Integrated Capture and Conversion of CO₂ to Methanol in a Post-Combustion Capture Solvent: Heterogeneous Catalysts for Selective C—N Bond Cleavage

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An efficient and selective heterogeneous catalyst is identified for the condensed-phase hydrogenation of captured CO₂ in the presence of an advanced water-lean post-combustion capture solvent, (N-(2-EthoxyEthyl)-3-MorpholinoPropan-1-Amine), 2-EEMPA. The catalysts commonly used for gas-phase CO₂ hydrogenation (e.g., Cu/Zn/Al₂O₃) cause deactivation of amine promoters via N-methylation by C—O cleavage of formamide intermediates. A heterogeneous catalyst system that suppresses N-methylation of amine solvents is identified, demonstrating how Pt, supported by reducible metal oxides CeO₂ or TiO₂, can be selective for C—N cleavage to produce methanol. This is the first known demonstration of integrated low-temperature thermocatalytic capture and conversion of CO₂ to methanol in an economically viable CO₂ capture solvent. Technoeconomic analyses performed on the state-of-technology suggest that methanol can be produced with a minimum selling price of $4.4/gallon ($1,460/metric ton) when using CO₂ captured from a 650 MW natural gas combined cycle plant. Ultimately, a road map of how realistic and achievable improvements to space velocity and methanol selectivity of this integrated process can enable near cost parity to fossil-derived methanol, with a selling price of ≈$1.4/gal ($470/metric ton), is presented.

1. Introduction

Continuous anthropogenic emissions of CO₂ into the atmosphere since the industrial revolution have been associated with ongoing environmental issues such as global warming and climate change. While we transition from fossil energy to renewable energy sources to reduce CO₂ emissions, massive deployment of carbon capture, utilization, and storage (CCUS) technologies are needed to limit the global temperature rise (1.5–2 °C).[1–3] Thus, direct air capture and flue gas capture technologies have recently been gaining considerable attention. Compared to direct air capture (containing ≈400 ppm CO₂), post-combustion CO₂ capture from industrial flue gas (containing 4–15% CO₂) is an efficient and economic approach to curtail emissions to the atmosphere from industrial sources, such as fossil-powered power plants, cement, and steel industries.[4–7]
Particularly, the solvent-based post-combustion CO₂ capture technologies using amines (e.g., monoethanolamine [MEA]) are mature and considered to be the industrial benchmark.[8]

Upon the release of the captured CO₂ via thermal regeneration of the capture solvent at low pressure, the CO₂ can be compressed and then either stored underground for permanent CO₂ storage or used as a C₂ source to produce value-added chemicals/materials and fuels, such as formic acid, methanol, methane, ethanol, polycarbonates, and others.[9,10] However, the overall process of capture, compression, transportation, and storage of CO₂ is not energy efficient or cost-effective. To overcome these challenges, the integrated capture and conversion of captured CO₂ to materials (IC³M) has been identified as a key enabling platform technology for producing CO₂-derived chemicals economically and efficiently.[11] In the conventional CCUS approach, the cost of the capture process is mostly dominated by energy-intensive regeneration of the capture solvent. In the IC³M approach, the exothermic conversion process partially offsets the energy required for the regeneration of the capture solvent. In addition, because the captured CO₂ is converted directly in the capture solvent medium, there is also energy saved on the CO₂ compression and transportation that would otherwise be required with gas-phase conversion, thus reducing additional energy inputs and associated equipment costs. Further, the “activated” captured CO₂ species facilitate new reaction pathways and free-energy landscapes compared to free CO₂, thereby enabling enhanced reactivity and conversion even at low temperature and pressure.[10b] We have recently shown how synthetic methane could be produced by IC³M technology with improved thermal efficiencies of 5%, reduced capital cost of 32%, and reduced minimum product selling price of 12% relative to conventional amine amoxidation and the gas-phase Sabatier methanation process.[11a] The use of IC³M technology has the potential to enable our near-term goal of providing market incentives for carbon capture by selling CO₂-derived materials. Compared to conventional approaches, IC³M is capable of producing multiple products from a single CO₂ capture solvent process by varying the reagent co-feed and catalyst bed, thus providing superior economic incentives with the potential for multiple revenue streams as well as accommodating fluctuations in market demand.

The conversion of captured CO₂ to various C₄ chemicals such as methanol, formate, and CO has been demonstrated in the literature to be enhanced in the presence of amines, alcohols, and other organic solvents. However, most of these solvents are not viable for post-combustion capture because they are too viscous, costly, volatile, or have unknown physicochemical properties for a post-combustion CO₂ capture.[9,11h,12] Compared to the aqueous post-combustion solvents (e.g., aqueous 30 wt% MEA), water-lean post-combustion solvents are superior for the IC³M approach due to the following advantages: 1) have high CO₂ physical solubility, thereby enabling conversion at lower CO₂ pressure and temperature, 2) have lower operating temperatures that suppress the undesirable, endothermic reverse-water-gas-shift reaction (rWGS; \( \Delta H = 41.2 \text{ kJ mol}^{-1} \)) while enhancing desirable CO₂ hydrogenation reactions, 3) facilitate CO₂ hydrogenation reactions (e.g., to methane, methanol, ethanol, methyl formate, and others) that involve water as a byproduct, whereby the excess water in aqueous solvents reverses the equilibrium and can also block catalyst active sites, and 4) are more resistant to corrosion and solvent decomposition.[11b]

In the near term, among the CO₂-derived value-added chemicals, methanol is most attractive as a fuel and as a chemical platform feedstock to produce olefins, aromatics, and other chemicals to help pay for the costs of capture. Currently, methanol is produced industrially from a CO₂/CO and H₂ mixture using a ternary copper-based catalyst (Cu/ZnO/Al₂O₃) in the gas phase at high reaction temperature (>200 °C) and pressure (70–100 bar). In traditional gas-phase catalysis, there are three proposed mechanisms involving 1) a formate (HCOO⁻) intermediate, 2) a CO⁻ intermediate via rWGS, and 3) trans-hydroxycarbonyl (COOH). These intermediates are suggested depending on the catalysts and conditions (Figure 1A, formate and CO pathways shown).[13] In the condensed-phase hydrogenation in the presence of an amine-based capture solvent, the intermediates involved are ammonium carbamate, formate, and N-formamide (Figure 1B).[9,10,c,12,14] The final hydrogenation of the N-formamide intermediate can form many products such as methane, methanol, and N-methylation of the capture solvent. The N-methylation of the capture solvent causes solvent deactivation—therefore, the active –NH– unit of the capture solvent is unavailable for subsequent reuse during CO₂ capture. The C–N cleavage of the N-formamide intermediate forms methane or methanol, while the C–O cleavage cause N-methylation. In this study, we study in detail catalysts with different metal and support combinations to suppress the N-methylation of the capture solvent (via C–O cleavage) using 2-EEMPA, an advanced water-lean capture solvent with the lowest costs (19% cheaper than Cansolv) of capture for the reported CO₂ capture technologies.[15] The best catalysts identified from the batch experiments were explored further for continuous-flow testing for a range of operating temperatures and space velocities. TEA was then performed on the current state-of-technology (SOT) for the combined capture and conversion of CO₂ captured from flue gas from a 650 MW natural gas combined cycle (NGCC) plant using experimental data and two goal cases.

2. Results and Discussion

2.1. Batch Reactor Hydrogenation Studies

2.1.1. Cu- and Ag-Supported Heterogeneous Catalysts

The hydrogenation of captured CO₂ was studied using 2-EEMPA as a water-lean post-combustion capture solvent in a batch reactor (see Experimental Section for details). EEMPA was chosen as a solvent for this study because its molecular structure was derived optimal performance for carbon capture due to its low energy, costs of CO₂ capture, and high chemical durability. The solvent’s two ether groups were introduced to provide charge solvation and the combination and spacing between the 3° and 2° nitrogen atoms promote intramolecular hydrogen bond formation between the carbamate/ammonium of the captured CO₂ in a favorable 6-member ring to keep viscosity of the CO₂-loaded solvent sufficiently low. Furthermore, EEMPA has been shown to be highly durable under oxidative conditions in post-combustion carbon capture, and it is
known that ether and amine moieties are also highly stable under reducing atmospheres common for catalytic hydro-
genations. Details on EEMPA’s molecular design, testing, and performance for carbon capture can be found in our previous publications.[16]

First, CO2 captured in 2-EEMPA (10 wt% CO2 loading) was subjected to hydrogenation in the presence of an industrial gas-phase methanol catalyst, Cu/ZnO/Al2O3 (entry 1, Table 1). The undesired N-methylation of 2-EEMPA was observed by 1H nuclear magnetic resonance (NMR) as a major product. To confirm N-methylation, an operando NMR experiment was performed with 13C-enriched CO2 (shown in Figure 2). At 25 °C, under 13CO2 and H2 atmosphere, the 2-EEMPA+13CO2− (car-
bamate) species was mostly observed at 159.2 ppm in addition to 13CO2 at 125.2 ppm. Upon heating to 170 °C, the following new species were observed: 13CO, 2-EEMPA* H13CO2 (formate), H13CO2C2H5 (ester), 2-EEMPA-13CHO (formamide), and 2-EEMPA-13CH3 (N-methylated 2-EEMPA). The major species identified was 2-EEMPA-13CH3 (the 13CH3 signal observed at 41.7 ppm), which was formed as a result of 13CO2 acting as an N-methylating agent (Figure 1). Similar N-methylation of amines was reported in the literature with a Cu/Al2O3 catalyst.[17] Literature reports have also shown that the rate of formation of N-methylated amine increases (and methanol decreases) when operated at higher temperatures, but the mechanism for N-methylation is still not known.[18] It is also believed that the in situ formed methanol can act as an N-methylating agent. The fact that our operando NMR studies only showed traces of methanol but an excess of 2-EEMPA-13CHO species, N-methyl-
ation likely occurs through a formamide intermediate. Similar formamide intermediate has been identified by us previously in the hydrogenation of captured CO2 to methane.[11a] The for-
mamide can undergo C=O cleavage to form an N-methylated amine or C=N cleavage to form methanol (Figure 1B). In the present case, C=N cleavage is preferred because C=O cleavage results in deactivation of the capture solvent via N-methylation.

Under the experimental conditions shown in Table 1, entry 1, the C=N cleavage selectivity was ≈25% in the case of Cu/
ZnO/Al2O3. CO formation was also observed via the rWGS as a side product. The use of other amphoteric oxide supports such as hydrotalcite and ZrO2 resulted in suppression of methanol product, and only N-formamide and 2-EEMPA-Me products were observed in addition to CO (Table 1, entries 2 and 4). Decreased CO2 loading (5 wt%) improved the overall conver-
sion and reduced rWGS reaction, although the C=N cleavage selectivity remained mostly unchanged (Table 1, entry 1 vs. 3).

The CeO2 and TiO2 support completely suppressed both meth-
anol and 2-EEMPA-Me formation. However, 2-EEMPA-CHO was observed as a major product in both cases, which indicates that these supports in combination with Cu are not effective for
the hydrogenation of the formamide intermediate under these reaction conditions (Table 1, entries 5 and 6). Overall, the surface acidity/basicity of the oxide supports considerably influenced the performance and selectivity of the catalyst (Table 1, entries 1–6).

Milstein et al. have shown that the Ag/Al₂O₃ catalyst was effective for selective C=N cleavage in the case of hydrogenation of benzamides and aliphatic amides under basic conditions.[19] Because formamide is an important intermediate observed under our reaction conditions, 30 wt% Ag/Al₂O₃ was

**Table 1.** Hydrogenation of captured CO₂ in the presence of Cu- and Ag-supported heterogeneous catalysts using a batch reactor system.

| Entry | Cat. | CO₂ conv. [%] | Product selectivity [%] | Methanol Yield [%] | C─N cleavage selectivity [%] |
|-------|------|---------------|--------------------------|-------------------|-----------------------------|
|       |      | CO | CH₄ | 2-EEMPA-CHO | 2-EEMPA-Me | Methanol |                  |
| 1     | 64 wt% Cu/ZnO/Al₂O₃ | 40.2 | 21.4 | 0.0 | traces | 59.0 | 19.6 | 7.9 | 24.9 |
| 2     | 54 wt% Cu/ZnO/hydrotalcite | 34.2 | 16.3 | 4.7 | 15.7 | 63.3 | 0.0 | 0.0 | 0.0 |
| 3     | 64 wt% Cu/ZnO/Al₂O₃ | 62.3 | 14.2 | 0.0 | 0.0 | 65.8 | 20.0 | 12.5 | 23.3 |
| 4     | 64 wt% Cu/Zn/ZrO₂ | 60.5 | 10.7 | 0.0 | traces | 31.2 | 58.1 | 0.0 | 0.0 |
| 5     | 5 wt% Cu/CeO₂ | 3.4 | 0.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 | 0.0 |
| 6     | 35 wt% Cu/TiO₂ | 15.7 | 5.6 | 0.0 | 0.0 | 76.6 | 17.8 | 0.0 | 0.0 |
| 7     | 30 wt% Ag/Al₂O₃ | 30.6 | 0.0 | 1.0 | 0.0 | 72.8 | 26.3 | 0.0 | 0.0 |

Reaction conditions: Catalyst = 200 mg, 170 °C, 2-EEMPA-5g (CO₂ loaded 2-EEMPA used), initial P(H₂) = 60 bar, time = 12 h. a)2-EEMPA-(10 wt%CO₂); b)2-EEMPA-(6 wt%CO₂), 64% Cu/ZnO/Al₂O₃ = Cu (64 wt%)/ZnO (24 wt%)/Al₂O₃ (5 wt%), 64% Cu/Zn/ZrO₂ = Cu (64 wt%)/ZnO (15 wt%)/ZrO₂ (21 wt%), 56 wt% Cu/Zn/hydrotalcite = Cu(56 wt%)/ZnO(36 wt%)/Al₂O₃(8 wt%), C─N cleavage selectivity = (moles of methanol) × 100/(moles of 2-EEMPA-N-CH₃ + moles of methanol).

**Figure 2.** In situ ¹³C MAS-NMR during the hydrogenation of ¹³CO₂ in the presence of 2-EEMPA and the Cu/ZnO/Al₂O₃ catalyst at 170 °C under 60 bar H₂ (initial pressure) in ethanol co-solvent, 2-EEMPA: EtOH = 1:10 (molar ratio).
The selectivity and performance of 5 wt% Pd/ZnO/Al₂O₃ were significantly improved for hydrogenation of captured CO₂, 5 wt% Pd/ZnO/Al₂O₃, was also screened for the hydrogenation of captured CO₂ to improve the C=N cleavage selectivity for the hydrogenation of formamide intermediate formed in situ, 2-EEMPA-CHO (Table 1, entry 7). Unfortunately, Ag/Al₂O₃ was very slow for the hydrogenation of 2-EEMPA-CHO. In addition, there was no selectivity for C=N cleavage resulting in N-methylation of 2-EEMPA.

### 2.1.2. Pd-Supported Heterogeneous Catalysts

The other commonly used catalyst for methanol synthesis from hydrogenation of CO₂, 5 wt% Pd/ZnO/Al₂O₃, was also screened for hydrogenation of captured CO₂ (Table 2, entry 1). The selectivity and performance of 5 wt% Pd/ZnO/Al₂O₃ were comparable to that of Cu/ZnO/Al₂O₃. Upon testing the roles of Al₂O₃ and ZnO with 5 wt% Pd separately, it was revealed that the combination of both Al₂O₃ and ZnO was required for higher CO₂ conversion (Table 2, entries 2 and 3). In particular, C=N cleavage selectivity was further reduced with the 5 wt% Pd/Al₂O₃ catalyst. Pd on a Ga₂O₃ support predominantly formed methane and some amount of CO. No N-methylation was observed in this case. A lower CO₂ loading (Table 2, entry 5) showed no improvement in CO₂ conversion, unlike the Cu/ZnO/Al₂O₃ catalyst (in Table 1, entries 1 and 3). This suggests possibly different mechanistic pathways involved irrespective of similar product distributions with the Pd/Zn/Al₂O₃ and Cu/ZnO/Al₂O₃ catalysts.

The Pd on an inert carbon support formed 2-EEMPA-Me with good selectivity along with small amounts of CO and methane as side products (Table 2, entry 8). A basic support such as MgO significantly improved the C=N cleavage selectivity to ~55% (Table 2, entry 9), although the methanol yield was lower than entry 1, Table 2, with 5 wt% Pd/ZnO/Al₂O₃. Similarly, Pd supported by CeO₂, which is known to possess significant basicity as well as mild acidity, further improved the C=N cleavage selectivity to ~70%, resulting in significant suppression of N-methylation.

### 2.1.3. Pt-Supported Heterogeneous Catalysts

Followed by the good selectivity of the Pd/CeO₂ catalyst for C=N bond cleavage, Pt/CeO₂, was also screened under similar reaction conditions (Table 3, entry 1). Similar to Pd/CeO₂, Pt/CeO₂ formed methanol with high C=N bond cleavage selectivity. In addition, a considerable amount of CO was also formed in the gas phase by the rWGS reaction. Note that the CO formation via decarbonylation of methanol has also been reported in the literature. The TiO₂ support behaved similar to CeO₂, albeit with more methane formation and less CO production (Table 3, entry 2). While no methanol was formed in the case of Pt on a SiO₂ support, more CO was formed relative to Pt on a TiO₂ support (Table 1, entry 1 vs. 3). In order to understand the role of the support on the reaction mechanism, we performed CO₂-TPD (TPD = temperature programmed desorption) and NH₃-TPD to evaluate the acidic and basic nature of the Pt/TiO₂, Pt/SiO₂ and Pt/CeO₂ catalysts (Figure S7 and Table S2, Supporting Information). The TPD analyses showed that Pt/TiO₂ has both acidic and basic sites, while the Pt/CeO₂ catalyst contains mostly basic sites and the Pt/SiO₂ does not have any acidic or basic sites. This suggests that the basicity offered by the TiO₂ and CeO₂ supports suppresses N-methylation (see Figure 1). Based on the experimental and TPD results, a plausible reaction mechanism for the methanol, CO and CH₄ formation from the captured CO₂ has been shown in Figure 3. First, the captured CO₂ (i.e., carbonate) coordinates to the catalyst surface, followed by hydrogenation with hydrogen activated by Pt to form a formate species, B. The in situ formed formate species, B, formylates the amine and forms an N-formamide intermediate, E. The nucelophilic attack of the lattice oxygen of the support on the carbonyl carbon of the N-formamide intermediate, E, and subsequent hydrogenation and deamination results in the formaldehyde intermediate, H, which then gets hydrogenated again to form methanol. We believe the participation of the lattice...
oxygen in the nucleophilic attack of the carbon of the N-formamide intermediate is the key to the C–N cleavage selectivity. Recent reports in the literature for alcoholysis of amides have indicated that both basic and acidic sites offered by CeO₂ surfaces are required for selective C–N cleavage. However, the mechanistic understanding on the synergistic effect between Pt and the acid–base pairs offered by the supports requires further investigation.

Because of the favorable chemical stability of TiO₂ in organic solvents, its strong metal–support interactions, and its acid–base properties, the Pt/TiO₂ system was explored further with different process conditions. The addition of ethanol

Table 3. Hydrogenation of captured CO₂ in the presence of Pt-supported catalysts using a batch reactor system.

| Entry | Cat.          | CO₂ conv. [%] | CO | CH₄ | 2-EEMPA-N-CHO | 2-EEMPA N-Me | Methanol yield [%] | C–N cleavage selectivity [%] |
|-------|---------------|---------------|-----|-----|---------------|---------------|-------------------|-----------------------------|
| 1     | 5 wt% Pt/CeO₂ | 29.7          | 49.5| 3.3 | 11.4          | 24.4          | 7.2               | 68.0                        |
| 2     | 5 wt% Pt/TiO₂ | 29.1          | 31.9| 19.8| 9.0           | 12.3          | 27.0              | 7.9                         |
| 3     | 5 wt% Pt/SiO₂ | 23.9          | 77.4| 0.0 | 15.3          | 7.3           | 0.0               | 0.0                         |
| 4     | 5 wt% Pt/TiO₂ | 42.4          | 15.6| 7.8 | 37.7          | 11.7          | 27.2              | 11.5                        |
| 5     | 5 wt% Pt/TiO₂ | 11.5          | 35.8| 25.6| traces        | traces        | 38.7              | 4.5                         |
| 6     | 5 wt% Pt/TiO₂ | 15.9          | 0.9 | 25.9| 18.1          | 26.4          | 28.6              | 4.5                         |
| 7     | 5 wt% Pt/TiO₂ | 12.2          | 25.5| 22.4| 15.0          | traces        | 37.1              | 4.5                         |
| 8     | 5 wt% Pt/TiO₂ | 44.7          | 5.8 | 1.6 | 38.1          | 5.9           | 7.6               | 3.4                         |
| 9     | 5 wt% Pt/TiO₂ | 19.3          | 29.8| 16.9| 10.6          | 10.1          | 32.6              | 6.3                         |

Reaction conditions: Catalyst = 200 mg, 170 °C, 2-EEMPA-5g (CO₂ loaded 2-EEMPA was used, 6 wt% CO₂ loading), initial P(H₂) = 60 bar, time = 12 h. a) ethanol (10.6 g); b) 3 h; c) 10 wt% CO₂; d) 30 bar H₂; e) 150 °C; f) 30 wt% MEA was used as a capture solvent; mostly MEA-formate and MEA-N-formamide species were observed; MEA decomposition products were also observed under the reaction conditions, C–N cleavage selectivity = (moles of methanol) × 100/(moles of 2-EEMPA-N-CH₃ + moles of methanol).

Figure 3. Proposed reaction mechanism for the hydrogenation of captured CO₂ in the presence of Pt/TiO₂ catalyst. Surface hydroxyl groups are not shown for simplicity.
as a co-solvent was also evaluated and improved the yields of the 2-EEMPA-CHO intermediate and methanol and decreased the yields of side products, CO, and methane (Table 3, entry 4). However, from the economic feasibility point of view, it is beneficial to avoid using ethanol as the co-solvent in the system. Because ethanol used for CO₂ conversion needs to be separated from the conversion products as well as from the carbon capture solvent, before recycling the carbon capture solvent to the CO₂ absorber. These separations are energy- and capital-intensive involving large distillation columns, big reboilers, and additional process units to break azeotropic between ethanol and water by-product.

At low reaction temperatures (e.g., 150 °C) and with short reaction times, methanol was formed with high selectivity, and 100% selectivity toward C–N bond cleavage was observed (Table 3, entries 5 and 7). Table 3, entry 5 clearly shows that N-methylation and methanol formation do not occur in parallel with Pt/TiO₂—instead, the methanol is likely acting as an N-methylation source. Thus, by avoiding the longer contact time between the methanol and catalyst, N-methylation can be avoided. On the other hand, at lower H₂ pressure, the methanol yield and C–N bond cleavage selectivity were decreased (Table 3, entry 6). The commonly employed post-combustion solvent 30 wt% MEA was also evaluated for the hydrogenation of captured CO₂ with a Pt/TiO₂ catalyst (Table 3, entry 8). ¹H NMR analysis revealed the formation of mostly MEA-formate, MEA-N-CHO species, and several MEA decomposition products (Figure S5, Supporting Information). This shows that the current approach of combined capture and conversion to methanol is not practical when using the conventional MEA solvent, in large part because the reaction involves elimination of water, and the formation of water is hindered in aqueous solution (Figure 1).

2.1.4. TiO₂ Supported Metal Catalysts

In additional batch reactor studies, the TiO₂ support was screened with different metals such as Ni, Ru, Cu, and Pd to understand the role of Pt in selective C–N bond cleavage (Table 4). In the reactions with Ni and Ru, methanol was formed with high selectivity and no methanol was observed (Table 4, entries 2 and 3). To the best of our knowledge, this is the first example of methane formation from captured CO₂ using a non- noble metal catalyst in the presence of a capture solvent. No methanol was observed in the presence of a Cu/TiO₂ catalyst, but only N-methylation was observed via undesired C–O bond cleavage (Table 3, entry 4, also shown in Table 1, entry 6). High Cu content on the TiO₂ support could have limited the availability of the TiO₂ support for the C–N cleavage selectivity. It is also important to note that low Cu content (3 wt%) in Cu/CeO₂ catalyst was not sufficient to hydrogenate the EEMPA-CHO intermediate (Table 1, entry 5).

When Pd was used in place of Pt, the Pd/TiO₂ was less active for the final formamide hydrogenation step (Table 2, entry 5) because Pd has a low concentration of hydrogen atoms on the surface compared to Pt. Therefore, the results in Tables 3 and 4 clearly show that the combination of Pt and TiO₂ or CeO₂ supports is best suited for methanol production with reduced or negligible deactivation of the capture solvent.

Operando ¹³C NMR was performed with ¹³C-enriched CO₂ in the presence of a Pt/TiO₂ catalyst to understand the reaction pathway in the condensed phase and confirm the absence of N-methylation. The NMR analysis showed ¹³CO, 2-EEMPA-¹³CHO, ¹³CH₂OH, and ¹³CH₄ as predominant species at 183.1, 164.4, 49.1, and –11 ppm, respectively, at 170 °C. Simultaneous formation of all these species suggests that methanol can form via both CO and N-formamide intermediates. CO could also form from the decarbonylation of methanol. It is very important to note that no detectable amount of the undesired 2-EEMPA-¹³CH₃ species was observed, unlike the Cu/ZnO/Al₂O₃ catalyst under similar reaction conditions (Figure 2 vs. Figure 4).

2.2. Continuous Flow Reactor Hydrogenation Studies

The most promising catalyst formulation Pt/TiO₂ identified in batch reactor studies was then evaluated under continuous-flow operation for a range of operating temperatures and space velocities using CO₂ captured in neat 2-EEMPA solvent (Table 5). When operating at 140 °C, the CO₂ conversion was very low (2%) (Table 5, entry 1). However, the catalyst was highly selective toward methanol, with 93% selectivity. Interestingly, the remaining product was primarily propanol, with 7% selectivity. At higher temperatures (170 and 190 °C), ethanol and smaller amounts of butanol were also detected (Table 5, entries 2–8). While the mechanism for their formation is not yet clear, we can learn from decades of research on higher alcohol synthesis from the hydrogenation of CO and CO₂. For example, the

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**Table 4. Hydrogenation of captured CO₂ in the presence of metals with TiO₂ supports using a batch reactor system.**

| Entry | Cat. | CO₂ conv. [%] | CO₂ CH₄ | CO₂-EMPA-N-CHO | CO₂-EEMPA-N-CHO | Methanol yield [%] | C–N cleavage selectivity [%] |
|-------|------|--------------|--------|----------------|-----------------|-------------------|--------------------------|
| 1     | 5 wt% Pt/TiO₂ | 29.1       | 31.9   | 19.8          | 9.0             | 12.3              | 27.0             | 0                      | 7.9                    | 68.7                  |
| 2     | 35 wt% Ni/TiO₂ | 77.9       | 0.0    | 91.4          | 6.4             | 0.0               | 0.0           | 0.0                    | 2.2                    | –                     |
| 3     | 5 wt% Ru/TiO₂ | >99        | 0.0    | >90           | 0.0             | 0.0               | 0.0           | >10                    | 0.0                    | –                     |
| 4     | 35 wt% Cu/TiO₂ | 15.7       | 5.6    | 0.0           | 76.6            | 17.8              | 0.0           | 0.0                    | 0.0                    | 0.0                   |
| 5     | 5 wt% Pd/TiO₂ | 19.9       | 3.7    | 16.2          | 80.1            | 0.0               | 0.0           | 0.0                    | –                     | –                     |

Reaction conditions: Catalyst = 200 mg, 170 °C, 2-EEMPA-5g (CO₂ loaded 2-EEMPA used, 6 wt% CO₂ loading), initial P(H₂) = 60 bar, time = 12 h, C–N cleavage selectivity = (moles of methanol) × 100/(moles of 2-EEMPA-N-CH₃ + moles of methanol).
synergistic effects between metal nanoparticles and the underlying TiO\textsubscript{2} support, especially the anatase crystal phase with abundant oxygen vacancies, have been reported to facilitate ethanol formation from CO\textsubscript{2} and H\textsubscript{2}.[27] Thus, this is a very important finding because the production of higher alcohols from syngas and/or CO\textsubscript{2} has been the subject of significant research in the area of conventional thermochemical catalysis. Furthermore, no CO or CO\textsubscript{2} was observed in the gas phase for any of the conditions evaluated. Confirmation that the reaction is primarily occurring in the condensed phase is significant, because any loss of carbon in the form of gas-phase CO or CO\textsubscript{2} would require additional energy and cost for recapture and conversion.

Also, when the operating temperature was increased from 140 to 190 °C (Table 5, entry 5), the CO\textsubscript{2} conversion modestly increased from 2% to 12%. However, the methanol selectivity was reduced from 93% to 78%. When higher alcohols were formed in addition to methanol, the generation of methane with 15% selectivity was also observed. While methane is considered an undesired side product in alcohol production reaction, the production of methane could have its advantages as a CO\textsubscript{2}-neutral fuel. When operating at 190 °C, the space velocity was decreased by a factor of 10 and the conversion increased from 12% to 86% (Table 3, entries 4 and 6). However, methanol selectivity decreased from 78% to 52% because of increasing methane and ethane formation.

Table 5. Hydrogenation of captured CO\textsubscript{2} over a Pt/TiO\textsubscript{2} catalyst over a range of operating temperatures and space velocities using a continuous-flow reactor system.

| Entry | Reaction temperature [°C] | CO\textsubscript{2} Conversion [%] | WHSV [g CO\textsubscript{2}/g cat/h] | TOS [h] | Selectivity [mol C%] |
|-------|---------------------------|-----------------------------------|-------------------------------------|---------|----------------------|
|       |                           |                                   |                                     |         | MeOH | EtOH | PrOH | BuOH | CH\textsubscript{4} | C\textsubscript{2}H\textsubscript{6} |
| 1     | 140                       | 2.2                               | 0.15                                | –       | 92.7 | 0.0  | 7.3  | 0.0  | 0.0  | 0.0  |
| 2     | 170                       | 7.7                               | 0.15                                | –       | 66.5 | 4.3  | 2.5  | 0.7  | 26.0 | 0.0  |
| 3     | 170                       | 29.1                              | 0.015                               | –       | 57.0 | 4.5  | 0.8  | 1.4  | 26.7 | 8.7  |
| 4     | 190                       | 11.8                              | 0.15                                | –       | 78.0 | 4.3  | 0.0  | 2.5  | 15.1 | 0.0  |
| 5     | 190                       | 26.9                              | 0.015                               | 40      | 63.6 | 4.6  | 0.2  | 1.9  | 26.4 | 3.3  |
| 6     | 190                       | 85.7                              | 0.015                               | 80      | 51.5 | 9.7  | 0.6  | 1.9  | 27.1 | 9.3  |
| 7     | 190                       | 75.9                              | 0.015                               | 60      | 50.2 | 8.6  | 0.7  | 2.0  | 29.2 | 9.3  |
| 8     | 190                       | 65.2                              | 0.015                               | 80      | 46.0 | 8.0  | 1.1  | 4.7  | 29.8 | 10.5 |

Liquid feed: Captured CO\textsubscript{2} in 2-EEMPA solvent (5 wt% CO\textsubscript{2}) over 5 wt% Pt/TiO\textsubscript{2} catalyst. Reaction conditions: 1.0 g catalyst, 870 psig; Gas feed: 38 sccm H\textsubscript{2}, 5 sccm N\textsubscript{2}. Change in weight hour space velocity (WHSV) is achieved by changing the liquid feed flow (0.05, 0.025, 0.005 mL min\textsuperscript{-1}). TOS = time on stream. Catalyst was pretreated in situ overnight at 120 °C under reducing flow (50 sccm 10% H\textsubscript{2} in N\textsubscript{2}).

Figure 4. In situ 13C MAS-NMR during the hydrogenation of 13CO\textsubscript{2} in the presence of 2-EEMPA and a 5 wt% Pt/TiO\textsubscript{2} catalyst at 170 °C under 60 bar H\textsubscript{2} (initial pressure) in an ethanol co-solvent, 2-EEMPA: EtOH = 1:10 (molar ratio).
2.3. Catalyst Characterization Studies

Catalytic performance results in Table 5 (entries 6–8) show how the activity of Pt/TiO₂ decreases over time (CO₂ conversion steadily drops from 85.7% to 65.2% over 80 h of reaction). To understand possible underlying deactivation mechanisms, we performed postmortem characterization of the catalyst used in this reaction using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), temperature-programmed oxidation with mass spectrometry (TPO-MS), X-ray powder diffraction (XRD), and inductively coupled plasma (ICP) and compared the results with those of the fresh catalyst. DRIFTS of the fresh and spent catalysts showed the presence of adsorbed water (Figure 5). The spent catalyst also showed alkane C–H stretching bands between 3000 and 2800 cm⁻¹, which corresponds to the capture solvent (EEMPA). The main infrared features of the spent catalyst are the presence of CO adsorbed on Pt and of carbonate-like species in different adsorption modes (note that these carbonate-like species are also present in the fresh catalyst sample). The spent catalyst showed the presence of a terminal Pt–CO (2116 cm⁻¹) and a weak band at 1873 cm⁻¹ for bridged Pt–CO. Multiple bands appeared in the carbonate region between 1700 and 1200 cm⁻¹, correspondingly to the carbonates, carbamates, and bicarbonates.²⁸ Both species (CO and carbonates) have been described in the literature as reasons for metal/support catalyst deactivation—in the case of CO due to a reduction of active sites on the Pt surface and in the case of carbonates due to a reduced number of interface Pt–TiO₂ active sites where they are preferentially formed.²⁸ Physical changes to the catalyst (e.g., sintering/leaching of platinum particles) cannot be discarded, despite the mild conditions used. There was no appreciable change in the Pt dispersion between the fresh and spent catalysts based on the CO chemisorption (Table S3, Supporting Information), suggesting no Pt sintering during the reaction. The presence of organic residue on the spent catalyst makes ICP (for Pt) and elemental analysis (C, H, N, S) quantification difficult or inconclusive. The Pt content of the fresh and spent Pt/TiO₂ catalysts was 5.6% and 4.5%, respectively. The capture solvent absorbed on the spent catalyst could be the reason for the low Pt content (and high C, H, N content) in the spent catalyst. The Pt crystal size as determined by XRD remained below the detection limit. Further, XRD did not indicate any change in the TiO₂ support predominantly anatase phase after reaction. The XRD and elemental analysis (CHNSO) results are presented in the Supporting Information.

The TPO-MS analysis of the fresh Pt/TiO₂ catalyst showed signals for the loss of water between 150 and 500 °C (Figure 6). The spent catalyst showed the presence of water, CO₂, and a small amount of CO. The metal-bound CO is possibly formed from the rWGS reaction. The following could be potential CO₂ sources: 1) the 2-EEMPA carbamate species bound to the Pt, which can release CO₂ with an increase in temperature (2-EEMPA-CO₂⁻ to 2-EEMPA + CO₂), 2) surface bicarbonate species formed upon the reaction of CO₂ or 2-EEMPA carbonate with water. The bicarbonate species can decompose to produce CO₂, water, and carbonate species (2HCO3⁻ to CO₂ + H₂O + CO₂⁻), 3) oxidation of adsorbed organic species such as HCO₂⁻, 2-EEMPA, 2-EEMPA-CHO and 2-EEMPA-CH₃. The concurrent formation of water and CO₂ points to the oxidation of these organic species, 4) oxidation of adsorbed CO—under TPO conditions (10% O₂/He), the surface-bound CO species could oxidize to give CO₂ (2CO + O₂ to 2CO₂). In addition, the TPO profile of the spent catalyst (Figure 6) shows that desorption and oxidation of adsorbed species occur at moderate temperatures (<300 °C) and that CO gets desorbed at temperatures slightly higher than the reaction temperature (190 °C). This relatively strong (and extended) CO adsorption is consistent with literature reports, which indicate this as the main reason for Pt deactivation at these mild reaction temperatures (<200 °C) and...
for weaker CO–Pt adsorption at higher temperatures.[28] Solvent adsorbed on the catalyst (3000–2800 cm\(^{-1}\)) infrared bands in Figure 5) decomposes also at moderate oxidation temperatures (NO peak max at 290 °C in Figure 6). Both DRIFTS and TPO-MS analyses suggest that CO and carbonates are blocking the active sites of the spent catalyst. However, our operando \(^{13}\)C MAS-NMR showed only the presence of metal-bound CO under the reaction conditions (at 170 °C) and that the carbonate/carbonate/bicarbonate species are formed only at room temperature (Figure 4). CO-TPD was performed on the CO chemisorbed Pt/TiO\(_2\) catalyst to further evaluate strong CO adsorption. CO-TPD results suggest that CO is strongly bound to the catalyst surface (CO-Pt) even at the reaction temperature of 190 °C (Figure S8, Supporting Information). Overall, based on DRIFTS, in situ \(^{13}\)C MAS-NMR, and TPO-MS, we conclude that the catalyst is most likely poisoned by the strong adsorption of CO on Pt. Regeneration/reativation is possible at relatively moderate oxidation/desorption temperatures, which will be addressed in our future research.[28,29] The optimization of this Pt/TiO\(_2\) formulation (and reduced CO poisoning) may be targeted toward decreased CO adsorption.[30]

2.4. Technoeconomic Analyses

A technoeconomic analysis (TEA) was conducted for the combined CO\(_2\) capture and conversion to methanol process, as shown in Figure 7. Here, 90% CO\(_2\) in the flue gas from a NGCC power plant was captured in the absorber by countercurrent contact with 2-EEMPA. Instead of sending the CO\(_2\)-rich solvent to a solvent regenerator and producing low-pressure pure CO\(_2\) for downstream conversion to methanol at high pressure, the entire condensed-phase rich solvent is pumped to the desired pressure to avoid the use of a capital and energy-intensive CO\(_2\) compressor. The pressurized rich solvent is then heated and fed to the main reactor packed with Pt/TiO\(_2\) catalyst at 190 °C, 60 bar along with H\(_2\). In this analysis, H\(_2\) is produced off-site from either fossil or renewable pathway, which is outside the system boundary. It is assumed that H\(_2\) is delivered at the conversion plant at pressure as required for H\(_2\) transportation[31] and the associated compression cost is included in the cost of delivered H\(_2\). The reactor product contains CO\(_2\)-lean solvent, unconverted H\(_2\), methanol, C\(_2\)\(_x\), alcohol, CH\(_4\), and light hydrocarbons. The product is first sent to a high-pressure flash drum, where the gas phase goes to the pressure swing adsorption (PSA) unit to separate H\(_2\) from CH\(_4\) and light hydrocarbons. H\(_2\) is recycled back to the reactor, while CH\(_4\) and light hydrocarbons are used as fuel gas to supply heat and energy for other unit operations. The liquid phase from the high-pressure flash drum is sent to the solvent recovery column to separate alcohols from the lean solvent. The lean solvent from the bottom is recycled back to the absorber for CO\(_2\) capture. Wet alcohols from the top contain mainly methanol, ethanol, and water. Because of the existence of azeotrope between these components, extractive distillation is used for alcohols and water separation, where ethylene glycol is used as an entrainer.

A process model of the flowsheet (Figure 7) was developed in Aspen Plus V11, as summarized in Table S4, Supporting Information, to estimate the mass and energy balance and provide basic information for equipment sizing. The ENRTL-RK property method with electrolyte chemistry was used to calculate the thermal and transport properties of the entire flowsheet. Particularly, the energy balance around the integrated solvent regeneration and CO\(_2\) conversion reactor is evaluated using the Aspen built-in enthalpy model at given CO\(_2\) loading, conversion, and product selectivity. For the 2-EEMPA-CO\(_2\)-H\(_2\)O system, the parameters in the property models were regressed available in the Aspen property database were directly used. Flue gas from a 650 MW NGCC plant was used as the CO\(_2\) resource in this study. The flue gas composition (4 mol% CO\(_2\)) and plant scale (224 metric ton CO\(_2\)/h) were set based on Case B31B in the NETL Rev4 report for all cases evaluated in this study.[32] The capital cost of equipment was evaluated using the Aspen Process Economic Analyzer V11. The minimum selling price (MSP) of methanol was evaluated via a simple annualized costs approach used by the PEP Yearbook (IHS Market, PEP Yearbook, 2020) based on the economic assumptions listed in Table S5, Supporting Information. Four cases were evaluated as listed in Table 6: two SOT cases using experimental data, and two goal cases with improved catalyst performance (faster kinetics and/or higher). For the two SOT cases, the operating condition (temperature, pressure, WHSV) and reactor performance (single-pass conversion and product selectivity) were set based on the
The experimental data collected from the continuous flow reactor system (entries 5 and 6 in Table 5). It was assumed that catalyst deactivation could be overcome via regeneration under moderate conditions, under which the regeneration cost is negligible compared to the cost of Pt/TiO₂ catalyst. A detailed cost estimate about the catalyst regeneration will be conducted along with experimental study in our future research.

The key performance and economic measures and breakdown in MSP of methanol are presented in Table 6 and Figure 8 for the four cases. The results suggest that the MSP of methanol at the SOT is ≈$4.4/gal ($1,470/metric ton), which is slightly lower than that of renewable methanol ($1,600/metric ton) assuming CO₂ is sourced from a carbon capture facility at a cost of $50/metric ton CO₂.[33] For the SOT cases, catalyst cost is the major contributor to the MSP of methanol, especially at low WHSV, because the precious metal Pt is used in the catalyst. The two SOT cases suggest that trade-offs exist between WHSV and single-pass conversion with the current technology. Low WHSV leads to a much larger reactor and higher consumption of the expensive catalyst. High WHSV leads to a low single-pass conversion and additional equipment needed to recycle the reactor product and have overall conversion greater than 65%. Note that in the combined carbon capture and conversion process, the reactor has two functions: producing methanol as a final product and regenerating the carbon capture solvent to be sent back to the CO₂ absorber. A conversion greater than 65% is required to generate a CO₂-lean solvent for 90% CO₂ capture from NGCC flue gas with a CO₂ concentration of 4 mol%. The two goal cases suggest that the MSP of methanol can be significantly reduced and may reach price parity with conventional methanol synthesis ($1.2/gal in 2018) if faster kinetics and higher selectivity can be achieved with catalyst and reactor development, both of which are current efforts in our laboratory. Now that a catalyst system has been identified that facilitates selective C–N cleavage, we can work to tune the catalytic parameters to improve overall rate and methanol selectivity. As the delivered hydrogen price varies significantly with production pathways, fossil vs renewable, a sensitivity study as presented in Figure 9 was conducted for Case Goal 2 with high conversion and high selectivity at high WHSV, which illustrates the linear dependence of the MSP of methanol on hydrogen price.

### 3. Conclusions

In summary, we have demonstrated an integrated capture and utilization approach to produce methanol directly from the captured CO₂ inside an economically viable water-lean post-combustion capture solvent, that in time, may achieve cost parity with fossil-derived methanol. We have identified that traditional gas-phase CO₂ hydrogenation catalysts deactivated the solvent via N-methylation of the 2°amine moiety. Upon screening different catalyst formulations, we discovered that the Pt catalysts on reducible metal oxides (TiO₂ or CeO₂) suppress undesirable N-methylation of the capture solvent, showing high selectivity.

![Figure 8. Breakdown in MSP of methanol.](image-url)
for C–N bond cleavage. The most promising catalyst, Pt/TiO₂, with its known favorable chemical stability in organic solvents, strong metal–support interaction, and acid–base properties were further evaluated under continuous-flow operation, which produced a single-pass CO₂ conversion of 29% with 70% selectivity to methanol at 170 °C. Further increase in the reaction temperature to 190 °C resulted in a decrease in methanol selectivity with an unprecedented single-pass CO₂ conversion of 86%. TGA for two SOT cases was performed using experimental data, and two goal cases assuming future improvements to catalytic performance were made. Trade-offs between single-pass conversion, WHSV, and H₂ cost on methanol MSP were evaluated. Assuming that processing advancements are made, which we believe is possible through improved catalyst design, the selling price of methanol can be reduced by nearly half. A detailed study to elucidate the reaction mechanism must be conducted for further understanding and improvement of the process as well as future catalyst design.

4. Experimental Section

Materials: 64 wt% Cu/Zn/Al₂O₃ was purchased from Alfa Aesar. 2-EEMPA was synthesized by following the procedure reported in the literature. Metal (Pt, Pd, Ni, Cu) supported on metal oxides (TiO₂, Al₂O₃, CeO₂, SiO₂, MgO) were prepared by incipient wetness impregnation of nitrate metal precursors followed by drying (8 h at 100 °C) and calcination at 400 °C (4 h under static air). Metal oxide supports: TiO₂ = Degussa P25 from Sigma Aldrich, Al₂O₃ = γ-Al₂O₃ from Engelhard, CeO₂ = nanopowder (<25 nm) from Sigma Aldrich, SiO₂ = Davissil 646 Silica gel from Sigma Aldrich, MgO = Nanoactive (R) MgO from Nanoscale Corporation. All other materials were purchased from commercial suppliers and used without further purification unless otherwise mentioned. All deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. 1,3,5-Trimethoxybenzene (TMB) was added as an internal standard for NMR spectroscopy. The rotor was charged with a 13CO₂ (0.28 mmol) and H₂ (0.8 mmol) and using a 5 mm Chemmagnetics design HXY probe. The rotors were Varian/Agilent style cavern rotors (Revolution NMR LLC), modified for high-pressure samples as described previously[35] 2-EEMPA (0.16 mmol), Cu/ZnO/Al₂O₃ or Pt/TiO₂ (8 mg), and ethanol (1.6 mmol) were transferred to a MAS-NMR rotor in a N₂-atmosphere glovebox. The rotor was charged with a 13CO₂ (0.28 mmol) and H₂ (0.8 mmol) at room temperature and heated to 170 °C. When the set temperature was reached, the rotor was kept at this temperature while an array of 13C NMR spectra was collected. A 45° pulse was used. A recycle delay of 30 s and a spinning speed of 5 kHz were applied. The spectra were acquired with 64 scans and an acquisition time of 300 ms.

Standard Procedure for Continuous-Flow Experiments: Fixed-bed experiments were performed in a stainless-steel tubular reactor (3/8 nominal OD, 0.305 ID), the reactor wall was heated with a stainless-steel block (3 in) wrapped with a fiberglass heating tape (OmegaLux) (Figure S6, Supporting Information). Liquid was fed to the reactor using a high-pressure Isco pump (Teledyne), and gases (H₂, N₂) were fed using mass flow controllers (Brooks). In a typical experiment, 1 g of catalyst (60–100 mesh) was loaded between quartz wool in the heated part of the reactor. Reaction conditions: pressure (60 bar) was controlled using a Tescom back pressure regulator, and temperature (120–190 °C) was controlled using a derga-digital R/S controller. After reaction, liquid products were condensed and collected in a stainless-steel 50 mL cylinder maintained at 0 °C using a recirculatory thermostat (WVR). Gas products were analyzed using a 4-channel Fusion MicroGC (Inficon), and liquid products were analyzed using liquid chromatography.

Catalysts: Characterization: Fresh and spent samples of Pt/TiO₂ catalyst were studied using DRIFTS, TPO-MS, XRD, ICP, and CHNSO elemental analysis. The DRIFTS accessory was a Harrick Praying Mantis with a reaction chamber and zinc selenide windows adapted to a Bruker IFS 66/S spectrometer. The spectra of the untreated samples were recorded with the sample at room temperature (21 °C) and at atmospheric pressure using a background with potassium bromide powder and dry nitrogen purge. The instrument resolution was 4 cm⁻¹ with an 8 mm aperture, and 1024 scans were co-added for the spectrum. A silicon carbide source was used with a KBr beam splitter and a liquid-nitrogen-cooled MCT detector. The scanner velocity was 60 kHz. The phase resolution was 32 cm⁻¹ with a Mertz phase correction. A Blackman-Harris-3-term apodization function was used with 2x zerofill. The nonlinearity correction was turned on.

TPO-MS was performed using a Micromeritics Autochem II 2920 chemisorption analyzer coupled with a Cirrus 2 Mass Spectrometer. 50 mg of sample was loaded under 50 sccm 10%O₂/He for 40 min, and without any preliminary thermal treatment, the sample was ramped up to 600 °C at a rate of 10 °C min⁻¹ and held at this temperature for 20 min. Effluent gases were monitored using mass spectrometry.

TPD and CO Chemisorption were performed using a Micromeritics Autochem II 2920 chemisorption analyzer. 100 mg of sample was loaded and was purged under flowing He (25 sccm) for 10 min. Samples were pretreated in situ at above 200 °C with 10%O₂/He for 2 h, followed by reduction at 200 °C with 10%H₂/N₂ for 20 min, He purged at 200 °C for 10 min, then cooled to 40 °C for N₂, or CO for chemisorption. After the adsorption, samples were purged under flowing He (25 sccm) for
10 min, then the samples were heated up to 500 or 250 °C at a rate of 10 °C min⁻¹. XRD patterns were recorded using a Philips X’pert MPD (Model PW3040/00) diffractometer with a copper anode (Kα = 0.15405 nm) and a scanning rate of 0.0013° per second between 2 h = 10° and 90°. Jade 5 (Materials Data Inc., Livermore, CA) and the Powder Diffraction File database (International Center for Diffraction Data, Newtown Square, PA) were used to analyze the diffraction patterns.

The carbon, hydrogen, nitrogen, and sulfur composition of the Pt/TiO₂ catalyst before and after reaction was determined using a Thermo Fisher Flash 2000 CHNS/O organic elemental analyzer (Thermo Fisher Scientific, Inc., Waltham, MA). About 10 mg of sample was used for each analysis.

ICP was used to quantify the amount of Pt present on the Pt/TiO₂ catalyst before and after reaction. ICP used a Perkin-Elmer 3000DV with an AS90 Autosampler, which has an instrument detection limit of ~1 ppb. About 10 mg of solid sample was prepared via microwave digestion in concentrated acid and then diluted to volume.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
CO₂ captures, CO₂ catalysis, CO₂ utilizations, hydrogenation, methanol, selective C–N cleavage, techno-economic analysis

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