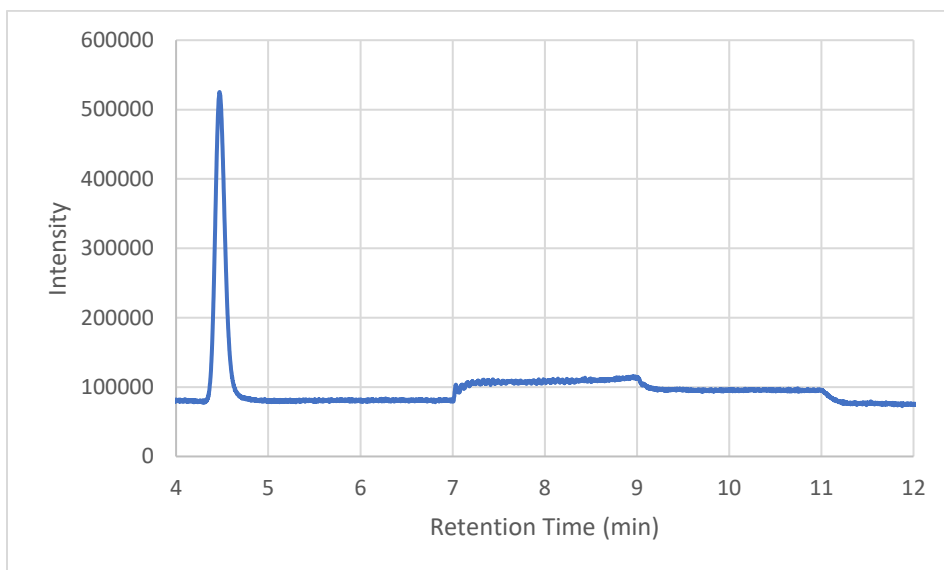


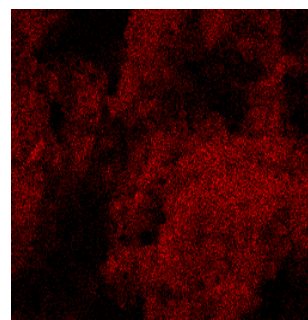
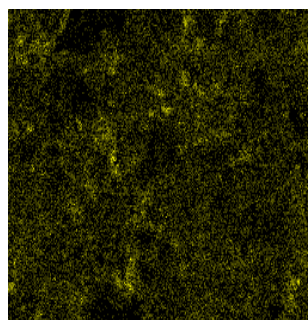
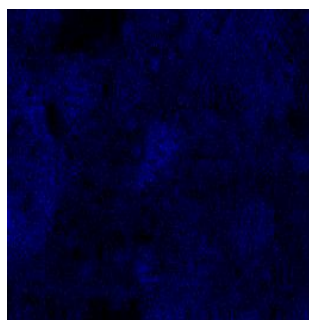
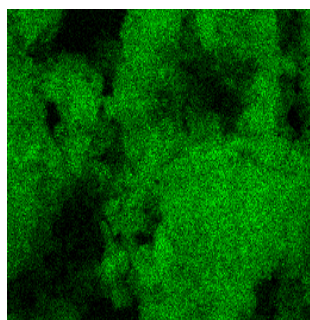
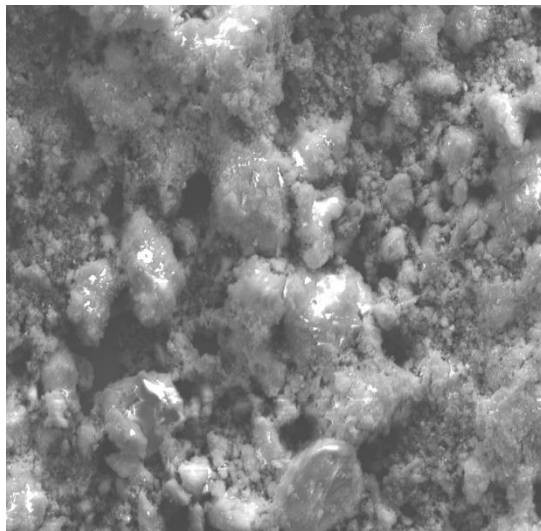
Figure S4. A representative GC spectrum of the reaction with conditions of 48 hours, 300mg Ni/Al₂O₃, 225° C, 10 mL H₂O, 50 bar H₂, 10 mmol K₂CO₃ zoomed between 4 and 12 minutes. Peak at 4.5 min corresponds to the reaction product, CH₄.

To calculate the amount of methane that was produced, the integration values were obtained from the gas chromatography spectrum. For example, the chromatograms shown in figures S3 and S4 have 99.85% H₂ and 1.15% CH₄. 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 95.75% H₂ and 4.25% CH₄. The pressure prior to releasing the gas was recorded and utilized for the next step of the calculation. The pressure of 655 psi at the time of release is multiplied by the percentage of methane. This results in 27.83 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. 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 10 mmol of methane in the gas released from the reactor. This provides the 100% yield that was observed.

$$\text{mol of methane} = \frac{(1.894 \text{ atm})(0.130 \text{ L})}{(27.0 \text{ }^\circ\text{C} + 273.15)(0.0821 \frac{\text{atm} * \text{L}}{\text{mol} * \text{K}})}$$

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.

2.3 SEM/XRF data of the catalysts



Aluminum

Calcium

Nickel

Oxygen

Figure S5. A SEM image and EDS mapping of the Ni/CaAl₂O₄ catalyst after activation

The weight concentrations were 27.4% Ni, 11.95% Ca, 38.17% Al, and 23.47% O as determined by Energy Dispersion X-Ray Spectroscopy.

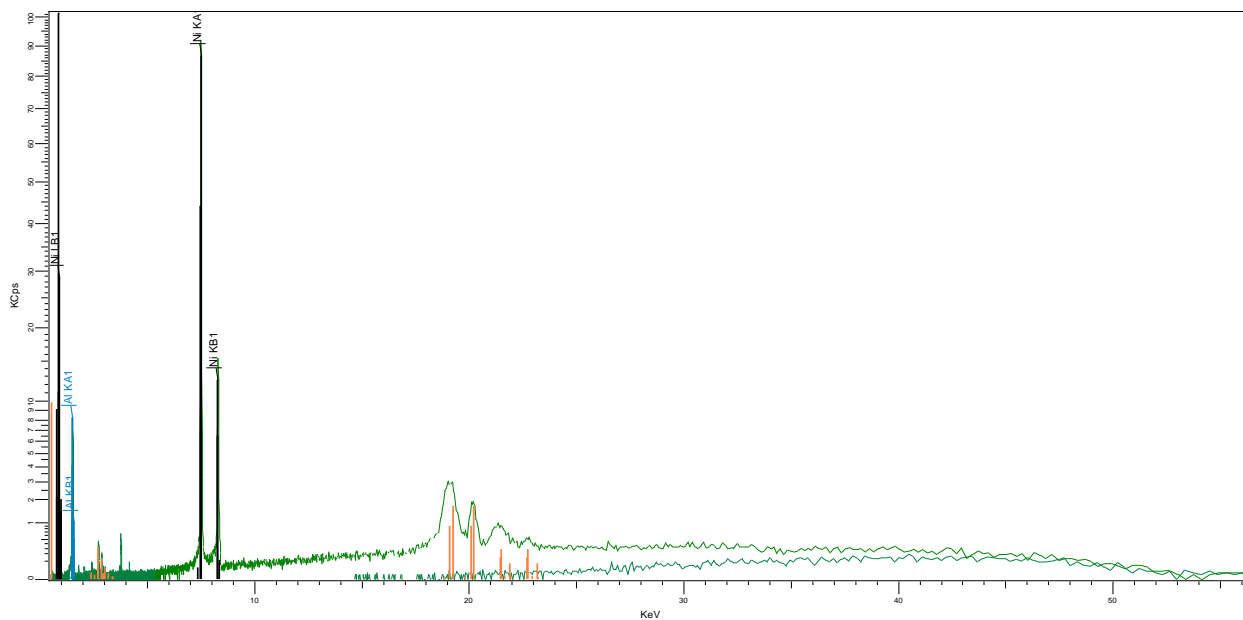


Figure S6. XRF of 25%Ni/Al₂O₃ after activation under H₂

The nickel signals are marked with black markings. Aluminum is marked with blue markings. The residual rhodium peaks are marked with orange markings. The rhodium peaks are present because the X-Ray source is rhodium.

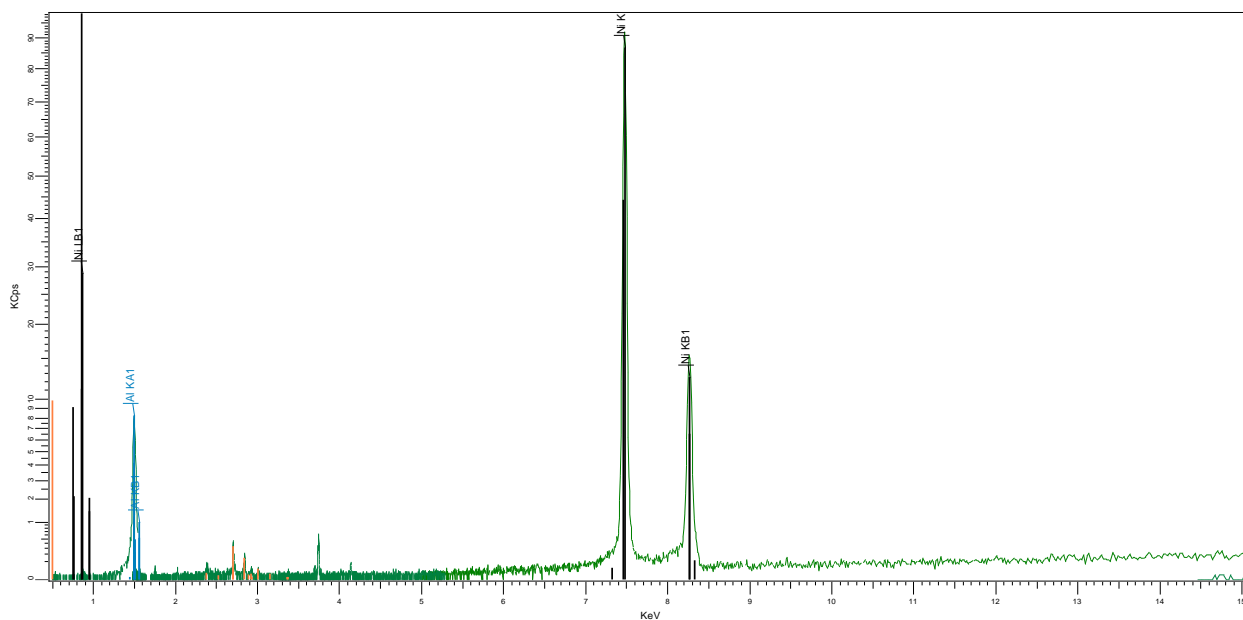


Figure S7. XRF spectra of 25%Ni/Al₂O₃ after activation zoomed into 0-15KeV

Table S2. Weight concentration of Ni/Al₂O₃

Catalyst	Nickel (% w)
Ni/Al ₂ O ₃	25.80±0.35

2.4 NMR data

A ^{13}C NMR spectra of the solution after capture of CO_2 from the air (DAC) with KOH following the procedure described in 1.5 was collected and is presented in Figure S8. For this, a small aliquot of the solution (100 μl) was dissolved in 1 mL of D_2O . 100 mg of imidazole was used as an internal standard. The obtained peak at 164.8 ppm corresponds to a mixture of potassium bicarbonate/carbonate that was produced as a result of the capture. Nuclear Overhauser Effects were excluded from the program and the peaks were integrated to determine the amount of CO_2 captured.

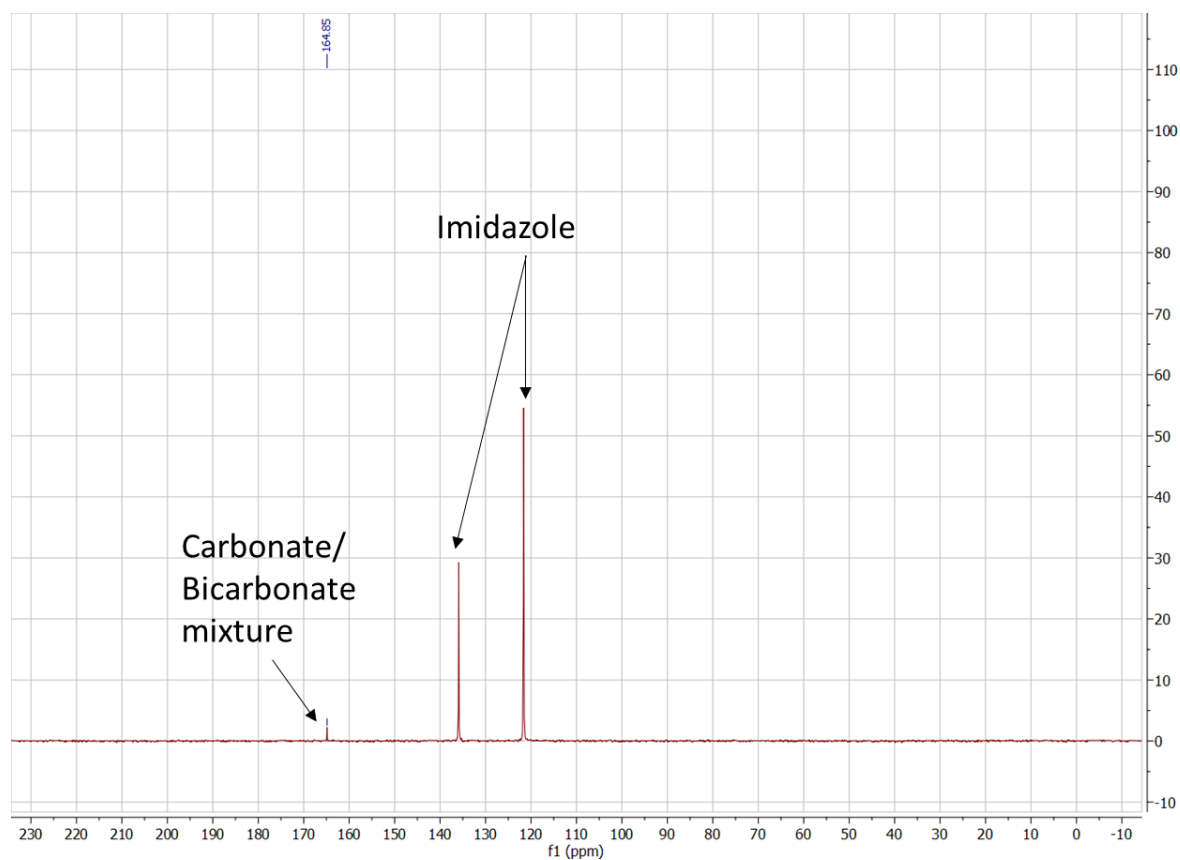


Figure S8. Proton decoupled ^{13}C NMR of the DAC solution after capture (in D_2O with imidazole as internal reference).

Figure S9 shows the proton decoupled ^{13}C NMR spectra of a 1/1 mixture of potassium carbonate/potassium bicarbonate ($\text{K}_2\text{CO}_3/\text{KHCO}_3$), whose ^{13}C signals appear as a single peak in D_2O at 164.04 ppm. Imidazole was used as the internal standard. This peak matches closely the peak shown in Figure S8.

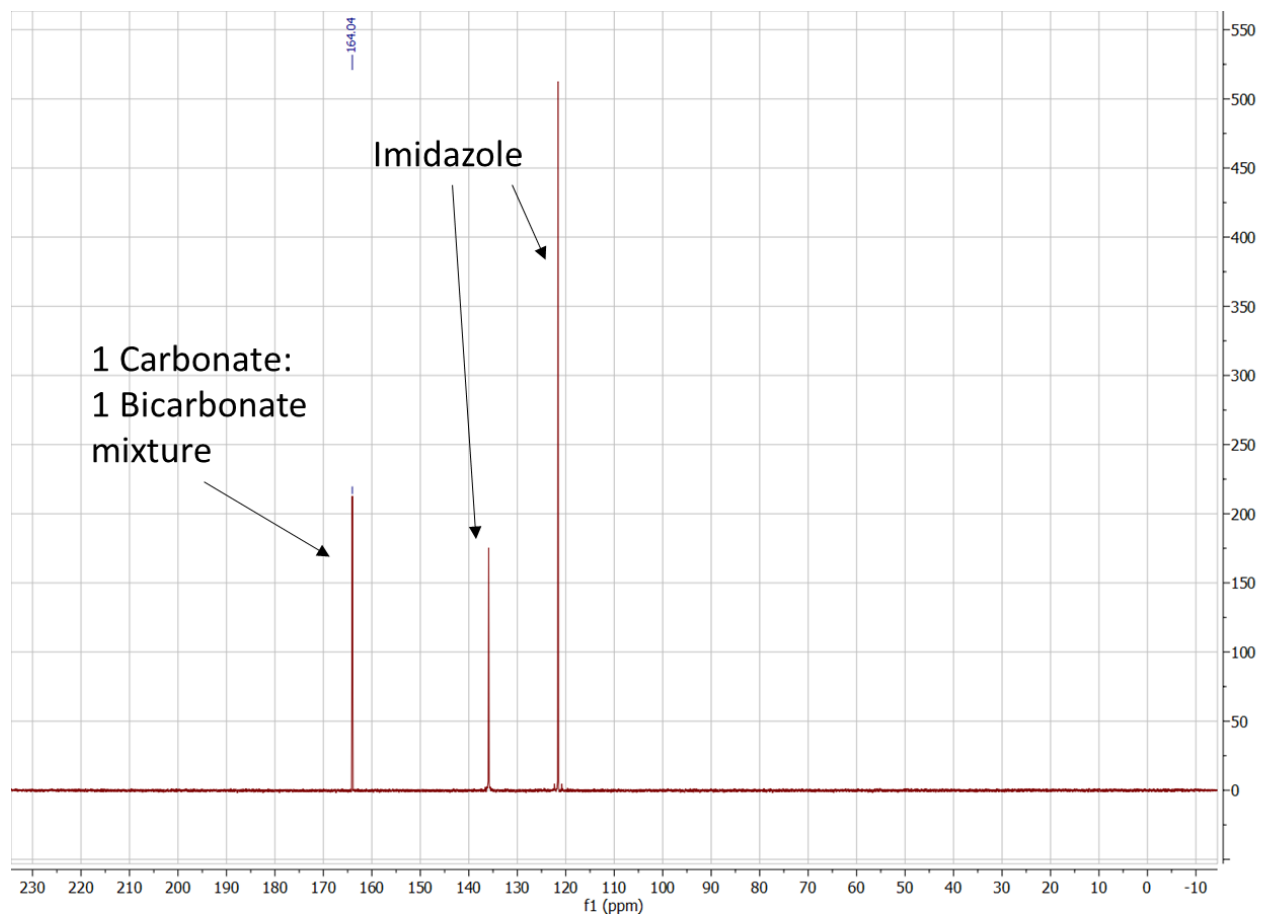


Figure S9. Proton decoupled ^{13}C NMR of a 1:1 mixture of potassium carbonate/potassium bicarbonate (in D_2O with imidazole as internal reference).

Figure S10 shows the ^{13}C NMR spectra of a sample of potassium bicarbonate, KHCO_3 , in D_2O . Imidazole was used as the internal standard.

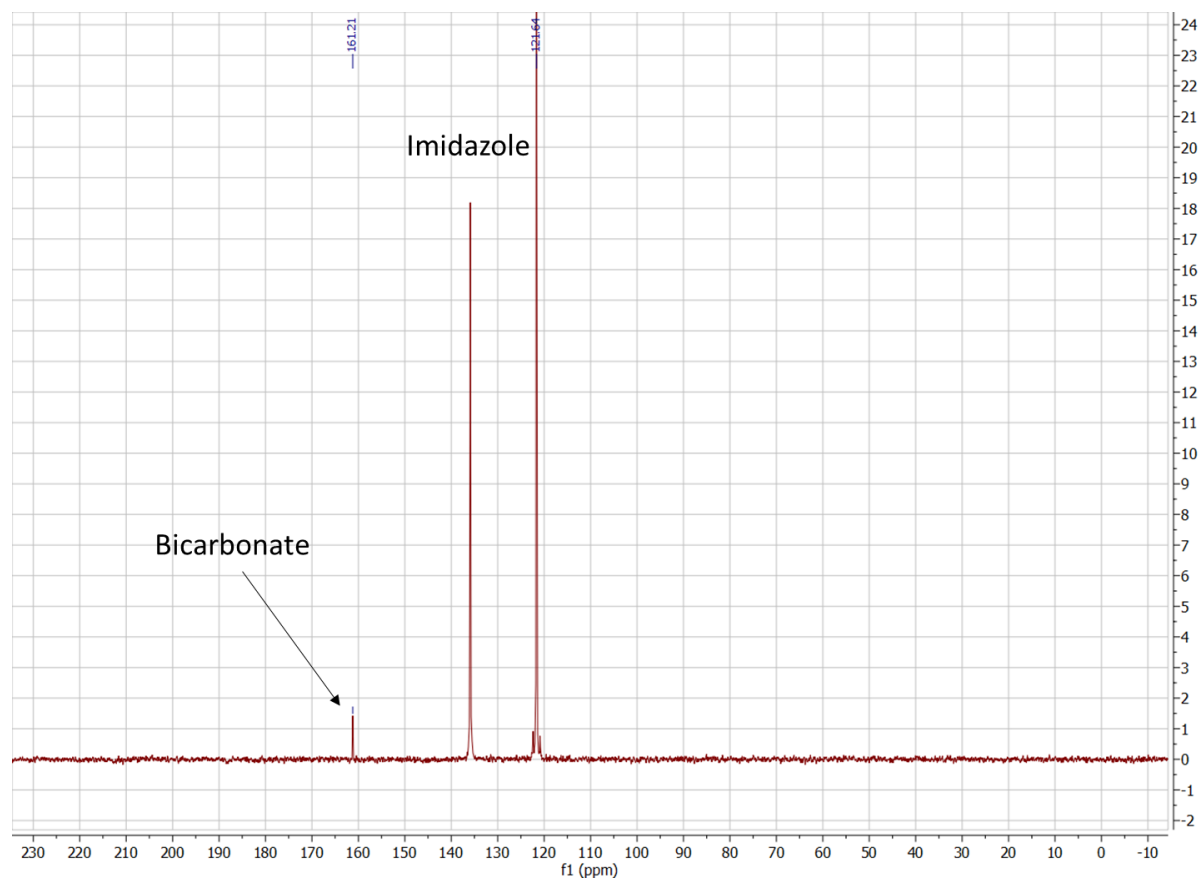


Figure S10. Proton decoupled ^{13}C NMR of a potassium bicarbonate, KHCO_3 (in D_2O with imidazole as internal reference)

Figure S11 shows the Proton decoupled ^{13}C NMR spectra of a sample of potassium carbonate, $\text{K}_2^{13}\text{CO}_3$, in D_2O . Imidazole was used as the internal standard.

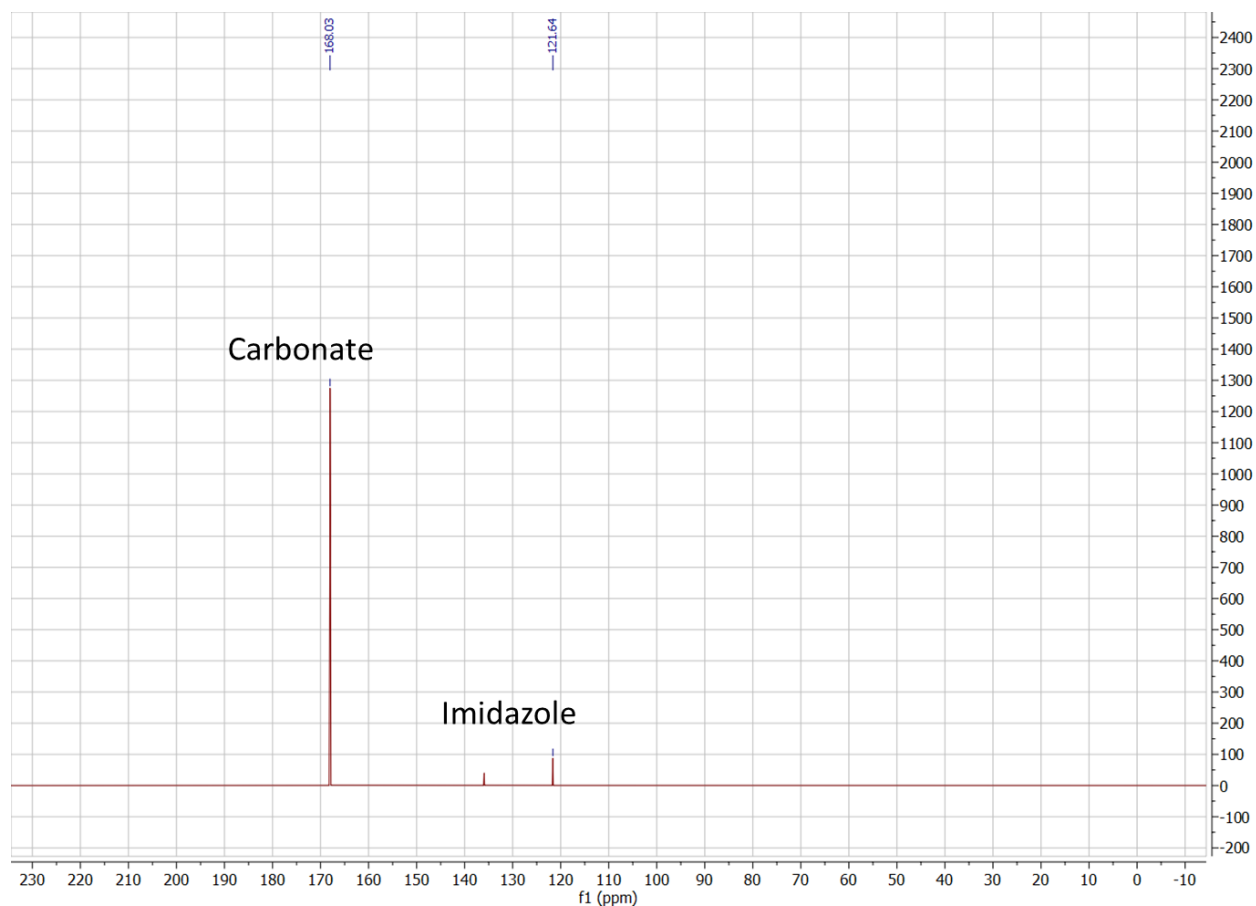


Figure S11. Proton decoupled ^{13}C NMR of potassium carbonate, $\text{K}_2^{13}\text{CO}_3$ (in D_2O with imidazole as internal reference)

A reaction with ^{13}C labeled $\text{K}_2^{13}\text{CO}_3$ was performed to determine whether the resulting methane would be ^{13}C -labelled (following the condition in Table 3, entry 3). For this, part of the gas mixture after the reaction with $\text{K}_2^{13}\text{CO}_3$ was bubbled through a solution of deuterated toluene and a ^1H NMR spectrum was collected. Methane is known to appear at about 0.17 ppm in toluene- d_8 .^{1,2} With ^{13}C -labelled methane, the methane peak would appear as a doublet. And this was indeed what was observed in the spectrum (Figure S12 and S13 A), showing that the methane resulting from the reaction was ^{13}C -labelled. The $^1\text{J}_{\text{CH}}$ value obtained was equal to 125.7 Hz. There was also a trace amount of ^{12}C -methane (due to the presence of $\text{K}_2^{12}\text{CO}_3$ in the carbonate which was 98.7% ^{13}C according to the manufacturer).

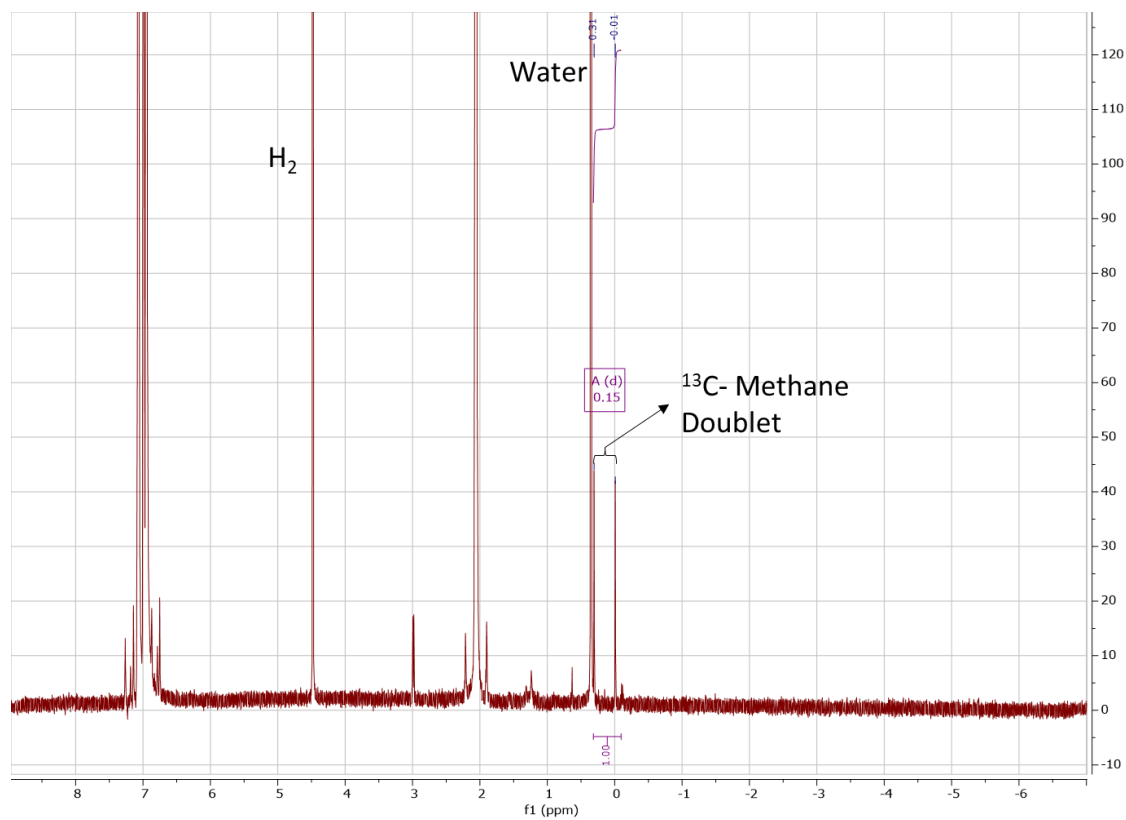


Figure S12. ^1H NMR of the gas mixture after reaction with $\text{K}_2^{13}\text{C}\text{O}_3$ showing the ^{13}C -methane peaks around 0.17 ppm (as well as the peak corresponding to H_2 at 4.48 ppm due to the presence of H_2 in the gas phase) in toluene- d_8 . The expansion of the methane region is shown in Figure S13 A.

Following a similar procedure, where methane from the reaction mixture is bubbled through deuterated toluene to obtain a methane signal, ^1H NMR was also obtained for pure ^{13}C -methane and ^{12}C -methane to confirm that the methane in the reaction gas mixture was ^{13}C labelled. Figure S13-C shows that the ^{12}C -methane peak is at 0.16 ppm. Figure S13-A and S13-B show the $^{13}\text{CH}_4$ peaks in the same positions (~ 0.01 and 0.31 ppm) and with the same $^1J_{\text{CH}}$ coupling constant of 125.7 Hz. Thus, it was confirmed that we can synthesize ^{13}C labelled methane from ^{13}C labelled carbonate salts.

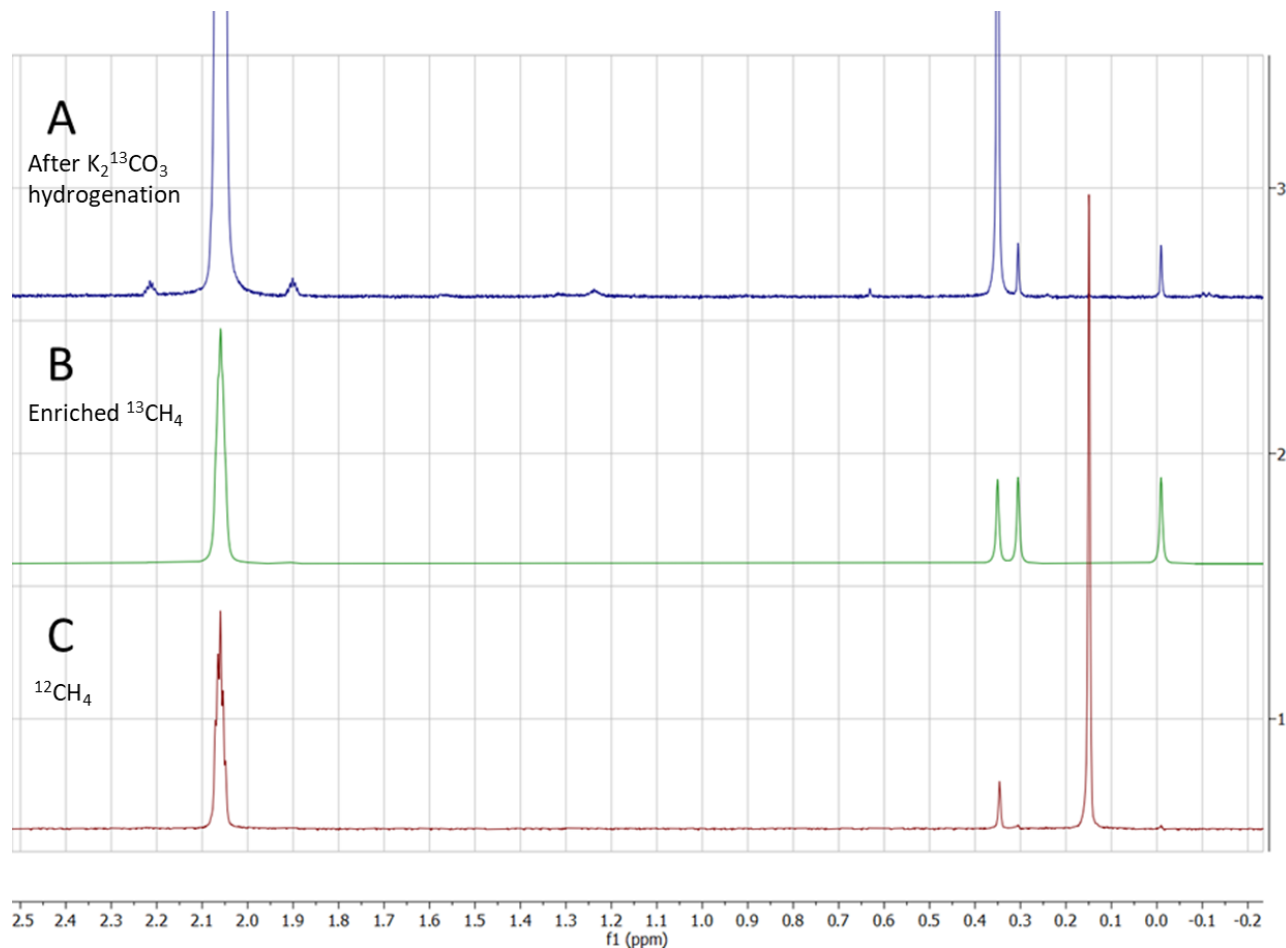


Figure S13. ^1H NMR of methane in toluene from various methane sources shown from -0.2 ppm to 2.5 ppm [A] from reaction gas mixture as shown in Figure S12 [B] from 99% ^{13}C pure ^{13}C -methane [C] From ^{12}C -methane. Taken in toluene- d_8 .

A ^{13}C NMR spectrum was also collected after the reaction with $\text{K}_2^{13}\text{CO}_3$ to determine whether the resulting methane was ^{13}C -labelled (Figure S14). The gas mixture after the reaction was bubbled through a solution of deuterated toluene. There is a peak at 0 ppm, which corresponds to methane, as verified by analyzing 99% ^{13}C methane (Figure S15).

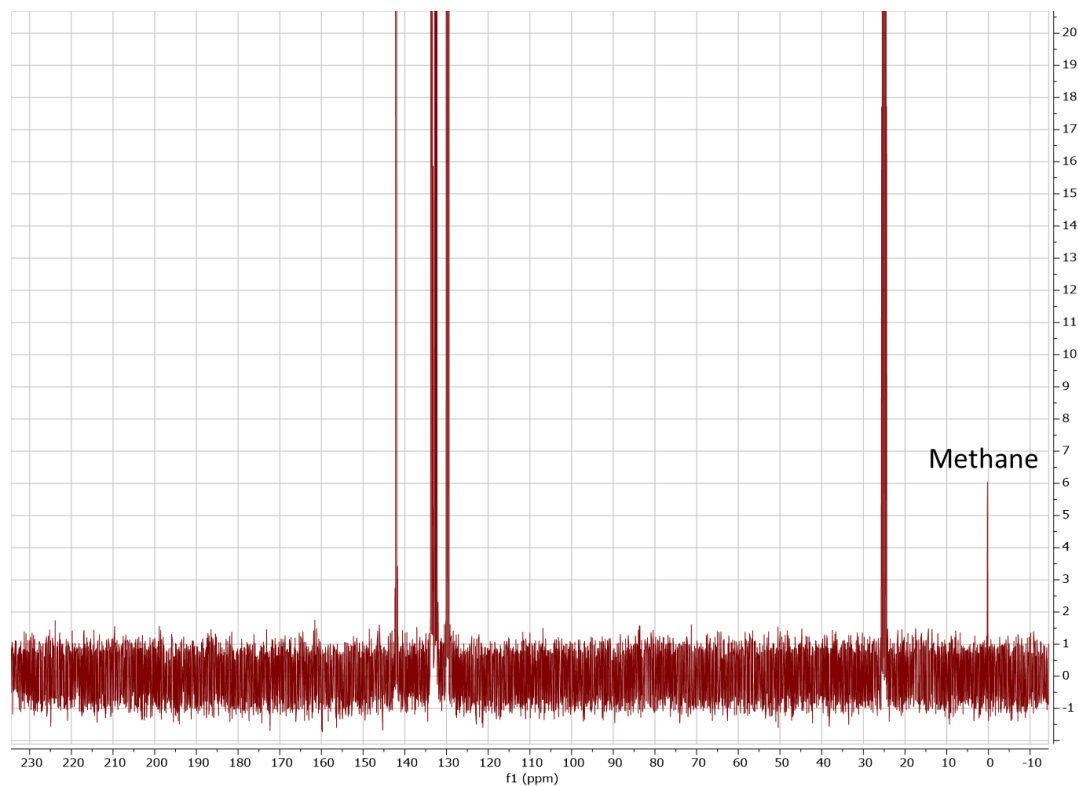


Figure S14. Proton decoupled ^{13}C NMR of the gas mixture after reaction with $\text{K}_2^{13}\text{C}\text{O}_3$ showing the ^{13}C -methane peaks around 0 ppm. Taken in toluene- d_8 .

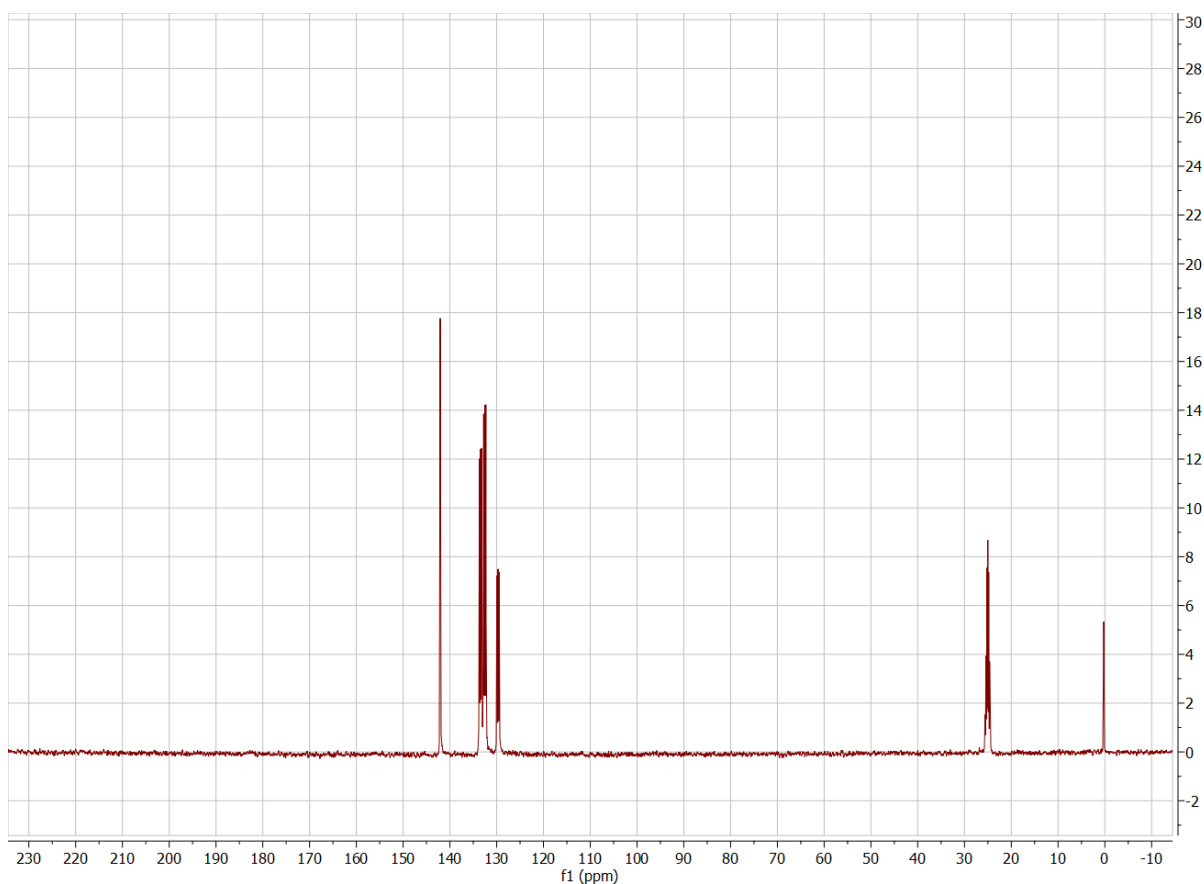


Figure S15. Proton decoupled ^{13}C NMR of $^{13}\text{CH}_4$ (99% ^{13}C) showing the ^{13}C -methane peaks around 0 ppm. Taken in toluene- d_8 .

References

- (1) Chen, J. Y. C.; Martí, A. A.; Turro, N. J.; Komatsu, K.; Murata, Y.; Lawler, R. G. Comparative NMR Properties of H_2 and HD in Toluene- d_8 and in $\text{H}_2/\text{HD}@C60$. *Journal of Physical Chemistry B* **2010**, *114* (45), 14689–14695. <https://doi.org/10.1021/jp102860m>.
- (2) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176–2179. <https://doi.org/10.1021/om100106e>.