Synthesis of monocarboxylic acids via direct CO2 conversion over Ni–Zn alloy catalysts

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Article

**Keywords:** CO2, hydrogenation, acetic acid, propanoic acid, Ni–Zn alloy

**DOI:** [https://doi.org/10.21203/rs.3.rs-49347/v1](https://doi.org/10.21203/rs.3.rs-49347/v1)

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Abstract

The direct conversion of CO$_2$ to methane, gasoline-to-diesel range fuels, methanol, and light olefins using renewable electricity sources is considered a promising approach for mitigating global warming. Nevertheless, the direct conversion of CO$_2$ to high value-added chemicals, such as acetic and propanoic acids (AA and PA, respectively), has not been explored to date. Herein, we report a Ni–Zn alloy/Zn-rich Ni$_x$Zn$_y$O catalyst that directly converted CO$_2$ to AA and PA with an overall selectivity of 77.1% at a CO$_2$ conversion of 13.4% at 325 °C. The surface restructuring of the ZnO and NiO phases during calcination and subsequent reduction led to the formation of a Ni–Zn alloy on the Zn-rich Ni$_x$Zn$_y$O phase. Surface-adsorbed ($^\cdot$CH$_x$)$_n$ species were formed via the reverse water-gas shift reaction and subsequent CO hydrogenation. Afterward, monocarboxylic acids were produced via the direct insertion of CO$_2$ into the ($^\cdot$CH$_y$)$_n$ species and subsequent hydrogenation. The synthesis of monocarboxylic acid was highly stable up to 216 h on-stream over the Ni–Zn alloy catalyst, and the catalyst maintained its phase structure and morphology during long-term CO$_2$ hydrogenation. The high selectivity toward monocarboxylic acids and high stability of the Ni–Zn alloy demonstrated its excellent potential for the conversion of CO$_2$ into value-added chemicals.

Introduction

The direct conversion of CO$_2$ into fuels and chemicals using renewable H$_2$ that can be produced via water electrolysis or biomass conversion has received considerable attention because of its potential to mitigate global warming$^{1-3}$. Different catalysts have been developed to effectively convert CO$_2$ into C$_1$ chemicals (e.g., methanol$^{4-6}$, CO$^7,8$, CH$_4^9,10$, and formic acid$^{11-13}$). However, because of the inherent inertness of CO$_2$ ($\Delta G^0_{298K} = -394.4$ kJ mol$^{-1}$) and high energy barrier of the C–C coupling reaction$^{14}$, it is challenging to directly synthesize long-chain hydrocarbons and oxygenated species from CO$_2$, with high selectivity. Recently, cascade tandem catalysis strategies have been used to demonstrate that high-yield hydrocarbons and oxygenated species, such as lower olefins$^{15,16}$, C$_5^+$, aromatics$^{19,20}$, and long-chain alcohols$^{21,22}$, can be produced directly via the hydrogenation of CO$_2$. Although many efforts have been dedicated to the direct conversion of CO$_2$ to long-chain hydrocarbons and alcohols, less attention has been paid to the synthesis of monocarboxylic acids, such as acetic and propionic acids (AA and PA, respectively), via direct CO$_2$ conversion.

Acetic acid is an important building block or solvent for producing value-added chemicals, such as vinyl acetate monomers, alkyl acetates, acetic anhydride, and terephthalic acid, which are widely used in the polymer, chemical, textile, and display industries$^{23}$. AA has been mainly produced via methanol carbonylation over Rh- or Ir-based homogeneous catalysts using specially designed reactor systems$^{24}$. An alternative method for producing AA is the fermentation of ethanol$^{25}$ or other biomass-derived species$^{26}$; however, the contribution of the biological process to the total production of AA is small. Similar to AA,
PA is an important chemical that is directly used as a preservative in the food industry or building block for the production of polymers and pharmaceuticals\textsuperscript{26}. The main PA synthesis method consists of the hydrocarboxylation of ethylene using nickel carbonyl as catalyst\textsuperscript{27}. The global productions of AA and PA are approximately 20 and 16 Mton/year, respectively, and their corresponding market values are approximately 690 and 2300 US$/ton, respectively (Supplementary Fig. S1)\textsuperscript{26,28}. The use of CO\textsubscript{2} as reactant to produce AA has been proposed as a sustainable and low-carbon alternative to the conventional petroleum-based route, and previously reported data are summarized in Supplementary Table 1. First, the direct C–C coupling of CO\textsubscript{2} and CH\textsubscript{4} is an attractive method because it uses low-cost CH\textsubscript{4} as a H source and presents an atomic efficiency of 100\%\textsuperscript{29,30}. However, the extremely high stability of CO\textsubscript{2} and CH\textsubscript{4} causes the reaction to be highly unfavorable thermodynamically (Eq. (1)). Thus, the thermochemical conversion of CO\textsubscript{2} and CH\textsubscript{4} resulted in an extremely low CH\textsubscript{4} conversion and AA formation rate (0.05–0.395 mmol g\textsuperscript{−1} h\textsuperscript{−1}) even in stepwise, cyclic reaction mode to alleviate thermodynamic limitations\textsuperscript{31–34}.

\[
\text{CO}_2 + \text{CH}_4 \rightarrow \text{CH}_3\text{COOH} \quad (\Delta G_{298K} = 71.17 \text{ kJ mol}^{-1}, \Delta H_{298K} = 35.3 \text{ kJ mol}^{-1}) \quad (1)
\]

Thermodynamic analysis indicated that even under harsh reaction conditions (10 MPa, 725 °C, CO\textsubscript{2}:CH\textsubscript{4} = 95:5), the fractional conversion of CH\textsubscript{4}/CO\textsubscript{2} was very low ($1.6 \times 10^{-6}$, Supplementary Fig. S2)\textsuperscript{32}. To mitigate the unfavorable thermodynamic C–C coupling between CO\textsubscript{2} and CH\textsubscript{4}, the use of O\textsubscript{2}\textsuperscript{35,36}, methanol\textsuperscript{37}, and plasma was proposed\textsuperscript{35,36,38}; however, overcoming the thermodynamic limitations is still challenging. The second approach is the reverse water-gas shift (RWGS) reaction of CO\textsubscript{2} or dry reforming of CH\textsubscript{4} to produce syngas, followed by the conversion of syngas to AA (Eqs. (2a–c)):\textsuperscript{39–41}

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}, \quad \Delta G_{298K} = 28.63 \text{ kJ mol}^{-1}, \Delta H_{298K} = 42.1 \text{ kJ mol}^{-1}; \quad (2a)
\]

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2, \quad \Delta G_{298K} = 170.59 \text{ kJ mol}^{-1}, \Delta H_{298K} = 247 \text{ kJ mol}^{-1}; \quad (2b)
\]

and

\[
2\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{COOH}, \quad \Delta G_{298K} = -135 \text{ kJ mol}^{-1}, \Delta H_{298K} = -105.8 \text{ kJ mol}^{-1}. \quad (2c)
\]

However, the RWGS reaction for the production of syngas is highly endothermic (Eq. (2a)), and therefore, it is highly energy- and cost-intensive. Third, CO\textsubscript{2} can be directly hydrogenated to AA and PA (Eqs. (3) and (4), respectively):

\[
2\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}, \quad \Delta G_{298K} = -43.08 \text{ kJ mol}^{-1}, \Delta H_{298K} = -64.7 \text{ kJ mol}^{-1} \quad (3)
\]

and

\[
3\text{CO}_2 + 7\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + 4\text{H}_2\text{O}, \quad \Delta G_{298K} = -98.01 \text{ kJ mol}^{-1}, \Delta H_{298K} = -80.07 \text{ kJ mol}^{-1} \quad (4)
\]
In the temperature range of 300–340 °C, the formation of AA and PA could be thermodynamically more feasible than the formation of methanol (Supplementary Fig. 2). In 1994, Ikehara et al.\textsuperscript{34} suggested the possibility of obtaining AA via the direct hydrogenation of CO\textsubscript{2}; it was hypothesized that AA could form over Ag-promoted Rh/SiO\textsubscript{2} via the direct incorporation of CO\textsubscript{2} into methyl groups to form acetate groups. However, the formation rate of AA was extremely low (~0.035 mmol g\textsuperscript{−1} h\textsuperscript{−1}). In addition, the direct conversion of CO\textsubscript{2} to PA has never been reported.

In this study, we demonstrated that the direct CO\textsubscript{2} hydrogenation over Ni–Zn alloy deposited on Zn-rich Ni\texttextsubscript{x}Zn\textsubscript{y}O produced AA and PA with high selectivity (58.9% and 18.2%, respectively) at a CO\textsubscript{2} conversion of 13.4%. The catalyst was highly stable for up to 216 h on-stream and the variations in CO\textsubscript{2} conversion and product selectivity were negligible. The Ni–Zn alloy/Zn-rich Ni\textsubscript{x}Zn\textsubscript{y}O catalyst was synthesized via the co-precipitation of Ni and Zn precursors followed by calcination and subsequent reduction. The formation of the Ni–Zn alloy was monitored using in situ X-ray diffraction (XRD) analysis. The mechanisms and reasons for the high selectivity toward monocarboxylic acids of the CO\textsubscript{2} and CO hydrogenation reactions were analyzed using in situ near-ambient pressure X-ray photoelectron spectroscopy (NAP–XPS) and operando diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS). Lastly, plausible pathways for the production of AA were proposed using density functional theory (DFT) calculations.

**Results And Discussion**

**Performance of hydrogenation of CO\textsubscript{2} to monocarboxylic acids.** Ni–Zn alloy catalysts with different Ni/Zn molar ratios were synthesized via the coprecipitation of Ni(NO\textsubscript{3})\textsubscript{2} and Zn(NO\textsubscript{3})\textsubscript{2} precursors followed by calcination at different temperatures in the range of 500–900 °C for 6 h under air flow and subsequent reduction at 450 °C for 10 h under 5% H\textsubscript{2}/Ar flow. The CO\textsubscript{2} hydrogenation reactions were performed over Ni–Zn alloy catalysts at 325 °C, 3.0 MPa, using a H\textsubscript{2}/CO\textsubscript{2} ratio of 1:2, and gas hourly space velocity (GHSV) of 5400 mL g\textsuperscript{−1} h\textsuperscript{−1}. The Ni–Zn alloy catalysts with Ni/Zn ratios of 1:3 calcined at 500, 600, 700, 800, and 900 °C, followed by reduction were denoted N\textsubscript{1}Z\textsubscript{3}-500, N\textsubscript{1}Z\textsubscript{3}-600, N\textsubscript{1}Z\textsubscript{3}-700, N\textsubscript{1}Z\textsubscript{3}-800, and N\textsubscript{1}Z\textsubscript{3}-900, respectively. Among these, the N\textsubscript{1}Z\textsubscript{3}-900 catalyst presented high AA and PA selectivities of 58.9% and 18.2%, respectively (excluding CO) at a CO\textsubscript{2} conversion of 13.4% (Fig. 1a). The amounts of formic acid and C\textsubscript{4+} acids (e.g., butyric acid, valeric acid) formed were negligible (<1.5%). The total monocarboxylic acid selectivity of the reaction reached 77.1% (excluding CO). Conversely, the selectivities toward CH\textsubscript{4} and C\textsubscript{2}−C\textsubscript{4} were highly suppressed to 17.0% and 5.0%, respectively. Consequently, high space time yields (STYs) of 0.405 and 0.125 mmol g\textsuperscript{−1} h\textsuperscript{−1} were achieved for AA and PA, respectively (Supplementary Table 1). Although numerous reports have been published on the direct hydrogenation of CO\textsubscript{2} to methanol\textsuperscript{5,42–45}, C\textsubscript{5+} liquid hydrocarbons\textsuperscript{46–50}, and aromatics\textsuperscript{19,20,51–53}, studies dedicated to the direct CO\textsubscript{2} conversion to monocarboxylic acids have been extremely rare. A single article, which described the possibility of forming AA over a Ag-promoted Rh/SiO\textsubscript{2} catalyst, was published in the early 1990s\textsuperscript{34}; however, the reported production rate of AA was very low (~0.035 mmol g\textsuperscript{−1} h\textsuperscript{−1}).
Furthermore, this is the first reported synthesis of PA via the direct catalytic hydrogenation of CO$_2$. Even though ZnO is known to be an active catalyst for the synthesis of methanol via the hydrogenation of CO and CO$_2$, the formation of methanol or higher alcohols over Ni–Zn alloy catalysts has not been reported$^6$, $^{54}$, $^{55}$.

To analyze the effect of the calcination temperature on the CO$_2$ hydrogenation, we used Ni–Zn alloy catalysts calcined at different temperatures in the range of 500–1000 °C (Fig. 1a). As the calcination temperature increased from 500 to 700 °C, the CO$_2$ conversion slightly increased from 9.5–10.1%, whereas the AA, PA, and CH$_4$ selectivities increased significantly from 39.5–61.7%, increased significantly from 8.4–15.2%, and decreased significantly from 51.0–21.8%, respectively. Further increasing the calcination temperature to 1000 °C resulted in the increase in CO$_2$ conversion to 14.7%, slight decrease in AA selectivity to 56.1%, and slight increase in PA selectivity to 20.9%. For all catalysts calcined in the temperature range of 500–1000 °C, the C$_2$–C$_4$ selectivity was suppressed, and ranged between 1.0–7.1%. As discussed below, the formation of the Ni–Zn alloy, which played an important role in increasing the selectivity of the reaction toward the formation of monocarboxylic acids, occurred at calcination temperatures above 700 °C.

To further elucidate the role of Ni–Zn alloys for producing monocarboxylic acids with high selectivity, the performance of the N$_1$Z$_n$-900 (n = 2, 3, 4) catalysts was compared with that of monometallic ZnO, and the results are presented in Fig. 1b. The use of the monometallic ZnO catalyst prepared via precipitation resulted in a very low CO$_2$ conversion of 2.0% and high methanol selectivity of 81.3%; moreover, no monocarboxylic acids were formed. Therefore, Ni and Zn presented a strong synergistic effect during the selective conversion of CO$_2$ to monocarboxylic acids. To investigate the synergistic effect, Ni–Zn alloy catalysts with different Ni/Zn ratios were tested for the CO$_2$ hydrogenation reaction. As the Ni/Zn ratios changed from 1:2 to 1:3, the AA and CH$_4$ selectivities increased from 47.2–58.9% and decreased from 28.7–17.0%, respectively, which indicated that the methanation reaction over the Ni-deficient catalyst was suppressed to some extent. This suggested that the Ni/Zn ratios of the Ni–Zn alloy catalysts should be carefully adjusted to obtain catalysts with active sites that could lead to the selective production of monocarboxylic acids. As the Ni/Zn ratio further changed from 1:3 to 1:4, the changes in CO$_2$ conversion and product selectivity were negligible.

The N$_1$Z$_3$-900 catalyst presented excellent long-term stability for the CO$_2$ conversion reaction and remarkable selectivity toward monocarboxylic acids (Fig. 1c). The initial CO$_2$ conversion activity of the N$_1$Z$_3$-900 catalyst was maintained for up to 216 h on-stream. After 216 h on-stream, the CH$_4$ and AA + PA selectivities slightly increased from 17.0–21.6% and slightly decreased from 77.1–71.5%, respectively. However, even after the long-term catalytic run, the production of methanol and long-chain alcohols were not observed.

**Process optimization.** The aforementioned experiments demonstrated that the use of the N$_1$Z$_n$-900 (n = 2, 3, 4) catalysts produced monocarboxylic acids directly via the hydrogenation of CO$_2$ with high selectivity.
For the process optimization experiments, CO₂ hydrogenation was performed under different reaction conditions to optimize the CO₂ conversion and monocarboxylic acid selectivity. First, the effect of temperature on the CO₂ conversion over the N₁Z₃-900 catalyst was analyzed (Supplementary Fig. 3a). As the temperature was increased from 280 to 325 °C, the CO₂ conversion increased from 8.8–13.4% and the AA + PA selectivity (excluding CO) increased from 64.3–77.1%. As the temperature was further increased to 350 °C, the CO₂ conversion, AA + PA selectivity, and CH₄ selectivity slightly increased to 13.6%, decreased significantly to 55.4%, and increased significantly from 17.0–38.5%, respectively. The increase in CH₄ selectivity with the temperature could be attributed to the high availability of dissociated H on the surface of the catalyst. When the pressure was increased from 1.5 to 3.0 MPa, the CO₂ conversion increased from 8.6–13.4% and the change in AA + PA selectivity was negligible (Supplementary Fig. 3b). At a high pressure of 4.0 MPa, the AA + PA and CH₄ selectivities decreased to 60.8% and increased to 35.1%, respectively. The increase in CH₄ formation at high H₂ partial pressure was ascribed to the increase in the availability of dissociated H on the surface of the catalyst, which increased the possibility of hydrogenation of the *CO species (* denotes surface-adsorbed species). As the H₂/CO₂ ratio increased from 1:1 to 2:1, the CO selectivity decreased from 86.5–63.4% and the CO₂ conversion and AA + PA selectivity remained almost the same (Supplementary Fig. 3c). The increase in the H₂/CO₂ ratio to 3:1 resulted in the decrease in the AA + PA selectivity to 45.3% and significant increase in the CH₄ selectivity to 45.7%, which was caused by the enhanced methanation reaction under a sufficient H₂ supply. As the GHSV increased from 2800 to 8000 mL g⁻¹ h⁻¹, the CO₂ conversion, AA + PA selectivity, and CO selectivity decreased from 18.6–11.1%, decreased from 80–65.1%, and increased from 63.7–72.6%, respectively (Supplementary Fig. 3d). The enhanced desorption of *CO adsorbed on the catalyst surface at high GHSV could be responsible for the decrease in AA + PA selectivity.

Characterization of active phases. To analyze the active sites for the effective conversion of CO₂ to monocarboxylic acids, the crystallinity and phase structure of the catalysts were examined using XRD analysis. We assumed that a new alloy-based active phase was formed during the calcination and reduction of the catalysts because neither metallic Ni⁰ nor ZnO were the active sites for the formation of the monocarboxylic acids. The XRD patterns of the N₁Z₃ catalysts calcined at temperatures in the range of 500–900 °C under air flow, followed by reduction at 450 °C under pure H₂ flow, are presented in Supplementary Fig. 4. The peaks at 36.5°, 57.2°, and 63.1°, which were associated with the respective (101), (110), and (103) planes of pure ZnO, and the 44.7° peak, which was ascribed to the (111) plane of pure metallic Ni⁰, shifted toward lower 2θ angles in the XRD spectra of the reduced N₁Z₃ catalysts (Supplementary Figs. 4c–e). In addition, a new peak at 43.0° appeared in the XRD spectrum of the N₁Z₃-900 catalyst. This suggested that the intermetallic diffusion of the Zn and Ni atoms occurred during the high-temperature calcination and subsequent reduction, which led to the formation of a Ni–Zn alloy phase. The migration of Ni atoms into the ZnO phase during calcination formed the Zn-rich NiₓZnₙO phase⁵⁶. The XRD peaks associated with the Zn-rich NiₓZnₙO phase became sharper and narrower as the calcination temperature increased. The decrease in the full-width at half-maximum indicated that the
crystallinity of the Zn-rich Ni$_x$Zn$_y$O phase increased at high calcination temperatures, and the shifting of the peak positions toward lower 2θ angles suggested that the Ni atoms in the Zn-rich Ni$_x$Zn$_y$O phase were located in the interstitial sites of ZnO$^{57-59}$. Further, the shifting of the Ni$^0$ peak toward a lower 2θ angle by approximately 0.5° indicated the partial dissolution of Zn$^0$ in the Ni$^0$ crystalline structure$^{60}$. The diffusion of Zn into the NiO phase during calcination followed by reduction could produce the Ni–Zn alloy phase. The crystal structure of the Ni–Zn alloy with a Ni/Zn ratio of 1:3, which was predicted using the Reflex plus program of the Material Studio software, was estimated to be Ni$_4$Zn$_{22}$ (Supplementary Table 2, Supplementary Fig. 4b, Supplementary Fig. 5b)

To further investigate the formation mechanism of the Ni–Zn alloys, in situ XRD patterns of the N$_1$Z$_3$ precursor collected under calcination and reduction conditions were analyzed. First, the intermetallic diffusion of Ni and Zn into the ZnO and NiO phases, respectively, was investigated by collecting XRD patterns during the calcination of the co-precipitated N$_1$Z$_3$ precursor at temperatures in the range of 27–900 °C under air flow (Supplementary Fig. 6). As the calcination temperature increased to approximately 230 °C, dehydration of the co-precipitated Ni(CO$_3$)$_3$ and Zn(CO$_3$)$_2$ species and subsequent formation of the NiO and ZnO phases were observed. As the calcination temperature further increased to 900 °C, the positions of the peaks of the pure ZnO and NiO phases progressively shifted toward lower 2θ angles, which indicated that Zn and Ni diffused into the interstitial sites of NiO and ZnO, respectively. During calcination, the Zn atoms in the four-coordinated tetrahedral sites migrated into the tetrahedral NiO$_4$ sites and formed a Ni-rich Ni$_x$Zn$_y$O phase. Because the ionic radius of Zn$^{2+}$ (74 pm) was larger than that of Ni$^{2+}$ (69 pm), the unit cell of NiO was expanded, which resulted in the shifting of the peaks ascribed to the (111), (200), and (220) planes of pure NiO toward lower 2θ angles. The unit cell expansion of the Zn-rich Ni$_x$Zn$_y$O phase implied that Ni atoms could be present in the interstitial lattice sites of the ZnO phase.

After the N$_1$Z$_3$ sample calcined at 900 °C was cooled to 25 °C, in situ XRD patterns were collected as the temperature was increased to 450 °C under H$_2$ flow (Supplementary Fig. 7). The peaks of pure metallic Ni$^0$ (44.8°, 52.1°, and 76.9°, Supplementary Fig. 3) were not observed in the XRD pattern of the reduced N$_1$Z$_3$-900 catalyst, which indicated that pure Ni$^0$ phase did not form during the reduction process. Instead, the peaks associated with the (111) and (220) planes of the Ni-rich Ni$_x$Zn$_y$O phase shifted toward lower 2θ angles, from 37.1° to 36.8° and from 62.9° to 62.7°, respectively. In addition, the 43.1° peak ascribed to the (200) plane of the Ni-rich Ni$_x$Zn$_y$O phase shifted to 42.7° in the XRD pattern of the Ni–Zn alloy. The peaks associated with the (101) and (103) planes of the Zn-rich Ni$_x$Zn$_y$O phase shifted toward lower 2θ angles—from 36.4° to 36.2° and from 62.5° to 62.2°, respectively.

The local chemical environments of Ni and Zn in the N$_1$Z$_3$-700 and N$_1$Z$_3$-900 catalysts were analyzed using X-ray absorption spectroscopy (XAS). The Ni K-edge X-ray absorption near edge structure (XANES) spectra of N$_1$Z$_3$-700 and N$_1$Z$_3$-900 were similar to that of a reference Ni foil, which confirmed the presence of Ni$^0$ in the structure of the catalysts (Fig. 2a). A close inspection of the XANES profile revealed that the onset of the adsorption edge downshifted slightly compared to that of the Ni foil (inset of
Fig. 2a). In addition, the height of the white line peak of the N$_1$Z$_3$-900 catalyst was lower than that of the Ni foil. These results indicated that Ni in the N$_1$Z$_3$-900 catalyst presented a slightly negative charge compared to that of Ni in the Ni foil, which was attributed to the electron transfer from Zn to Ni. The Fourier-transform magnitudes of the Ni K-edge extended X-ray absorption fine structure (EXAFS) spectra of the catalysts were similar to that of Ni foil (Fig. 2b). This was ascribed to the similar scattering parameters of Ni and Zn owing to the close proximity of Ni and Zn in the periodic table$^{61}$. The two main peaks of NiO at 1.65 and 2.57 Å, which were assigned to the Ni–O and Ni–Ni bonds in the rocksalt crystal structure, respectively$^{62}$, were not observed in the profile of the N$_1$Z$_3$ catalysts. Moreover, a peak at 2.2 Å appeared in the spectrum of the catalysts, which indicated the presence of Ni or Zn in the nearest Ni neighbors. The Zn K-edge XANES spectra of the N$_1$Z$_3$-700 and N$_1$Z$_3$-900 catalysts are illustrated in Fig. 2c. The onset of the adsorption edge downshifted and the height of the white line peak decreased compared to that of the ZnO reference, which indicated that the valence of Zn in the catalysts was lower than that in ZnO. The Zn K-edge EXAFS spectra presented two main peaks centered at 1.55 and 2.93 Å, which corresponded to the Zn–O and Zn–Ni(Zn) bond lengths. A new peak centered at 4.08 Å was observed in the spectra of the N$_1$Z$_3$-700 and N$_1$Z$_3$-900 catalysts and was assigned to the Zn–Ni coordination.

The morphology of the N$_1$Z$_3$ catalysts calcined at different temperatures was analyzed using field-emission scanning electron microscopy (FE–SEM) analysis, and the images are presented in Supplementary Figs. 8 and 9. Prior to calcination, the coprecipitated Ni(CO$_3$)$_3$ and Zn(CO$_3$)$_2$ particles were needle-shaped (Supplementary Fig. 8a). At a low calcination temperature of 500 °C, agglomerated spherical-shape particles with an average particle size of 25 nm formed (Supplementary Fig. 8b), and the degree of interparticle agglomeration increased at 900 °C (Supplementary Fig. 8c). The elemental mapping and energy-dispersive X-ray spectroscopy (EDX) analysis results (Supplementary Figs. 8d–g) revealed that the Ni and Zn species were well-distributed in the co-precipitated precursor and the Ni/Zn ratio was approximately 1:3. After the reduction of the calcined catalysts at 450 °C under H$_2$ flow, no noticeable changes were observed in the morphology of the catalyst (Supplementary Fig. 8). The primary particle size of the catalysts increased from 25–30 to 100–400 nm as the calcination temperature increased from 500 °C (N$_1$Z$_3$-500) to 900 °C (N$_1$Z$_3$-900). For the N$_1$Z$_3$-900 catalyst, the primary particles were highly agglomerated and converted to secondary micron-sized particles (Supplementary Fig. 9e). Furthermore, as the calcination temperature increased from 500 to 900 °C, the Brunauer–Emmet–Teller (BET) surface area of the catalysts decreased from 42.1 to 14.6 m$^2$ g$^{-1}$ (Supplementary Fig. 10 and Supplementary Table 3).

The diffusion of Zn into the NiO phase during calcination and formation of the Ni–Zn alloy during the reduction were analyzed using high-resolution transmission electron microscopy (HR–TEM) and high-angle angular dark field–scanning transmission electron microscopy (HAADF–STEM), and the results are presented in Fig. 3. The formation of uniform nano-sized 10–30 nm particles was observed at the surface of the 100–400 nm spherical ZnO particles. Some nano-sized particles were in close contact with each other, which suggested that the nanoparticles migrated during calcination owing to their high surface
energy. The Zn and O species were well-distributed throughout the micron- and nano-sized particles. In contrast, the Ni species were predominantly distributed throughout the nano-sized particles, and only a few Ni species were distributed throughout the Zn-rich micron-sized particles. This indicated that most micron- and nano-sized particles of the N$_1$Z$_3$-900 catalyst were low-level Ni-doped ZnO and Ni–Zn alloy, respectively. Two different lattice parameters of the nano-sized Ni–Zn alloy particles, 7.71 and 2.29 Å, were observed in the HR–TEM images of the N$_1$Z$_3$-900 catalyst. The presence of the enlarged interplane spacing of 7.71 Å, which was approximately three times larger than that of pure ZnO (2.5 Å$^{63}$), suggested the formation of a Ni–Zn alloy$^{64}$. In addition, the interlayer spacing of 2.29 Å of the N$_1$Z$_3$-900 catalyst was larger than that of pure metallic Ni (2.03 Å), which agreed well with the XRD results. To further investigate the formation of the Ni–Zn alloy, the elemental compositions of the nano-sized particles of the N$_1$Z$_3$-900 catalyst were analyzed using EDX line scanning (Supplementary Fig. 11). The elemental concentrations of Zn, Ni, and O measured over the lateral distance of 40 nm confirmed that the nano-sized particles on the surface of ZnO were O-deficient Ni–Zn alloy species. Unlike the Ni and Zn species in N$_1$Z$_3$-900, those in N$_1$Z$_3$-700 were well distributed throughout the catalyst (Supplementary Figs. 12a–l). The segregation of the nano-sized Ni–Zn alloy phases was first observed for the N$_1$Z$_3$-800 catalyst (Supplementary Figs. 12g–i). Therefore, highly active nano-sized Ni–Zn alloy particles were formed via calcination at the high temperatures of 800 and 900 °C followed by reduction at 450 °C.

We used the aforementioned results to propose a schematic of the Ni–Zn alloy formation (Fig. 4). During the calcination of the co-precipitated product at temperatures of up to 230 °C, Ni(CO$_3$)$_3$ and Zn(CO$_3$)$_2$ were transformed into NiO and ZnO, respectively. As the temperature further increased up to 900 °C, the intermetallic diffusion was enhanced and Ni- and Zn-rich Ni$_x$Zn$_y$O phases formed. Furthermore, the degree of intermetallic diffusion increased with increasing the calcination temperature. The amount of Zn that could diffuse into NiO could reach 40 mol% when a mixture of ZnO and NiO with a ZnO/NiO ratio of 3:1 was calcined at 900 °C$^{56}$. During the reduction reaction in the presence of H$_2$, the Ni-rich Ni$_x$Zn$_y$O phase lost its O either via the formation of water or the generation of O vacancies to form Ni–Zn alloy species. The structural rearrangement of the Ni and Zn atoms in the unit cell of the catalyst was examined using the Reflex plus program of the Material Studio software utilizing experimental XRD data (Supplementary Fig. 4b). The predicted atomic arrangement on the Ni–Zn alloy phase indicated that Ni-centered pentagonal and hexagonal structures could be present in the alloy phase, and majority of the Ni–Zn alloy species presented (111) and (200) facets (Fig. 4b).

To gain insight regarding the synthesis mechanisms of monocarboxylic acids, the chemical state of the N$_1$Z$_3$ catalyst under CO$_2$ hydrogenation conditions was monitored using NAP–XPS, and the results are presented in Fig. 5. All peaks were referenced to the C 1 s spectrum at 284.8 eV. In the presence of a H$_2$ and CO$_2$ mixture at 0.2 mbar and 25 °C, the high-resolution Zn 2p spectra presented Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ peaks at 1021.8 and 1045.0 eV, respectively, which indicated the presence of Zn($^{2+}$)O at the surface of the catalyst (Fig. 4a). The divalent oxidation state of Zn($^{2+}$)O shifted toward higher binding energy levels when the reaction was performed at 325 °C and after the evacuation of gases at 325 °C; this could
be attributed to the catalyst surface interacting with the electronegative C and O species. The metallic Ni$^{0}$ peak at 852.6 eV was the major Ni species identified in the Ni 2p spectrum of the reduced N$_{1}$Z$_{3}$ catalyst (Fig. 5b). In addition, the Ni$^{2+}$ 2p$_{3/2}$ and Ni 2p$_{1/2}$ peaks at 856.1 and 873.0 eV, respectively, and satellite peak associated with the Ni$^{2+}$ 2p$_{3/2}$ peak were observed. The intensity of the Ni$^{2+}$ peaks decreased during the hydrogenation of CO$_{2}$, owing to the reduction reaction promoted by the presence of H$_{2}$. Under ultra-high vacuum (UHV) conditions, several sub-peaks were observed in the Ni 2p spectra of N$_{1}$Z$_{3}$-900, which indicated that different chemical states of Ni were present in this catalyst (Supplementary Fig. S13b). The Ni 2p$_{3/2}$ peak collected under UHV conditions was deconvoluted into three peaks: Ni$^{0}$, Ni$^{+}$, and Ni$^{2+}$ at 852.0, 853.3, and 855.4 eV, respectively. The peaks of the Ni species in the N$_{1}$Z$_{3}$-900 catalyst downshifted compared with those of Ni$^{0}$, Ni$^{2+}$, and Ni$^{3+}$ (852.6, 853.7, and 855.6 eV, respectively)$^{65,66}$. This could be caused by the interaction of less electronegative Zn with Ni. Additionally, the increase in the electron density on the surface of the Ni atoms could be caused by the electrons donated by the O vacancies in the ZnO lattice$^{67}$. Under CO$_{2}$ hydrogenation conditions, the peaks of metallic Ni$^{0}$ and Ni$^{2+}$ upshifted, which could be caused by interaction of Ni with the O-containing intermediates (Fig. 5b). The O 1 s ultra-high vacuum (UHV) XPS profiles of the catalysts were deconvoluted into three sub-peaks at 529.0, 530.9, and 531.8 eV, which corresponded to the lattice oxygen anions (O$^{2-}$) in the wurtzite structure, oxygen defects caused by O vacancies (O$_{\text{v}}$)$^{68,69}$, and adsorbed oxygen species at the surface (O$_{a}$)$^{68,69}$, respectively, (Supplementary Fig. S13c). The %areas of the O vacancies of the N$_{1}$Z$_{3}$-700 and N$_{1}$Z$_{3}$-900 catalysts were 34.3% and 44.7%, respectively. In the presence of H$_{2}$/CO$_{2}$ under the reaction conditions (Fig. 5c), the peaks associated with the O$_{2}^{-}$ species shifted to 529.8 eV. This upshift, which was caused by the oxidation of the catalyst surface, could be ascribed to the surface O$^{*}$ being produced either via the formation of CO$^{*}$ or further CO$^{*}$ dissociation. In addition, the formation of CO$_{2}$-adsorbed intermediates (e.g., carbonate, bicarbonate, and formate, which will be discussed further) caused the O vacancy peak to upshift to 531.1 eV via increasing the electron density. The C 1 s spectrum of the fresh N$_{1}$Z$_{3}$ catalyst obtained under UHV conditions presented two peaks at 284.8 and 289.3 eV, which corresponded to the surface organic contaminants and residual carbonate species on the surface of catalysts (Supplementary Fig. S13d)$^{70,71}$. When the catalyst was exposed to a mixture of H$_{2}$ and CO$_{2}$ at 25 °C, an additional peak at 292.7 eV appeared, which could be attributed to the gaseous CO$_{2}$ in the in situ cell (Fig. 5d)$^{72}$; this peak almost disappeared after the cell was evacuated. In the presence of H$_{2}$ and CO$_{2}$ at 325 °C, several adsorption peaks of reaction intermediates, which were produced via CO$_{2}$ hydrogenation, were observed. The peaks at 291.4 and 288.2 eV corresponded to the adsorbed CO and formate species, respectively.$^{73}$ In addition, a carboxylate peak was observed at 291.1 eV$^{74}$.

To investigate the interactions between the surface Ni species and ZnO, the hydrogen temperature-programmed reduction and desorption (H$_{2}$–TPR and H$_{2}$–TPD, respectively) profiles of the N$_{1}$Z$_{3}$ catalysts were analyzed. The N$_{1}$Z$_{3}$ catalysts prepared at temperatures in the range of 500–800 °C exhibited three peaks at low, medium, and high temperatures (100–200, 200–500, and > 500 °C, respectively) in the H$_{2}$–
TPR profile (Supplementary Fig. 14a). Typically, the H$_2$–TPR profile of bulk NiO particles, in the absence of supports, presents an asymmetric peak in the temperature range of 250–500 °C, which corresponds to the overlapped reduction of Ni$^{3+}$ to Ni$^{2+}$ and Ni$^{2+}$ to Ni$^{0}$ 75–78. When NiO interacts strongly with a support (e.g., γ-Al$_2$O$_3$ or ZnO), the difficulty in reducing the NiO phase generates broad high-temperature peaks above 500 °C 67, 79. The high-temperature reduction peaks could also be ascribed to the reduction of Zn$^{2+}$ to metallic Zn in the presence of Ni, although bulk ZnO is barely reducible 60, 80. For highly-dispersed NiO nanoparticles that interact weakly with their support, the reduction temperature range was lower (200–250 °C) than that of the bulk NiO particles 79, 81. Thus, it was reasonable to assign the low-, medium-, and high-temperature peaks of the N$_1$Z$_3$ catalysts to the reduction of highly-dispersed NiO nanoparticles that interacted weakly with ZnO, bulk NiO phases, and NiO phases that interacted strongly with ZnO, respectively. The low-temperature peak at 230–290 °C, which were observed in the H$_2$–TPR profiles of the N$_1$Z$_3$ catalysts prepared at low calcination temperatures of 500–800 °C shifted to higher temperatures in the range of 436–484 °C in the H$_2$–TPR profile of N$_1$Z$_3$-900, and the peak intensity of the highly dispersed NiO nanoparticles at 175 °C decreased significantly. In addition, the amount of H$_2$ consumed in the medium temperature range increased with increasing the calcination temperature (Supplementary Table 4). This indicated that the highly dispersed NiO nanoparticles were converted into Ni-rich Ni$_x$Zn$_y$O phase via the enhanced diffusion of the Zn$^{2+}$ cations into the NiO lattice during calcination. Further, high reduction temperatures were required to reduce the lattice O of the Ni-rich Ni$_x$Zn$_y$O phase to form Ni–Zn alloy, because of the Zn$^{2+}$ doping. The H$_2$–TPD profiles of the N$_1$Z$_3$ catalysts presented a low-temperature desorption region (< 400 °C), which corresponded to the H atoms that were either weakly or moderately adsorbed on the surface of the catalyst, and a high-temperature desorption region (> 401–900 °C), which corresponded to the strongly adsorbed H atoms (Supplementary Fig. 14b). The N$_1$Z$_3$ catalysts prepared at calcination temperatures above 700 °C exhibited similar H$_2$ desorption behavior.

To gain insight into the CO$_2$ adsorption behavior and active sites for the CO$_2$ conversion reaction, the O$_2$ temperature-programmed desorption (O$_2$–TPD) profiles of the catalysts were obtained (Supplementary Fig. 15). Depending on the number of gained electrons, the O species at the surface of metal oxides can be categorized into physically adsorbed oxygen (O$_{\text{ads}}^{(\text{phys})}$) at temperatures below 100 °C, superoxide species (O$_{\text{ads}}^{(\text{superoxide})}$) in the temperature range of 100–200 °C, monatomic oxygen (O$_{\text{ads}}^{(\text{monatomic})}$) in the temperature range of 200–400 °C, lattice oxygen at the surface (O$_{\text{latt(surface)}}^{(\text{surface})}$) in the temperature range of 400–700 °C, and lattice oxygen in the bulk (O$_{\text{latt(bulk)}}^{(\text{bulk})}$) at temperatures above 700 °C 82–84. The surface-adsorbed O$_{\text{ads}}^{(\text{phys})}$ and O$_{\text{ads}}^{(\text{superoxide})}$ species, which were associated with surface vacancies, were weakly bonded to the catalyst surfaces and thus, were relatively easy to desorb; however, the lattice O species were difficult to extract 82, 83, 85. Broad peaks centered at 360–370 °C, which were associated with the desorption of O$_{\text{ads}}^{(\text{phys})}$ species, were observed in the O$_2$–TPD profiles of the N$_1$Z$_3$-500 and N$_1$Z$_3$-600 catalysts. A low-temperature O$_{\text{ads}}^{(\text{phys})}$ peak at 310 °C appeared in the O$_2$–TPD profile of the N$_1$Z$_3$-700 catalyst, and a low-temperature more intense O$_{\text{ads}}^{(\text{phys})}$ peak at 321 °C was observed in the O$_2$–TPD profile of the N$_1$Z$_3$-800 catalyst. This
suggested the formation of more easily desorbed $O_{(\text{ads})}$ species on the surface of catalysts prepared at higher calcination temperatures. Conversely, the high-temperature $O_{(\text{ads})}$ peaks in the temperature range of 360–385 °C, which were the major desorption peaks in the $O_2$–TPD profiles of the $N_1Z_3$-500, $N_1Z_3$-600, and $N_1Z_3$-700 catalysts calcined, were less prominent in the $O_2$–TPD profile of the $N_1Z_3$-800 catalyst. A remarkable change in the desorption of $O$ was observed in the $O_2$–TPD profile of the $N_1Z_3$-900 catalyst; the removal of $O_{\text{fatt(surface)}}$ from the metal oxide lattice was significantly increased from 0.033–0.059 mmol g$^{-1}$ (for the $N_1Z_3$-600, $N_1Z_3$-700, and $N_1Z_3$-800 catalysts) to 0.135 mmol g$^{-1}$ (for the $N_1Z_3$-900 catalyst), as listed in Supplementary Table 5. The presence of $O$ vacancies in metal oxides helps to create unsaturated metal centers, which renders the lattice $O$ adjacent to $O$ vacancies more active. The metal oxide can reserve some outer electrons that can be donated to the antibonding orbital of the $CO_2$ molecules on the metal surface to enhance $CO_2$ adsorption. Moreover, the presence of such $O$ vacancies on the catalyst surface increases the electron density at the metal centers, which can enhance the reactivity of $CO_2$. The creation of $O$ vacancies can facilitate the surface restructuring of Ni and Zn to form Ni–Zn alloys because of the differences between the ionic radii of the $O^{2-}$ ion (140 pm) and metal ions (Zn$^{2+}$, 74 pm and Ni$^{2+}$, 69 pm) and different diffusion paths could be accessible to the $O$ interstitials in the wurtzite lattice.

The $CO_2$ temperature-programed desorption ($CO_2$–TPD) profiles of the catalysts were used to examine the adsorption behavior of $CO_2$ on the catalyst surfaces, and the results are illustrated in Supplementary Fig. 16 and Supplementary Table 6. The desorption peaks in the $CO_2$–TPD profiles of the catalysts could be categorized into three regions: <250, 250–600, and >600 °C, which represented weak, medium, and strong basic sites. The main peak in the $CO_2$–TPD profiles of the $N_1Z_3$-500, $N_1Z_3$-600, and $N_1Z_3$-700 catalysts occurred in the temperature range of 535–555 °C and did not change significantly as the calcination temperature of the catalysts increased, which indicated that strong interactions were maintained between the adsorbed $CO_2$ and catalyst surfaces. However, the main desorption temperature of the $N_1Z_3$-900 catalysts shifted to 432 °C, which suggested that the surface basicity of the $N_1Z_3$-900 catalyst was significantly lower than those of the $N_1Z_3$-500, $N_1Z_3$-600, and $N_1Z_3$-700 catalysts. The favorable $CO_2$ adsorption on the surface of the $N_1Z_3$-900 catalyst at low temperatures could be attributed to the increase in the number of $O_{\text{fatt(surface)}}^2$ sites at the calcination temperature of 900 °C. The amount of $CO_2$ adsorbed at the medium basic sites of the $N_1Z_3$-900 catalyst was 0.158 mmol g$^{-1}$, which was significantly higher than those of the $N_1Z_3$-800 catalyst (0.102 mmol g$^{-1}$) and other lower-calcination-temperature catalysts (0.018–0.037 mmol g$^{-1}$). The high $CO_2$ hydrogenation activity of the $N_1Z_3$-900 catalyst suggested that the $CO_2$ adsorbed at the medium basic sites effectively participated to the reaction and the $CO_2$ adsorbed at the strong basic sites was less suitable for the subsequent conversion reaction. This hypothesis was supported by the strong interactions between the $CO_2$ molecules adsorbed at the medium basic sites and the catalyst surface at the reaction temperatures and facile desorption of the reaction products from the catalyst surface after the reaction.
To elucidate the reaction mechanism for the formation of monocarboxylic acids, in situ DRIFTS experiments were performed to analyze the evolution of the reaction intermediates over Ni–Zn alloy catalysts. To identify the chemical species derived from the adsorption of CO$_2$ on the surface of the N$_1$Z$_3$-900 catalyst, DRIFTS profiles were obtained by flowing CO$_2$ at 3.0 MPa through the DRIFTS cell that contained an in situ reduced N$_1$Z$_3$-900 catalyst sample, as presented in Fig. 6a. The detailed peak assignment is listed in Supplementary Table 7. As the temperature of the cell increased from 30 to 325 °C, the intensities of the infrared (IR) bands of CH$_4$ at 3015 and 1305 cm$^{-1}$ increased; however, further extending the adsorption time to 60 min at 325 °C led to a decrease in the intensity of CH$_4$ bands.

The reaction between the residual pre-adsorbed H$_2$ on the catalyst surface after reduction and adsorbed CO$_2$ species formed CH$_4$ even at a low temperature of 30 °C. As the temperature increased from 30 to 325 °C the intensities of the bands of the CO$_2$-adsorbed intermediate species (carbonate and bicarbonate) increased in the frequency range of 1800–1000 cm$^{-1}$. The bands at 1616 and 1293 cm$^{-1}$ were assigned to the asymmetric and symmetric vibrations of bidentate carbonate, respectively, and those at 1522 and 1327 cm$^{-1}$ corresponded to the asymmetric and symmetric vibrations of monodentate carbonate, respectively$^{90,91}$. The reaction between monodentate carbonate and adsorbed H$_2$ produced bicarbonate, which generated the peaks at 1636 cm$^{-1}$ ($\nu_{as}(O-C-O)$), 1419 cm$^{-1}$ ($\nu_s(O-C-O)$), and 1219 cm$^{-1}$ ($\delta(\text{COH})$)$^{90}$. In addition, the hydrogenation of bidentate carbonate produced formate, and its peaks were observed at 1577 cm$^{-1}$ ($\nu_{as}(O-C-O)$), 1388 cm$^{-1}$ ($\delta(C-H)$), and 1363 cm$^{-1}$ ($\nu_s(O-C-O)$)$^{92,93}$. The peaks of the CO formed via RWGS were observed at 2078 cm$^{-1}$ (linearly adsorbed CO, l-CO), 1933 and 1918 cm$^{-1}$ (bridge-adsorbed CO, b-CO), and 2055 cm$^{-1}$ (Ni(CO)$_4$)$^{94}$. Furthermore, the 1751 cm$^{-1}$ peak was ascribed to the formyl species produced via the hydrogenation of CO$^{95}$. In addition, the IR bands at 1080, 1050, 977, and 950 cm$^{-1}$ were associated with the bending of the = C–H groups and those at 1540 and 1340 cm$^{-1}$ were ascribed to the carboxylate species$^{92,96}$. The intermediates and products formed via the adsorption of CO$_2$ on the reduced N$_1$Z$_3$-900 catalyst (Fig. 6a) were different from those formed on the reduced N$_1$Z$_3$-500 catalyst (Fig. 6b). First, the formation of a large amount of CH$_4$ was observed at 150 °C over the N$_1$Z$_3$-500 catalyst; however, the formation of CH$_4$ was suppressed on the N$_1$Z$_3$-900 catalyst, and these results were in good agreement with the CO$_2$ hydrogenation data (Fig. 1a). This indicated that the metallic Ni particles on the N$_1$Z$_3$-500 catalyst surface facilitated methanation$^{97,98}$, and the formation of the Ni–Zn alloy suppressed the methanation reaction. Second, the formation of CO$_2$-adsorbed intermediates (i.e., carbonate, bicarbonate, and formate) on the surface of the N$_1$Z$_3$-500 catalyst was less favored than on the surface of the N$_1$Z$_3$-900 catalyst. This implied that the adsorption of CO$_2$ on the Zn-rich Ni$_x$Zn$_{1-x}$O phase was more favorable than that on the ZnO phase.

H$_2$ at 325 °C and 3.0 MPa was used as flow gas in the DRIFTS cell immediately after CO$_2$ flow, and the Fourier-transform infrared (FT–IR) spectra of the N$_1$Z$_3$-900 catalyst were collected to investigate its hydrogenation behavior (Fig. 7a). As the H$_2$ flow time increased to 15 min, the formation of CH$_4$ began to be favored, and the intensity of the IR band associated with the = C–H groups decreased significantly.
addition, the amounts of CO$_2$-adsorbed intermediate species, RWGS-formed gaseous CO (2200–2100 cm$^{-1}$), and water (1653 cm$^{-1}$)\textsuperscript{99}, which could be produced via the re-adsorption of OH from the decomposition of formate species\textsuperscript{100, 101}, began to increase. This indicated that progressive CO$_2$ hydrogenation occurred after 15 min of H$_2$ flow, after changing the flow gas from CO$_2$ to H$_2$. After 140 min of H$_2$ flow, the peaks of gaseous CO and I-CO almost disappeared from the FT-IR spectra of the N$_1$Z$_3$-900 catalyst, and the intensity of the CH$_4$ peak began to decrease. Moreover, residual CO$_2$ intermediate species were present on the surface of the N$_1$Z$_3$-900 catalyst. The CO$_2$ hydrogenation behavior over the N$_1$Z$_3$-500 catalyst was similar (Fig. 7b).

A distinct difference in the catalytic behaviors of the N$_1$Z$_3$-900 and N$_1$Z$_3$-500 catalysts was observed using their operando DRIFTS profiles collected utilizing a mixture of H$_2$ and CO$_2$ with a H$_2$/CO$_2$ ratio of 2:1 at 325 °C and 3.0 MPa as flow gas. After 15 min of H$_2$ and CO$_2$ flow, the formation of gaseous CO and CH$_4$ on the surface of N$_1$Z$_3$-500 was highly favored and the formation of CO and CH$_4$ on the surface of N$_1$Z$_3$-500 was suppressed (Supplementary Fig. 17). As presented in Fig. 8, the time evolution of the formation of CO indicated that the amount of gaseous CO produced during the initial stage of reaction over the N$_1$Z$_3$-900 catalyst continuously decreased, which suggested that CO was actively transformed into next-stage hydrogenated products. After 90 min of reaction, the amount of gaseous CO remained almost unchanged, which indicated that the rates of the hydrogenation of CO and formation of CO reached steady-state. In contrast, the amount of gaseous CO reached a maximum after 30 min of reaction over the N$_1$Z$_3$-500 catalyst and progressively decreased as the reaction continued for 300 min. This indicated that the N$_1$Z$_3$-500 catalyst could not convert CO to next-stage hydrogenated products during the initial reaction stage. The CO$_2$-adsorbed reaction intermediates (i.e., carbonate, bicarbonate, and formate) and double-bonded hydrocarbons reached steady-state peak intensities after 15 min of reaction over both catalysts (Supplementary Fig. 17).

To further elucidate the reaction behavior of the N$_1$Z$_3$-900 catalyst, CO adsorption on the in situ reduced catalyst followed by CO hydrogenation using a flow of H$_2$ were performed. As presented in Supplementary Fig. 18a, during the CO adsorption reaction, as the temperature increased from 30 to 325 °C, the amount of formed CO$_2$ increased, and that could be caused by the removal of the surface lattice O from the Zn-rich Ni$_x$Zn$_y$O (CO + ZnO $\rightarrow$ CO$_2$ + Zn). The produced CO$_2$ could be adsorbed to form carbonate, bicarbonate, and formate species. In contrast to the CO$_2$ adsorption, the formation of double-bonded hydrocarbons (1080–950 cm$^{-1}$) and CH$_4$ (3105 and 1305 cm$^{-1}$) was not observed during the CO adsorption reaction, which could be ascribed to the low hydrogenation reactivity of the adsorbed CO. The increase in the amount of formed CO$_2$ (which was generated via the water-gas shift reaction) was observed in the 30–40 min interval of H$_2$ flow at 325 °C (Supplementary Fig. 18b); moreover, CH$_4$ began to form simultaneously. In addition, CO$_2$-adsorbed intermediates (i.e., carbonate, bicarbonate, and formate) and CO-hydrogenated intermediate (formyl) began to form after 30 min of H$_2$ flow; this was attributed to the formation of CO$_2$. 


To further elucidate the adsorption behavior of hydrocarbon species formed on the N$_1$Z$_3$ catalysts, we used CH$_4$ temperature-programed desorption (CH$_4$–TPD) experiments; the results are presented in Supplementary Fig. 19 and Supplementary Table 8. The presence of the high-temperature desorption peaks at 450–541 °C in the CH$_4$–TPD profiles of the N$_1$Z$_3$ catalysts suggested that dissociated CH$_4$ adsorption occurred on the surface of the catalysts; furthermore, the methyl groups and H atoms generated by CH$_4$ could be adsorbed on the Zn centers and surface O sites of the N$_1$Z$_3$ catalysts, respectively.$^{86}$ The activation of CH$_4$ via dissociative adsorption on the Ni–Zn alloy catalyst suggested the participation of *CH$_x$ in the formation of monocarboxylic acids.

**Reaction mechanism.** Based on the TPD profiles of the N$_1$Z$_3$ catalysts, in situ NAP–XPS, and in situ DRIFTS, a plausible reaction pathway was proposed (Fig. 9a). First, molecular H$_2$ was activated via heterolytic cleavage on the Ni centers in the Zn-rich Ni$_x$Zn$_y$O and Ni–Zn alloy. Next, CO$_2$ molecules were adsorbed on the surface of the Zn-rich Ni$_x$Zn$_y$O to form carbonate, bicarbonate, and subsequently, formate species. Afterward, the formate species were hydrogenated to form gaseous CO. Subsequently, the produced CO was re-adsorbed on the Ni centers on the Ni–Zn alloy surface, and then it was hydrogenated to *CH$_x$ species via the formation of formyl species. Thereafter, the adsorbed *CH$_x$ species were hydrogenated to form *CH$_3$. Next, a CO$_2$ molecule was adsorbed on the Zn site of the Ni–Zn alloy surface, which was subsequently inserted into the adsorbed *CH$_3$ species to form the *CH$_3$COO intermediate. The subsequent hydrogenation of *CH$_3$COO generated the final CH$_3$COOH product. For PA, C–C coupling between the surface-adsorbed *CH$_x$ species could form *CH$_x$CH$_x$ and the subsequent hydrogenation of *CH$_x$CH$_x$ could produce *CH$_2$CH$_3$ species. The surface-adsorbed CO$_2$ inserted into the *CH$_2$CH$_3$ species formed *CH$_3$CH$_2$COO, and the subsequent hydrogenation of *CH$_3$CH$_2$COO produced CH$_3$CH$_2$COOH. Similarly, a small amount of butyric acid was produced over the N$_1$Z$_3$–900 and Ni$_1$Zn$_4$–900 (0.7% and 1.4% selectivity, respectively) catalysts via the CO$_2$ insertion into *CH$_3$CH$_2$CH$_2$ species to form CH$_3$CH$_2$CH$_2$COO* species. The subsequent hydrogenation of CH$_3$CH$_2$CH$_2$COO* could produce CH$_3$CH$_2$CH$_2$COOH. The presence of alcohols, such as methanol and ethanol, was not observed in the reaction product, which implied that typical methanol pathways (e.g., formate and carboxylic pathways)$^{102}$ might not be responsible for the production of monocarboxylic acids.

To further examine the possibility of direct C–C coupling of CO$_2$ and the surface adsorbed *CH$_3$ species, we used DFT simulation (Fig. 9b). The detailed steps of the hydrogenation of CO$_2$ to AA are presented in Supplementary Fig. 20. Based on the experimental XRD data (Supplementary Fig. 4a), the (111) plane of Ni$_4$Zn$_{22}$ was used for the simulation. The electron transfer from the metal surface to CO$_2$ facilitated the chemisorption of CO$_2^{δ−}$ as a tridentate configuration on the Ni center and two adjacent Zn atoms. The Ni–C, Zn–O*, and Zn–O** bond lengths were 1.947, 1.992, and 2.039 Å, respectively. The adsorbed H* at the Ni center was subsequently reacted with the chemisorbed CO$_2^{δ−}$ to form carboxylate species (*COOH) as bidentate configurations with bond lengths of 1.910 and 2.038 Å for Ni–C and Zn–O, respectively. The
*COOH species were subsequently dissociated into CO and hydroxyl groups, which were adsorbed on the Ni and Zn sites, respectively. Subsequently, CO was hydrogenated to form *HCO by combining H with C or O atoms, and then, it was further hydrogenated and deoxygenated to form *CH_x species. During the hydrogenation of CO, C was shifted from the Ni center to a Zn site, and the subsequent hydrogenation of Zn–CH_x produced Zn–CH_3 species. The bond length of Zn–C in the Zn–CH_3 species was 1.956 Å. This was slightly longer than that of [ZnCH_3]^+ (1.93 Å)\textsuperscript{103}, which suggested that the Zn–C bonds at the Ni\textsubscript{4}Zn\textsubscript{22} catalyst sites were slightly more activated. For the adjacent Zn–CH_3 species, CO\textsubscript{2} was adsorbed on the Zn sites and the adsorbed CO\textsubscript{2} was tilted toward the Zn–CH_3 bonds, and therefore, the Zn–CH_3 bond length increased to 2.015 Å. Subsequently, the activated CO\textsubscript{2} was inserted into the Zn–C bond of the Zn–CH_3 species to produce surface acetate species (Zn–OOCCH_3). Afterward, the surface Zn–OOCCH_3 species were hydrogenated to produce AA, which desorbed from the catalyst surface. The total Gibbs free energy for the formation of AA from CO\textsubscript{2} was −1.03 eV, which indicated that the reaction was thermodynamically feasible on the surface of the Ni\textsubscript{4}Zn\textsubscript{22} alloy. Similar alky group carboxylations using CO\textsubscript{2} have been observed using homogeneous organometallic catalysts\textsuperscript{104,105} and heterogeneous Zn-doped CeO\textsubscript{2}\textsuperscript{86} and Zn-doped H-ZSM-5 catalysts\textsuperscript{106}.

**Stability of the N\textsubscript{1}Z\textsubscript{3}-900 catalyst.** The stability of the crystal structure of the N\textsubscript{1}Z\textsubscript{3}-900 catalyst during the CO\textsubscript{2} hydrogenation reaction was tested using in situ XRD, and the results are depicted in Supplementary Fig. 21. The phase structure of the N\textsubscript{1}Z\textsubscript{3}-900 catalyst did not change as the temperature increased up to 400 °C under a H\textsubscript{2}/CO\textsubscript{2} flow, which indicated that the Ni–Zn alloy and Zn-rich Ni\textsubscript{x}Zn\textsubscript{y}O phases were stable during the CO\textsubscript{2} hydrogenation reaction. This suggested that the water molecules formed via the RWGS reaction did not alter the phase structure of the catalyst. The XRD pattern of the spent N\textsubscript{1}Z\textsubscript{3}-900 catalyst, which was collected after a 216 h on-stream test, was almost identical to that of the fresh catalyst. This demonstrated the robust structure of the N\textsubscript{1}Z\textsubscript{3}-900 catalyst under the reaction conditions (Supplementary Fig. 21b). In addition, the Ni–Zn alloy structure on the surface of the Zn-rich Ni\textsubscript{x}Zn\textsubscript{y}O phase in the spent catalyst was maintained after the long-term test (Supplementary Fig. 21c). The high stability of the N\textsubscript{1}Z\textsubscript{3}-900 catalyst under the reaction conditions caused the CO\textsubscript{2} conversion and product selectivity of the catalysts to remain unchanged (Fig. 1c).

In summary, we demonstrated that a Ni–Zn alloy/Zn-rich Ni\textsubscript{x}Zn\textsubscript{y}O catalyst could be used to produce AA and PA with high selectivity (58.9% and 18.2%, respectively) via direct CO\textsubscript{2} hydrogenation at a CO\textsubscript{2} conversion of 13.4% and by suppressing the selectivity toward CH_4 (17.0%) and C_2–C_4 (5.0%). The STYs of AA and PA were 0.405 and 0.125 mmol L\textsuperscript{−1} h\textsuperscript{−1}, respectively. The mutual diffusion of Ni into the ZnO phase and Zn into the NiO phase during calcination at temperatures of up to 900 °C and formation of Ni–Zn alloy during the reduction produced the Ni–Zn alloy/Zn-rich Ni\textsubscript{x}Zn\textsubscript{y}O catalyst. The numerous O vacancies in the Zn-rich Ni\textsubscript{x}Zn\textsubscript{y}O phase facilitated the adsorption of CO\textsubscript{2}. The presence of CO\textsubscript{2}-adsorbed species (i.e., carbonate, bicarbonate, and formate) and gaseous CO indicated that the RWGS reaction converted CO\textsubscript{2} to CO. Subsequently, CO was hydrogenated to formyl species and then to surface-
adsorbed \((^\text{CH}_3)n\) species. AA and PA were produced via the direct C–C coupling of \(\text{CO}_2\) to the surface-adsorbed \((^\text{CH}_3)n\) species. The \(\text{CO}_2\) conversion and monocarboxylic acid selectivity were maintained for up to 216 h on-stream, and the morphology and phase structure of the Ni–Zn alloy/Zn-rich Ni\(_x\)Zn\(_y\)O catalyst were maintained during the long-term stability test, which demonstrated the robust nature of the Ni–Zn alloy catalyst. Considering that, to date, direct \(\text{CO}_2\) conversion has mostly been used for the production of liquid fuels, methanol, and light olefins, the possibility of producing value-added monocarboxylic acids from \(\text{CO}_2\) demonstrated the novelty and usability of the Ni–Zn alloy catalyst.

**Materials And Methods**

**Catalyst preparation.** Ni–Zn alloy catalysts with different Ni/Zn ratios were synthesized via co-precipitation using Ni(III) and Zn(II) nitrates. For a typical synthesis, \(\text{Ni(NO}_3)_3\cdot9\text{H}_2\text{O}\) (99.9% purity, Alfa Aesar, USA) and \(\text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O}\) (99.9% purity, Alfa Aesar, USA) at experimentally desired molar ratios of 1:2, 1:3, and 1:4 were dissolved in 100 mL of deionized and distilled (DDI) water at 60 °C. Subsequently, a 1.5 mol L\(^{-1}\) \(\text{Na}_2\text{CO}_3\) (99.98% purity, Sigma-Aldrich, USA) aqueous solution was added dropwise to the \(\text{Ni(NO}_3)_3\cdot9\text{H}_2\text{O}\) and \(\text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O}\) mixture under vigorous stirring until the pH of the suspension reached 8. After the turbid liquid was aged at 70 °C for 12 h, the formed suspension was centrifuged and washed with DDI water to remove the unreacted \(\text{Na}_2\text{CO}_3\). The product was dried in an oven at 100 °C overnight and subsequently calcined at 500, 600, 700, 800, and 900 °C for 6 h in air at a flow rate of 50 mL min\(^{-1}\). The calcined catalyst was reduced at 450 °C for 10 h under pure \(\text{H}_2\) at a flow rate of 50 mL min\(^{-1}\) and a ramping rate of 10 °C min\(^{-1}\).

**Catalyst characterization.** The crystal structures of the Ni–Zn alloy catalysts were examined using an ex situ D/Max–2500V/PC (Rigaku, Japan) XRD instrument with Ni-filtered Cu K\(\alpha\) (\(\lambda = 1.5418\) Å) radiation at 40 kV and 50 mA. The diffraction patterns were collected in the 2\(\theta\) range of 10–80° at a scanning speed of 0.02°/s. Temperature-dependent time-resolved X-ray diffraction (TR–XRD) experiments were conducted using an R-AXIS IV++ (Rigaku, Japan) XRD apparatus. The TR–XRD data were collected using Mo K\(\alpha\) (\(\lambda = 0.7107\) Å) radiation and were recorded on an image plate detector with an exposure time of 100 s. After the data were collected, the 2\(\theta\) angles of all XRD patterns were converted to Cu K\(\alpha\) radiation with a wavelength of 1.54 Å. For the TR–XRD experiments, the catalyst samples were loaded in a quartz tube with an inner diameter of 1.5 mm, which was fixed on both sides using quartz wool. Both ends of the quartz tube were connected with gas inlet and outlet lines, and air (99.999% purity, Shinyang Sanso Co., South Korea) was passed through the tube at a flow rate of 10 mL min\(^{-1}\). The quartz tube was subsequently mounted on the thermal stage of the XRD instrument and diffraction data were collected as the temperature was increased from 27 to 900 °C at a ramping rate of 2 °C min\(^{-1}\). The temperature was decreased to 30 °C, the gas was switched to \(\text{H}_2\) (99.999% purity, Shinyang Sanso Co.) with a flow rate of 10 mL min\(^{-1}\), and then, diffraction data were collected as the temperature was increased from 27 to 450 °C at a ramping rate of 2 °C min\(^{-1}\). To study the phases that formed during the \(\text{CO}_2\) hydrogenation, the reduced catalyst sample was exposed to a flow of 75% \(\text{H}_2\) (99.999% purity, Shinyang Sanso Co.) and
25% CO₂ (99.999% purity, Shinyang Sanso Co.); flow rate of 10 mL min⁻¹, as the temperature was increased from 27 to 400 °C at a ramping rate of 2 °C min⁻¹.

The N₂ adsorption–desorption isotherms of the catalysts were obtained using a Belsorp-mini II (BEL Inc., Japan) apparatus at the liquid N₂ temperature of −196 °C. The specific surface areas of the catalysts were calculated using the multipoint BET method, and the average pore diameters (D_p, nm) and pore size distributions were calculated using the Barrett-Joyner–Halenda method and isotherm data. The external surface area and volume of the micropores were determined using the t-plot method. The morphology of the catalysts was observed using an S-4100 (Hitachi, Japan) FE–SEM instrument and a Tecnai G2 (FEI Co. Ltd, USA) HR–TEM device. Samples were deposited from alcohol suspensions on holey carbon-coated Cu grids. The surface chemical characteristics of the catalysts were examined using a PHI 5000 Versa Probe (ULVAC-Phi Inc., Japan) UHV–XPS instrument. NAP–XPS measurements were performed using a SPECS (SPECS, GmbH, Germany) surface nano analysis apparatus. The details of the analysis and equipment are presented in the literature. In brief, the NAP-XPS system consisted of analysis and sample load-lock chambers. The analysis chamber was equipped with a micro-focused Al Kα X-ray source with a beam size of 300 μm and a PHOIBOS hemispherical electron analyzer. The NAP-XPS analysis was performed under H₂/CO₂ mixture gas with a ratio of 1:2 at 0.2 mbar by increasing the temperature from 25 to 325 °C. The in situ C 1 s, Zn 2p, Ni 2p, and O 1 s XPS profiles of the catalysts were recorded and the data were analyzed using the SpecsLab prodigy software. The peak assignments were referenced to the C–C bond at 284.8 eV.

XAS measurements, viz. EXAFS and XANES of the Zn and Ni K-edges, were performed at the 7–bm QAS beamline of the National Synchrotron Light Source 2. The XAS experiments were conducted in transmission mode and the energy was calibrated using standard Ni foil, NiO, and ZnO. The XANES and EXAFS data were processed using the Athena/Artemis software package. The extracted EXAFS signal, χ(k), was weighted by k² to emphasize the high-energy oscillations. A Fourier-transform was performed for the k-range of 3.0–11.0 Å using a Hanning window function to obtain the magnitude plot of the EXAFS spectra in the R-space.

TPD and TPR experiments were performed using a BELCAT (BEL Inc., Country) instrument. H₂–TPR was performed to assess the reduction behavior of the catalysts. Catalyst samples (50 mg) were loaded into the sample tube and thermally treated under Ar (99.999% purity, JC Gas Company, South Korea) flow at 400 °C for 2 h to remove the physiosorbed water and other gaseous impurities from the catalysts. The samples was subsequently cooled 23 ± 2 °C under an Ar gas flow. Afterward, the samples were oxidized using a pure O₂ (99.995% purity, JC Gas Company) flow at a flow rate of 30 mL min⁻¹ at 400 °C for 2 h followed by cooling to 50 °C, and then, the sample tubes were flushed with Ar. The pretreated samples were heated to 900 °C at a ramping rate of 10 °C min⁻¹ under a 5% H₂/Ar (JC Gas Company) flow at a flow rate of 30 mL min⁻¹. H₂ consumption was monitored using a thermal conductivity detector (TCD) and recorded as function of the temperature.
For the CO$_2$–TPD, O$_2$–TPD, and CH$_4$–TPD analyses, catalyst samples (50 mg) were pretreated at 500 °C at a ramping rate of 5 °C min$^{-1}$ under a He (99.999% purity, JC Gas Company) flow at a flow rate of 30 mL min$^{-1}$ for 1 h, and subsequently reduced at 450 °C under a 5% H$_2$/Ar flow at a flow rate of 30 mL min$^{-1}$ for 1 h. After the samples were naturally cooled to 50 °C, they were exposed to pure CO$_2$ (99.99% purity, JC Gas Company), pure O$_2$ (99.995% purity, JC Gas Company), and pure CH$_4$ (99.999% purity, JC Gas Company) flows at flow rates of 30 mL min$^{-1}$ for 1 h at 50 °C for the CO$_2$–TPD, O$_2$–TPD, and CH$_4$–TPD analyses, respectively. The system was subsequently flushed with ultra-high-purity He (99.999%) for 15 min at a flow rate of 50 mL min$^{-1}$ to remove any physisorbed CO$_2$, O$_2$, or CH$_4$ molecules. The CO$_2$, O$_2$, or CH$_4$ desorption steps of the CO$_2$–TPD, O$_2$–TPD, and CH$_4$–TPD experiments were performed by increasing the sample temperature from 50 to 900 °C at a heating rate of 10 °C min$^{-1}$, under a He flow at a flow rate of 30 mL min$^{-1}$.

For the H$_2$–TPD analysis, each catalyst sample (50 mg) was placed in a sample tube, and the tube was purged with Ar at a flow rate of 50 mL min$^{-1}$ for 30 min at room temperature. The catalyst was subsequently reduced at 450 °C for 4 h at a ramping rate of 5 °C min$^{-1}$ under a 5% H$_2$/Ar flow of 50 mL min$^{-1}$. The sample tube was naturally cooled to 50 °C under pure Ar flow. Next, the catalyst was completely saturated using a 5% H$_2$/Ar flow for 30 min at 50 °C. The system was subsequently flushed with pure Ar for 15 min at a flow rate of 50 mL min$^{-1}$ to remove any physisorbed H$_2$ molecules at 50 °C. The desorption of H$_2$ was performed by increasing the sample temperature from 50 to 1000 °C at a ramping rate of 10 °C min$^{-1}$ under a pure Ar flow at a flow rate of 30 mL min$^{-1}$.

In situ CO$_2$– and CO–DRIFTS analyses were performed to identify the reaction intermediate species formed during the hydrogenation of CO$_2$. The DRIFTS profiles were collected using a Frontier (PerkinElmer, USA) spectrometer equipped with a Praying Mantis (Harrick, USA) cell and a mercury cadmium telluride detector cell connected to a gas flow system. All catalyst samples were mixed with KBr at catalyst:KBr weigh ratios of 1:4. The catalyst sample was pre-reduced in the cell at 450 °C and 0.1 MPa under a H$_2$ flow at a flow rate of 50 mL min$^{-1}$ for 6 h. After reduction, the cell was flushed with N$_2$ gas and allowed to cool to room temperature. Subsequently, the cell was purged with N$_2$ for 2 h and then the background spectra were recorded. First, CO$_2$-DRIFTS analysis was performed by flowing CO$_2$ (99.995% purity) at a flow rate of 50 mL min$^{-1}$ and 3.0 MPa as the temperature was increased from 30 to 325 °C at a ramping rate of 10 °C min$^{-1}$. The pressure of the cell was controlled using a 26-2300 Series (Tescom, USA) back-pressure regulator. Once the temperature reached 325 °C at 3.0 MPa, the IR spectra were collected for the next 2 h under a continuous steady-state CO$_2$ flow. Subsequently, the CO$_2$ flow was switched to H$_2$ flow at 325 °C, 3.0 MPa, and a flow rate of 50 mL min$^{-1}$, and the IR spectra were collected during the hydrogenation of CO$_2$ for 4 h. A similar procedure was used to perform CO-DRIFTS analysis, in which 5% CO/Ar was used to investigate the CO adsorption and subsequent CO hydrogenation behaviors of the catalysts. For the second set of measurements, after the pre-reduction of the catalysts at 450 °C
and 0.1 MPa, the DRIFTS cell was pressurized with CO$_2$ at a flow rate of 25 mL min$^{-1}$ and H$_2$ at a flow rate of 50 mL min$^{-1}$ (H$_2$/CO$_2$ ratio of 2:1) to 3.0 MPa. When the pressure reached 3.0 MPa, the temperature of the cell was increased to 325 °C at a ramping rate of 10 °C min$^{-1}$. At 325 °C, the IR spectra during the hydrogenation of CO$_2$ were collected for 300 min.

**Catalyst evaluation.** The hydrogenation of CO$_2$ was conducted in a high-pressure continuous-flow fixed-bed reactor setup. The reactor consisted of gas feeding lines, mass flow controllers, a stainless-steel fixed-bed catalytic reactor with an inner diameter of 10 mm, a back-pressure regulator, and a condenser. For a typical run, 500 mg of catalyst was mixed with 500 mg of silicon carbide (S/0365/60, Fisher Chemicals, USA) which was used as thermal diluent, and the mixture was charged in the reactor. The catalyst was placed in the tubular reactor between the quartz wool beds. Subsequently, the catalyst was reduced by flowing pure H$_2$ in the reactor at a flow rate of 50 mL min$^{-1}$ for 10 h at 450 °C at a ramping rate of 10 °C min$^{-1}$. Afterward, the catalysts were cooled to the experimentally desired temperatures of 280–350 °C, and the gas flow was switched to H$_2$/CO$_2$ (molar ratios of 1:1, 2:1, and 3:1). During CO$_2$ hydrogenation, the product stream was passed through the condenser, and the temperature of the condenser was maintained at 10 °C to liquefy the liquid products; furthermore, the residual gaseous stream was directed toward an Clarus 580 GC-Model Arnel 1115PPC (PerkinElmer, USA) refinery gas analyzer-gas chromatograph (RGA-GC). The RGA-GC was equipped with a TCD for the analysis of CO$_2$, CO, and H$_2$, and a flame ionization detector for the quantitative measurement of the C$_1$–C$_6$ gaseous hydrocarbons. The RGA-GC specifications are presented in detail in the literature.$^{109}$ The liquid products collected in the condenser were diluted with high-performance liquid chromatography (HPLC)-grade water and were directly injected into an Alliance, model e2695 (Waters, USA) HPLC instrument equipped with a ultraviolet–visible (UV–Vis) detector and an Aminex HPX-87H (Bio-Rad, USA) ion exclusion column (300 mm × 7.8 mm). The column and detector temperatures were maintained at 60 and 50 °C, respectively. The mobile phase consisted of a 0.15 N aqueous H$_2$SO$_4$ solution with a flow rate of 0.5 mL min$^{-1}$. A standard calibration curve was used to quantify the products.

The product selectivity was based on the carbon mole percentages (C-mol%) of all tested catalysts. After the gas and liquid products were quantified, the carbon balance obtained during the catalytic performance test for 24 h on-stream was 92–98%. The CO$_2$ conversion, monocarboxylic acid selectivity, and CO selectivity were calculated as follows:

\[
\text{CO}_2 \text{ conversion (C-mol\%)} = \frac{\text{CO}_2_{\text{in}} - \text{CO}_2_{\text{out}}}{\text{CO}_2_{\text{in}}} \times 100\% \quad (5)
\]

and

\[
\text{CO selectivity (C-mol\%)} = \frac{\text{CO}_{\text{out}}}{\text{CO}_2_{\text{in}} - \text{CO}_2_{\text{out}}} \times 100\% \quad (6)
\]
Monocarboxylic acid selectivity (C – mol%) excluding CO = 

\[
\frac{\text{Moles of monocarboxylic acid formed}}{\Sigma \text{Moles of hydrocarbons}} \times 100\%.
\]  

(7)

where CO\textsubscript{2 in}, CO\textsubscript{2 out}, and CO\textsubscript{out} are the mole fractions of CO\textsubscript{2} at the inlet, CO\textsubscript{2} at the outlet, and CO at the outlet, respectively.

**DFT calculations.** The crystal structure of Ni\textsubscript{4}Zn\textsubscript{22} was determined using the Reflex plus program of the Material Studio software. The powder diffraction pattern was indexed using the TREOR90 program inside the Reflex Powder Indexing module followed by the PowderSolve module to solve the structure using the simulated annealing method\textsuperscript{110,111}. The final structure was obtained using a powder solve module based on the Monte Carlo simulated annealing procedure\textsuperscript{112}. The similarity between the experimental and calculated XRD patterns was confirmed using Rwp values. The optimized structure solution was used as an initial structural model for the Rietveld refinement to obtain the final crystal structure solution and final Rwp value, which was calculated as follows:\textsuperscript{113}

\[
\frac{\Sigma m(y_i - y_0)^2}{\Sigma m(y_0)^2}
\]  

(8)

Then the final result of the Ni\textsubscript{4}Zn\textsubscript{22} spectrum were mixed with the ZnO spectrum and refined using the QPA module to find the final rwp value and the ratio between both the structures\textsuperscript{114,115}. The reaction pathway of CO\textsubscript{2} to AA was determined using the CASTEP module of the Materials Studio\textsuperscript{116,117}. Two layers of the (111) surface of Ni\textsubscript{4}Zn\textsubscript{22} were constructed and a 20 Å vacuum space was created to avoid self-interaction. The first layers were constrained and the top surface was unconstrained to facilitate the conversion reaction (Supplementary Fig. 22). The generalized-gradient approximation with the Perdew–Burke–Ernzerhof\textsuperscript{118} type exchange-correlation functions were used to calculate the interactions between atoms. The energy tolerance, maximum force tolerance, and maximum displacement tolerance were 10\textsuperscript{−5} eV atom\textsuperscript{−1}, 0.03 eV atom\textsuperscript{−1}, and 1 × 10\textsuperscript{−3} Å, respectively. The core electrons were described using ultra-soft pseudopotentials in conjunction with a cut-off energy of 300 eV. The k-point sampling of the Brillouin zone was performed according to the Monkhorst–Pack scheme using a 2 × 2 × 1 k-points mesh. The reaction energy was calculated as follows:

\[
E_{\text{reaction}} = \Sigma E_{\text{product}} - \Sigma E_{\text{reactant}}.
\]  

(9)

An adsorption locator module was used to find the adsorption site of the *CO\textsubscript{2} and H* on the surface of Ni\textsubscript{4}Zn\textsubscript{22} (111) plane. The Universal forcefield was employed to estimate the forces between the atoms within the lattice. The location was set to surface region defined by atom set to specify the region around the substrate in which adsorbate configurations was sampled. The most stable adsorption sites were then used to calculate the rest of the reaction pathway including the subsequent adsorption of *CO\textsubscript{2} and H*. 
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Figures

Figure 1

(a) Hydrogenation of CO2 over N1Z3 catalysts with Ni/Zn ratios of 1:3 synthesized at calcination temperatures of 500, 600, 700, 800, 900, and 1000 °C. (b) Hydrogenation of CO2 over N1Zn-900 (n= 2, 3, 4) catalysts with different Ni/Zn ratios calcined at 900 °C. (c) Long-term stability of the N1Z3-900
catalyst for the CO2 conversion reaction. Pretreatment conditions: 450 °C, 3.5 MPa, H2 flow rate of 50 mL min⁻¹ for 10 h. Reaction conditions: 325 °C, 3.0 MPa, H2/CO2 = 1:2, and gas hourly space velocity of 5400 mL g⁻¹ h⁻¹ (CO2 = 1800 mL g⁻¹ h⁻¹, H2 = 3600 mL g⁻¹ h⁻¹). Here, FA, AA, PA, C4+ acid, and MeOH denote formic acid, acetic acid, propionic acid, butyric and valeric acids, and methanol, respectively.

Figure 2
(a) Normalized Ni K-edge X-ray absorption near edge structure (XANES) spectra and (b) Fourier-transforms (FTs) of the normalized Ni K-edge extended X-ray absorption fine structure (EXAFS) spectra ($\kappa 3\chi(k)$) of N1Z3-700 and N1Z3-900. (c) Normalized Zn K-edge XANES spectra and (d) FTs of the normalized Zn K-edge EXAFS spectra ($\kappa 3\chi(k)$) of N1Z3-700 and N1Z3-900. Here, N1Z3-700 and N1Z3-900 are catalysts with Ni/Zn ratios of 1:3 calcined at 700 and 900 °C, respectively.

Figure 3

(a) Scanning electron micrograph, (b) and (c) high-resolution transmission electron micrographs, (d) fast Fourier transform pattern, and (e)–(i) high-angle angular dark field–scanning transmission electron micrographs and elemental mappings of the N1Z3-900 catalyst with a Ni/Zn ratio of 1:3 calcined at 900 °C.
Figure 4

(a) Schematic of the Ni–Zn alloy formation and (b) visualization of the (111) and (220) facets of the Ni$_4$Zn$_{22}$ alloy. Here, N1Z3-500, N1Z3-700, and N1Z3-900, are catalysts with Ni/Zn ratios of 1:3 calcined at 500, 700, and 900 °C, respectively.
Figure 5

(a) Zn 2p, (b) Ni 2p, (c) O 1s, and (d) C 1s in situ near-ambient pressure X-ray photoelectron spectroscopy profiles of the N1Z3-900 catalyst with a Ni/Zn ratio of 1:3 calcined at 900 °C. Reaction conditions: 325 °C, H2/CO2 = 1:2, and 0.2 mbar.
In situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) analysis of the CO2 adsorption process with increasing temperatures on the (a) N1Z3-900 and (b) N1Z3-500 catalysts with Ni/Zn ratios of 1:3 calcined at 900 and 500 °C, respectively. Prior to CO2 adsorption, the catalysts were reduced at 450 °C for 6 h under a H2 flow of 50 mL min\(^{-1}\) in the DRIFTS cell. After the reduction, the DRIFTS cell was evacuated and purged with a N2 flow of 30 mL min\(^{-1}\) for 2 h to remove H2, and was naturally cooled to 30 °C. Subsequently the DRIFTS cell was pressurized with CO2 at 3.0 MPa and the spectra were collected as the temperature was increased from 30 to 325 °C under a CO2 flow of 50 mL min\(^{-1}\). Here l-CO and b-CO denote linear and bridged CO, respectively.
Figure 7

In situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) analysis of CO2 hydrogenation after the adsorption of CO2 on the (a) N1Z3-900 and (b) N1Z3-500 catalysts with Ni/Zn ratios of 1:3 calcined at 900 and 500 °C, respectively. Prior to hydrogenation, the catalysts were reduced at 450 °C for 6 h under a H2 flow of 50 mL min−1. After reduction, the DRIFTS cell was evacuated and purged with a N2 flow of 30 mL min−1 for 2 h to remove H2, was and naturally cooled to 30 °C. Subsequently, the DRIFTS cell was pressurized with CO2 at 3.0 MPa and 50 mL min−1 as the temperature was increased from 30 to 325 °C. The CO2 flow of 50 mL min−1 was maintained at 325 °C for 2 h, then the flow gas was switched from CO2 to H2 at a flow rate of 50 mL min−1 at 325 °C and 3.0 MPa. Here, l-CO and b-CO denote linear and bridged CO, respectively, and g-CO denotes gaseous CO.
Figure 8

Time-dependent diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) profile of the N1Z3-900 catalyst with a Ni/Zn ratio of 1:3 calcined at 900 °C. Prior to hydrogenation, the catalyst was reduced at 450 °C for 6 h under a H2 flow of 50 mL min⁻¹. After the reduction, the DRIFTS cell was evacuated and purged with N2 for 2 h to remove H2 at 325 °C. Subsequently, the flow gas was switched from N2 to a H2/CO2 mixture with a ratio of 2:1, the pressure of the DRIFTS cell was increased to 3.0 MPa at 325 °C, and the spectra were obtained.
Figure 9

(a) Plausible reaction mechanism for the conversion of CO2 to acetic and propanoic acids. (b) Gibbs free energy profile of the CO2 conversion to acetic acid. Here, the Zn, Ni, H, O, and C atoms are depicted in light blue, yellow, white, red, and gray, respectively.

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