Direct Synthesis of Formamide from CO₂ and H₂O with Nickel—Iron Nitride Heterostructures under Mild Hydrothermal Conditions

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ABSTRACT: Formamide can serve as a key building block for the synthesis of organic molecules relevant to premetabolic processes. Natural pathways for its synthesis from CO₂ under early earth conditions are lacking. Here, we report the thermocatalytic conversion of CO₂ and H₂O to formate and formamide over Ni–Fe nitride heterostructures in the absence of synthetic H₂ and N₂ under mild hydrothermal conditions. While water molecules act as both a solvent and hydrogen source, metal nitrides serve as nitrogen sources to produce formamide in the temperature range of 25–100 °C under 5–50 bar. Longer reaction times promote the C–C bond coupling and formation of acetate and acetamide as additional products. Besides liquid products, methane and ethane are also produced as gas-phase products. Postreaction characterization of Ni–Fe nitride particles reveals structural alteration and provides insights into the potential reaction mechanism. The findings indicate that gaseous CO₂ can serve as a carbon source for the formation of C–N bonds in formamide and acetamide over the Ni–Fe nitride heterostructure under simulated hydrothermal vent conditions.

INTRODUCTION

Amides are an important class of compounds in biological and chemical sciences. They have been used in the manufacture of pharmaceuticals and agrochemicals, and they are also the basis of some versatile synthetic polymers. C–N coupling reaction that produces nitrogenous compounds including amides is one of the most fundamental reactions in the chemical industry. In life, amide functional groups are ubiquitous moieties in amino acids and the peptide bond. Formamide, the simplest amide, consists of the most common elements (C, H, N, and O) in the universe and is widely used for the synthesis of prebiotic molecules. Formamide can be considered as a multifunctional tool for prebiotic chemistry since its condensation and degradation products generate—in the presence of minerals and metal oxides—biologically relevant molecules including amino acids, cofactors, nucleobases, and carboxylic acids. Formamide produces the nucleosides adenine, purine, hypoxanthine, cytosine, thymine, and uracil. In 2008, Saladino et al. reported that the interaction of formamide with the hydrothermal vent mineral pyrite (FeS₂) yields purine and adenine, which are basic components of nucleic acids. Formamide was also reported to serve as a solvent for the phosphorylation of nucleosides to nucleotides. A recent study by Green et al. demonstrated the formation and the further conversion of aminonitriles in formamide. Furthermore, degradation products of formamide, formic acid, formaldehyde, HCN, ammonia, and CO₂ serve as substrates for the synthesis of other intermediates in prebiotic chemistry including sugars. Formamide is not only a parent molecule but also an intermediate in a series of reactions from very reactive small radicals to biologically significant molecules as implicated in Miller’s classical 1953 experiment. Computational studies suggested that formamide is a key intermediate in the Miller synthesis of glycine. Although a reducing gas mixture consisting of NH₃, CH₄, and H₂ was used in Miller’s experiment, a more oxidizing early atmosphere composed of N₂, CO₂, and H₂O is predicted by many geoscientists. Overall, formamide is a versatile compound in prebiotic chemistry that can generate a range of monomers, from amino acids to nucleic acids.

The synthesis of formamide under early earth conditions is of interest. Its formation has been studied starting from CO and NH₃ with UV light, from the conversion of aqueous acetonitrile by γ-irradiation, electrochemical synthesis from formic acid, and the electrosynthesis from methanol and ammonia. It can also be formed from formic acid and ammonia. Proposed reactions for the formation of formamide generally entail the presence of minerals, temperatures higher...
than 100 °C, and relatively high pH values, which are compatible with hydrothermal vent conditions.\textsuperscript{9} Additionally, it has been shown that the accumulation of formamide in hydrothermal vents via thermophoresis is possible.\textsuperscript{25} Its constituents are formate and ammonia. The former is common in hydrothermal vents, and the latter can be generated under hydrothermal vent conditions.\textsuperscript{26,27} The fixation of dinitrogen to ammonia in the presence of H\textsubscript{2}S and FeS under mild conditions (under atmospheric pressure at 70–80 °C), which are close to the biological conditions, has been experimentally simulated and shown to be feasible.\textsuperscript{28} In addition, recent laboratory-scale serpentinization reactions of peridotite, water, and N\textsubscript{2} generated up to 2 \( \mu \)mol of NH\textsubscript{3} per gram of peridotite after 30 days at 250 °C, with synthesis rates accelerated up to 10-fold with the addition of CO\textsubscript{2}.\textsuperscript{29} The formation of formate in hydrothermal vents is driven by the serpentinization process, which yields H\textsubscript{2} for the reduction of CO\textsubscript{2} and its dissolved forms.\textsuperscript{30} The oxidized carbon species are presumed to be the ultimate source of carbon for the abiotic synthesis of organic molecules.\textsuperscript{31,32} Several studies report the formation of formate from CO\textsubscript{2} with hydrothermal minerals under mild hydrothermal vent conditions.\textsuperscript{33–36} The formation of formate and acetate occurs via the gas-phase H\textsubscript{2}-dependent CO\textsubscript{2} reduction over silica-supported Co nanoparticles,\textsuperscript{37} and Ni–Fe nanoparticles are able to reduce CO\textsubscript{2} to the free intermediates of the acetyl-CoA pathway of CO\textsubscript{2} fixation—formate, acetate, and pyruvate—under mild hydrothermal conditions in the absence of the synthetic H\textsubscript{2}.\textsuperscript{38} The conditions of serpentinizing systems are reducing enough to have stable forms of Ni–Fe alloys and their native metal forms.\textsuperscript{39,40} Awaruite (NiFe) is known to exist in H\textsubscript{2}-rich serpentinizing systems.\textsuperscript{41,42} Furthermore, a recent study by Peters et al. reported that nickel–iron-containing meteoric catalyst (Campo del Cielo) yields methanol, ethanol, acetaldehyde, and alkanes from the hydrogenation of CO\textsubscript{2} under hydrothermal conditions.\textsuperscript{43}

While oxidized carbon species have been suggested to be the source of primordial carbon fixation pathways, there have been several proposals for the abiotic formation of reduced nitrogen species.\textsuperscript{44,45} One of the proposed sources of nitrogen is the release of N\textsubscript{2} or NH\textsubscript{3} from rocks and minerals, presumably from ammonium silicates or metal nitrides.\textsuperscript{46} In addition, the existence of the nitride mineral, siderazot, as a terrestrial mineral has been reported.\textsuperscript{47} Since the direct incorporation of N\textsubscript{2} gas into the CO\textsubscript{2} fixation system is very challenging due to the strong triple bond of N\textsubscript{2}, the oxidized carbon species are presumed to be the ultimate source of primordial carbon fixation pathways, there have been several proposals for the abiotic formation of reduced nitrogen species.\textsuperscript{47,48,49} On the other hand, nitridation of transition metals and their oxides under a gas flow of ammonia is a well-established process.\textsuperscript{50} Properties of the resulting metal nitrides depend on several factors including synthesis temperature, heating rate, and flow rates. To find optimal annealing temperatures, in situ X-ray diffraction (XRD) patterns of the Ni\textsubscript{3}Fe sample were collected under an ammonia flow in the temperature range of 30–400 °C. As seen in Figure S1, Ni\textsubscript{3}Fe formation began at a temperature of about 300 °C. Higher treatment temperatures as 400 °C can result in the catalytic decomposition of NH\textsubscript{3} to N\textsubscript{2} and H\textsubscript{2}, which is an undesirable byproduct due to its reducing effect.\textsuperscript{51}

After observing the optimum temperature range of 300–380 °C for ammonia treatment by in situ XRD, the treatment conditions were systematically varied to adjust the composition of the catalyst. First, a bimetallic NiFe sample was nitrided under an ammonia atmosphere in a quartz tube at 300 and 350 °C for 1 and 2 h. As shown in Figure S2, annealing at 300–350 °C for 1 or 2 h results in a heterostructure that consists of crystalline Ni\textsubscript{3}FeN and Ni\textsubscript{3}Fe phases while NiFe remained as the major phase. Reflection indices of (111), (200), and (220) planes could be assigned to the NiFeN (PDF: 00-050-1434) crystalline phase. The incorporation of more electronegative N atoms into parent metal structures increases the atomic distance between metal atoms in the crystal lattice. Therefore, reflections of NiFeN appear at lower 2\( \theta \) values compared to that of the NiFe alloy structure. The reflection ratios of NiFeN to NiFe were not altered significantly by changing the annealing temperature from 300 to 350 °C or increasing the treatment time from 1 to 2 h.

After confirming the formation of the Ni\textsubscript{3}FeN/NiFe heterostructure by XRD, textural parameters and elemental compositions of two selected samples (Ni\textsubscript{3}FeN/NiFe-300-2h and Ni\textsubscript{3}FeN/NiFe-350-2h) were further investigated by N\textsubscript{2}-sorption and scanning electron microscopy—energy-dispersive X-ray (SEM–EDX) spectroscopy, respectively. N\textsubscript{2}-sorption isotherms show hysteresis, which is related to the condensation of nitrogen within the interparticle porosity. The hysteresis loop in N\textsubscript{2}-sorption isotherms was maintained after the mild nitridation treatment at 300 and 350 °C; the NiFe morphology was not altered noticeably. The Brunauer–Emmett–Teller (BET) surface areas were found to be 28 and 27 m\textsuperscript{2}/g for NiFeN/NiFe-300-2h and NiFeN/NiFe-350-2h, respectively (Figure S3). Figure S4 displays the large-area (250 \( \mu \)m resolution) scanning electron microscopy—energy-dispersive X-ray (SEM–EDX) spectroscopy elemental mapping of these selected heterostructures with the distributions of Ni, Fe, and N atoms. The NiFeN/NiFe-300-2h sample has a slightly higher N content (7.4 atom %) than NiFeN/NiFe-350-2h (6.8 atom %). SEM–EDX mapping performed at a 100 nm range for the selected sample of NiFeN/NiFe-350-2h indicated a homogeneous distribution of Ni, Fe, and N atoms (Figure S5).

The morphology of the selected NiFeN/NiFe-350-2h sample was further analyzed by transmission electron
microscopy (TEM) where nanoparticles in the range of 15–30 nm could be imaged (Figures 1a and S6). After ammonia treatment, they maintained their initial morphology and shape. As seen in Figure 1b, high-resolution TEM (HR-TEM) imaging further supports the formation of crystalline Ni$_3$FeN with an interplanar spacing of 0.22 nm, which corresponds to the (111) plane of Ni$_3$FeN. Moreover, scanning transmission electron microscopy (STEM)–EDX mapping demonstrated the homogeneous distribution of N, Ni, and Fe atoms in the selected field (Figure 1c–f). More direct evidence of the homogeneous distribution of Ni, Fe, and N elements was obtained by STEM–EDX line scanning analysis along a linear path passing through central and peripheral parts of two arbitrary representative nanoparticles for the Ni$_3$FeN/Ni$_3$Fe-350-2h sample (Figure S7). Line scanning profiles of the composite particles show that Ni, Fe, and N signals are located homogeneously across the particles. The surface chemistry and composition of the selected Ni$_3$FeN/Ni$_3$Fe-350-2h heterostructure were probed by X-ray photoelectron spectroscopy (XPS). As shown in Figure 1g, the Ni 2p spectrum can be convoluted into two main features at 852.0 and 855.0 eV, which can be assigned to Ni$^0$ and Ni$^{2+}$ species, respectively. The satellite peak around 860 eV corresponds to the shake-up excitation of the high-spin nickel ions.

Figure 1h displays a high-resolution Fe 2p spectrum, which can be convoluted into two main peaks at 706.4 and 710.3 eV that can be assigned to metallic Fe and Fe$^{3+}$ species, respectively. The reason for the formation of Fe$^{3+}$ species on the metallic Fe surface could be the fast surface oxidation after the nitridation experiment. Furthermore, the N 1s spectrum of Ni$_3$FeN/Ni$_3$Fe-350-2h is shown in Figure 1i. The N 1s spectrum displays one peak, which can be convoluted into three components at 397.5, 399.2, and 401.6 eV that correspond to the nitrided composition. While the peak at 397.5 eV matches with the complete transformation to Ni–Fe nitride species, peaks at 399.2 and 401.6 eV can be assigned to –NH and –NH$_2$ surface moieties after the ammonia treatment, respectively. It can be concluded that the surface structure of Ni$_3$FeN/Ni$_3$Fe-350-2h consists of metal nitride species in addition to metallic Ni and Fe. In addition to bimetallic Ni$_3$FeN/Ni$_3$Fe heterostructures, mixed phases of monometallic nickel nitride and iron nitride were also prepared via ammonia treatment at 300 and 350 °C, respectively (Figure S8) to reveal differences in catalytic performances. Although heterostructures of monometallic Fe nitrides and bimetallic Ni$_3$Fe nitrides were successfully synthesized, this could not be achieved for Ni nitrides since it decomposes at a synthesis temperature of 350 °C due to the lower decomposition temperatures of nickel nitride. The XRD pattern of Ni samples treated at 300 °C for 2 h (Ni$_3$N/Ni-300) shows that Ni is still the main phase and small diffractions were observed at 38.9, 42.1, 44.5, and 58.5° corresponding to (110), (002), (111), and (112) planes of Ni$_3$N (PDF: 00-010-0280), respectively. As shown in Figure

\[ \text{Figure 1. TEM (a), HR-TEM (b), STEM (c), corresponding STEM–EDX elemental mapping (d–f), Ni 2p (g), Fe 2p (h), and N 1s (i) spectra of Ni$_3$FeN/Ni$_3$Fe prepared at 350 °C for 2 h.} \]
S8b. Fe₄N/Fe structures were successfully synthesized, Fe₄N (PDF: 00-006-0627) being the main component in addition to Fe₃N (00-049-1662).

After the structural analyses, the catalytic performances of the heterostructures were further investigated for CO₂ and H₂O conversion to oxygenates and amides by using a pressurized autoclave system, which can operate up to 400 bar and 300 °C. The experimental setup is shown in Figure S9.

The analyses of the formed liquid products were done by proton nuclear magnetic resonance (¹H NMR) and high-performance liquid chromatography (HPLC). Initially, standards of expected nitrogen and carbon fixation compounds were measured by ¹H NMR spectroscopy and results are displayed in Figures S10 and S11, respectively. Before the thermocatalytic survey, a series of control experiments were conducted to explore the potential catalytic background of the reactor system. First, a reaction was performed to check possible contaminations from the catalyst with water under 25 bar of Ar at 100 °C for 16 h. Another control reaction was performed with CO₂ and H₂ gases (25 bar, 3:2 ratio) at 100 °C in the absence of the metal catalyst. No formamide formation was detected, while a very low concentration of formate was found in control experiments (Figure S12). The trace formate might be possible contaminations from the air dissolved in Milli-Q water that was used as a solvent although the system was purged with Ar prior to the experiment.

With potential contamination sources from the reactor system characterized as negligible, thermocatalytic CO₂ fixation was performed in 2 mL of H₂O under 25 bar of CO₂ at 100 °C for 16 h over the Ni₃FeN/Ni₃Fe-350-2h heterostructure after 16 h in H₂O. Concentrations of obtained products (calculated from related ¹H NMR spectra) at different temperatures (d), diverse initial CO₂ pressures (e), and different reaction pH values (f). Ft: formate, Fd: formamide. Error bars represent the standard deviations of at least two independent reactions.

Figure 2. ¹H NMR spectra of the products (with their molecular structures) obtained under 25 bar CO₂ at different temperatures (a), under different initial CO₂ pressures at 100 °C (b), and at different initial pH values under 25 bar of CO₂ at 100 °C (c) over the Ni₃FeN/Ni₃Fe-350-2h heterostructure after 16 h in H₂O. Concentrations of obtained products (calculated from related ¹H NMR spectra) at different temperatures (d), diverse initial CO₂ pressures (e), and different reaction pH values (f). Ft: formate, Fd: formamide. Error bars represent the standard deviations of at least two independent reactions.
of nitrogen in Ni$_3$FeN/Ni$_3$Fe-300-2h (based on SEM−EDX analyses) might facilitate the C−C coupling toward the formation of C$_2$-compounds. It is known that introducing nitrogen atoms to the parent metal structure changes the energies of adsorption and desorption behaviors of reaction intermediates. The electronegative nitrogen atom alters the d-band energy density of the parent transition metal and improves the activity for electron donation reactions.

Previously, it was suggested by Moran and colleagues that acetate is formed via a formate pathway. Therefore, it is possible that formate was converted to acetate and therefore the low concentration of formate was detected with the Ni$_3$FeN/Ni$_3$Fe-300-2h sample.

After testing bimetallic Ni$_3$FeN/Ni$_3$Fe heterostructures, monometallic Ni$_3$N/Ni and Fe$_x$N/Fe heterostructures were further tested under the same reaction conditions, 25 bar of CO$_2$ at 100 °C for 16 h, to see performances of counterparts of the Ni$_3$Fe alloy. $^1$H NMR results of the obtained liquid products are shown in Figures S14 and S15. In both cases, formamide was not observed. Fe$_x$N/Fe yields very low amounts of carbon fixation products that were not detectable by HPLC (Figure S14). However, the formation of acetate and acetic acid was promoted over Ni$_3$N/Ni particles (Figure S15).

While 0.43 mM of formate was obtained over Ni$_3$N/Ni particles, which is almost one-fifth of the amount obtained over Ni$_3$FeN/Ni$_3$Fe particles, concentrations of acetate and formic acid were 0.07 and 0.19 mM, respectively. Overall, formamide formation was detected over only bimetallic heterostructures. The reason for this trend is discussed below in the catalyst alteration part in more detail. After observing that monometallic Ni$_3$N/Ni and Fe$_x$N/Fe heterostructures did not yield a significant amount of formamide, bimetallic Ni$_3$FeN/Ni$_3$Fe was chosen as a substrate and a catalyst for CO$_2$ fixation reactions. Due to the higher formamide selectivity with the Ni$_3$FeN/Ni$_3$Fe-350-2h heterostructure compared to that of Ni$_3$FeN/Ni$_3$Fe-300-2h, effects of reaction parameters on the product formation were further investigated by varying the temperature, the initial pH of the solution, and the initial CO$_2$ pressure by using Ni$_3$FeN/Ni$_3$Fe-350-2h. As seen in $^1$H NMR spectra in Figure 2a, both formate and formic acid were detected with the Ni$_3$FeN/Ni$_3$Fe-350-2h catalyst at temperatures of 25, 50, and 100 °C under 25 bar of initial CO$_2$ pressure after 16 h. Although the dissolution of CO$_2$ increases with decreasing temperatures in water, the obtained formate and formic acid amounts were lower at 25 and 50 °C compared to 100 °C (Figure 2d). The reason might be related to the formation of an additional compound peak at 7.79 ppm in $^1$H NMR (Figure 2a) at temperatures of 25 and 50 °C. This new peak at 7.79 ppm was assigned to 1,2,4-triazole, an aromatic nitrogen heterocycle with the formula C$_2$N$_3$H$_3$.

Computational studies of the possible formation of purine from formamide suggested that the ring closure reaction of formamide is thermodynamically favorable in the presence of water. Therefore, formamide generated from CO$_2$ and nickel−iron nitrides can be a building block for the formation of this type of cyclic nitrogen compound at low reaction temperatures. Another way to improve the solubility of CO$_2$ in water is by increasing the partial pressure of CO$_2$ according to...
Henry’s law.\textsuperscript{61} We performed a set of reactions under different initial CO\textsubscript{2} pressures in the range of 5–50 bar at 100 °C with a Ni\textsubscript{i}FeN/Ni\textsubscript{i}Fe-350-2h catalyst. As displayed in \textsuperscript{1}H NMR spectra in Figure 2b, formate and formamide were detected in all pressure values at 100 °C. Increasing the partial pressure of CO\textsubscript{2} to 25 bar from 5 bar led to the enhancement of the amount of formate and formamide from 0.43 to 2.06 mM and from 0.45 to 0.77 mM, respectively. However, a further increase in the initial CO\textsubscript{2} pressure to 50 bar results in the decrease of formate and formamide concentrations to 1.87 and 0.31 mM, respectively (Figure 2e). The reason might be associated with the excess amount of CO\textsubscript{2} that can block/occupy the active center of the Ni\textsubscript{i}FeN/Ni\textsubscript{i}Fe catalyst and causes its sudden deactivation, which is discussed below along with the catalyst alteration. Reaction pH is another key factor that can affect the solubility of CO\textsubscript{2} and its interaction with the solid catalysts, as well as the product spectrum.\textsuperscript{7} The effect of the initial pH of the reaction solution was investigated at a series of pH values from 6 to 11 (Figure 2c). The increase in the initial pH of the reaction solution resulted in the decrease of formate and formamide amounts from 2.06 to 0.54 mM and from 0.77 to 0.05 mM, respectively (Figure 2f). Notably, the formamide yield was about 10 times higher at pH 6. There could be several reasons for this trend: (i) change of carbonic acid equilibrium in water at different pH values, CO\textsubscript{2}\textsuperscript{-} ions tend to be formed in alkaline media,\textsuperscript{61} and different CO\textsubscript{2} forms in the aqueous phase at different pH values have different solubilities,\textsuperscript{57} (ii) potential decomposition of obtained compounds under alkaline conditions, especially hydrolysis of formamide in alkaline aqueous solutions can occur via the nucleophilic attack of an amide bond by hydroxide ion,\textsuperscript{64,65} (iii) catalyst alteration and stability of nitriles might be varied at different pH values.

After observing that the Ni\textsubscript{i}FeN/Ni\textsubscript{i}Fe-350-2h heterostructure yielded the highest amounts of products at the optimized conditions of 25 bar of CO\textsubscript{2} at pH 6 and 100 °C for 16 h, the impacts of the catalyst amount and the reaction time on product formation were further examined. In addition to the initial amount of 0.5 mmol (122 mg) of Ni\textsubscript{i}FeN/Ni\textsubscript{i}Fe-350-2h nanoparticles, 0.25 mmol (61 mg) and 1 mmol (244 mg) of the solid catalyst were tested under 25 bar of CO\textsubscript{2} at 100 °C for 16 h. The \textsuperscript{1}H NMR spectra in the range of 7.5 -- 9.5 ppm are provided in Figure 3a, and the whole spectral range is presented in Figure S16. As seen in Figure 3c, decreasing the catalyst amount from 0.5 to 0.25 mmol results in a decline in product concentrations (from 2.06 to 0.22 mM formate and from 0.77 to 0.2 mM formamide). Since H\textsubscript{2} can be obtained via the interaction of the metal with water due to water dissociation, the increase in metal loading increases the H\textsubscript{2} amount that shifts the reaction equilibrium toward products according to Le Chatelier’s principle. In addition, formic acid decomposition can occur at high temperatures via the decarboxylation pathway in aqueous solutions, which yield CO\textsubscript{2} and H\textsubscript{2} as products.\textsuperscript{66} Reaction equilibrium of formic acid decomposition can shift to the reactant side due to a higher amount of H\textsubscript{2}. However, a further increase in Ni\textsubscript{i}FeN/Ni\textsubscript{i}Fe-350–2h amounts to 1 mmol results in a decrease in formate and formamide concentrations (from 2.06 to 0.89 mM formate and from 0.77 to 0.19 mM formamide). Acetate and acetamide were detected as additional products with concentrations of 0.02 and 0.004 mM, respectively. To gain some insights into reaction intermediates and mechanism, CO\textsubscript{2} fixation was performed at longer reaction times of up to 7 days under 25 bar of CO\textsubscript{2} at 100 °C. Figure 3b displays the formate and formamide regions in \textsuperscript{1}H NMR; the whole \textsuperscript{1}H NMR spectra are provided in Figure S17. The quantitative analysis results of the obtained products are plotted in Figure 3d. When the reaction time is increased from 16 to 24 h, formate and formamide concentrations decreased to 0.82 and 0.43 mM, respectively, and acetate is formed as a new product (0.03 mM). This hints that formate is a substrate for the formation of acetate. When the reaction time was extended to 72 h, acetamide formation (0.15 mM) was confirmed. While the amounts of acetate and acetamide were enhanced up until 72 h, a further increase in the reaction time to 168 h led to a significant decrease in all product concentrations, likely due to product decomposition in aqueous media at high temperature and pressure. Formic acid and formamide are known to decompose to lower-molecular-weight compounds in water.\textsuperscript{16,66} In addition to liquid products, gas products of the reaction were also analyzed by gas chromatography (GC). Gas product analysis after a reaction time of 16 h reveals that methane and ethane were produced with 25 bar CO\textsubscript{2} at 100 °C using the Ni\textsubscript{i}FeN/Ni\textsubscript{i}Fe-350h-2h heterostructure (Figure S18a). There was no detectable additional gas product as the reaction time increased to 72 h (Figure S18b).

In previous studies with NiFe catalysts, it was shown that the addition of H\textsubscript{2} promotes formate formation from CO\textsubscript{2}.\textsuperscript{33,67} A control reaction was conducted with the addition of 10 bar of H\textsubscript{2} gas to study the role of H\textsubscript{2} versus water as a reductant. The catalytic reaction was performed with 0.5 mmol of Ni\textsubscript{i}FeN/ Ni\textsubscript{i}Fe-350-2h catalyst under 25 bar of CO\textsubscript{2} + H\textsubscript{2} mixture (3:2 ratio) at 100 °C for 16 h. As expected, the addition of H\textsubscript{2} had a positive effect on the formic acid formation, which was enhanced more than 20-fold (from 2.06 to 43.7 mM), and the generated formamide amount was more than doubled to 1.42 mM (Figure S19). Obviously, an increase in the formic acid amount promotes formamide formation. However, since nitrogen is the limiting reagent for the formation of formamide, the increase in concentration was much more significant for formate, suggesting that the reaction mechanism of CO\textsubscript{2} to formamide is H\textsubscript{2}-dependent.

Additional experiments were performed using formic acid and NH\textsubscript{4}OH as substrates to gain more insights into the reaction pathway of the reductive CO\textsubscript{2} conversion to formamide. Formic acid is commonly used as a substrate for amide synthesis.\textsuperscript{21,23} Moreover, a known method to prepare formamide is the reaction of formic acid and ammonia via ammonium formate formation as an intermediate product followed by dehydration to generate formamide at high temperatures.\textsuperscript{21} In order to investigate formic acid as a possible intermediate for formamide formation, we use 10 mM of formic acid as a carbon source (instead of CO\textsubscript{2}) since this concentration is close to the amount we have obtained in our reactions from CO\textsubscript{2} reduction. The reaction was performed for 16 h under ambient conditions with the Ni\textsubscript{i}FeN/Ni\textsubscript{i}Fe-350-2h catalyst. \textsuperscript{1}H NMR result (Figure S20) showed that almost all formic acids were consumed, and 4.85 mM of formamide was obtained. Moreover, a known method to prepare formamide is the reaction of formic acid and ammonia via ammonium formate formation as an intermediate product followed by dehydration to generate formamide at high temperatures.\textsuperscript{21} In order to investigate formic acid as a possible intermediate for formamide formation, we use 10 mM of formic acid as a carbon source (instead of CO\textsubscript{2}) since this concentration is close to the amount we have obtained in our reactions from CO\textsubscript{2} reduction. The reaction was performed for 16 h under ambient conditions with the Ni\textsubscript{i}FeN/Ni\textsubscript{i}Fe-350-2h catalyst. \textsuperscript{1}H NMR result (Figure S20) showed that almost all formic acids were consumed, and 4.85 mM of formamide was calculated to be produced. In addition to formamide, 1.1 mM of acetamide was detected. This experiment indicates that formic acid is an intermediate product in formamide synthesis from CO\textsubscript{2}. After the formation of formic acid, the subsequent reaction with lattice nitrogen yields formamide as the final product. Dehydration of ammonium formate, a product of formic acid and ammonia, can form formamide and some metal nitriles were reported to yield ammonia in water.\textsuperscript{68}
Therefore, it is possible that ammonia and formic acid are formed in water and yield formamide.

To reveal the role of nitrogen source, an additional experiment was conducted using 1 mM of NH$_4$OH solution as a nitrogen source instead of nitride mineral. The reaction was performed with 0.5 mmol of pristine Ni$_3$Fe nanoparticles (nitrogen-free) under 25 bar of CO$_2$ at 100 °C for 16 h. This results in only a small amount of acetamide, and no formamide formation could be detected based on $^1$H NMR analyses (Figure S21). The reason might be the increase in the pH of the solution; alkaline pH does not promote the formation of formamide as mentioned above. This suggests a route of the direct consumption of lattice nitrogen in the Ni$_3$Fe/Ni$_3$Fe heterostructure to produce formamide instead of ammonia as an intermediate product.

It is important to study the alteration of the catalyst for a better understanding of the reaction mechanism. The selected Ni$_3$Fe/Ni$_3$Fe-350-2h powders were subjected to structural characterization after different catalytic reactions. The main results are depicted in Figure 4. As presented in XRD patterns in Figure 4a, the Ni$_3$Fe/Ni$_3$Fe phase has not been altered noticeably at reaction temperatures of 25 and 50 °C; however, it started to decompose, and the FeCO$_3$ phase was formed at 100 °C. Postreaction SEM−EDX analyses indicated a clear compositional alteration after a reaction temperature of 25 and 100 °C. No nitrogen could be detected after the reaction at 100 °C (Figure S22), while about 5 atom % of nitrogen was found in the sample after the catalytic reaction temperature of 25 °C (Figure S23). EDX results also show that the Ni/Fe ratio was altered to be 5.5 and 4.4 after the reaction at 100 and 25 °C, respectively. This trend is expected due to the higher oxidation tendency of Fe compared to Ni in water. When the initial partial pressure of CO$_2$ in the reaction was increased from 5 to 50 bar, the formation of the FeCO$_3$ phase became more prominent as shown in XRD patterns in Figure 4b. At higher pressures, CO$_2$ can be adsorbed on the catalyst surface more strongly and can cause its sudden deactivation due to the saturation of water with dissolved CO$_2$. In addition, a higher amount of dissolved CO$_2$ can decrease the pH of the reaction solution slightly. The oxidation of transition metals is promoted by acidic conditions. This can be seen from the postreaction XRD pattern of Ni$_3$Fe/Ni$_3$Fe-350-2h after the reactions at different pH values (Figure 4c). The Ni$_3$Fe phase seems to be more durable under alkaline conditions of pH 9 and 11. Nitrides of Ni and Fe are reported to be less stable at acidic pH values. Nitrides of Ni and Fe are reported to be less stable at pH values lower than 9; Ni$_3$N can be oxidized to Ni$_3$O$_5$ while Ni$_3$N is stable at pH values around 9. Besides reaction temperature, pressure, and pH, the reaction time was also found to affect catalyst alteration. As seen in the XRD pattern in Figure 5a, FeCO$_3$ formation was observed after 16, 24, and 72 h subsequent to the catalytic reaction with 25 bar of CO$_2$ at 100 °C. The Ni$_3$Fe phase could be detected even after 72 h, while no metal nitride phase could be observed after longer reaction times. Alteration of the morphology of a selected sample (Ni$_3$Fe/Ni$_3$Fe-350-2h) after the particular reaction conditions (25 bar of CO$_2$ at 100 °C for 16 h) was further investigated by electron microscopy. SEM imaging shows significant alteration of the morphology and the formation of flake-like structures (Figure 4d). This structural alteration could be further supported by TEM where flake-like and aggregated nanoparticle structures were visualized (Figure 4e). As seen in Figure 4f, characteristic lattice fringes obtained from HR-TEM further support the formation of FeCO$_3$ for the solid sample after the catalytic reaction under 25 bar of CO$_2$ at 100 °C for 16 h. Overall, the formation of FeCO$_3$ alters the morphology of the Ni$_3$Fe/Ni$_3$Fe-350-2h heterostructure. Surface alteration of the selected sample (Ni$_3$Fe/Ni$_3$Fe-350-2h) after the catalytic reaction was further examined by XPS. As displayed in Figure
S25a, the Ni 2p spectrum contains a peak with maxima at 855.6 eV, which corresponds to Ni$^{2+}$ species. Additionally, there is a small shoulder at 851.6 eV that can be assigned to the metallic Ni. The Fe 2p spectrum (Figure S25b) displays a peak located at 711.3 eV, which can be attributed to Fe$^{2+}$. There was no detectable metallic Fe on the surface after the reaction. The surface Fe was completely oxidized, while the Ni surface was found to be more durable under the catalytic reaction conditions. No nitrogen species could be detected on the surface of this selected sample after the reaction, which further supports the consumption of nitrogen during the reaction. Alteration of monometallic FeN and Ni$_3$N provides further hints about their catalytic performance in CO$_2$ reduction. While the Ni$_3$N phase was transferred to Ni during the catalytic CO$_2$ reduction in the presence of water, the Fe$_3$N catalyst was completely converted to the FeCO$_3$ phase (Figure S26). Postreaction characterization of metal nanoparticles provided insights into the source of hydrogen and nitrogen for CO$_2$ fixation. The formation of FeCO$_3$ was observed after the catalytic reactions with Fe-containing catalysts. Interaction between carbonated water and Fe results in a redox reaction, which yields H$_2$ via water decomposition and Fe oxidation. When the concentrations of CO$_2$ and Fe$^{2+}$ ions reach the solubility limit in the reaction solution, the precipitation of FeCO$_3$ occurs. The precipitation of FeCO$_3$ depends on several parameters including temperature, pH, and the partial pressure of CO$_2$. At lower reaction temperatures, the dissolved CO$_2$ amount in water is higher according to Henry’s law, but the kinetics of the FeCO$_3$ formation are low. Therefore, the hydrogen formation rate is also low, which explains the lower concentrations of formate and formamide at lower reaction temperatures. In addition, the pH of the reaction affects the water dissociation rate over the metal catalyst. In alkaline regimes, the existence of OH$^-$ causes a lower concentration of H$^+$ in the solution, which could be the rate-limiting agent for CO$_2$ fixation to formate. The reaction path for CO$_2$ fixation to amides might follow a mechanism similar to Mars–van Krevelen, in which lattice nitrogen within nitrides involves C–N coupling and generation of nitrogen compounds. In the classical Mars–van Krevelen mechanism, after the adsorption of the substrate, an oxidation–reduction sequence occurs on the oxide surface whereby one of the lattice oxygens is consumed during the catalyst reduction step. In our reaction system, lattice nitrogen of Ni–Fe nitride heterostructures directly reacts with the CO$_2$ and other intermediates. A simplified proposed reaction pathway for the formation of amides over Ni$_4$FeN$_3$/Ni$_2$Fe nanoparticles via direct CO$_2$ reduction in H$_2$O is shown in Figure 5. CO$_2$ first can be converted to bonded CO or formyl group on the metal surface. The formyl group is either detached and forms formate or further converted to acetate. An amide formation pathway was confirmed by the reaction of formic acid and ammonia in our control experiment. Formic acid could be an intermediate during formamide formation. When the nitrogen source was replaced with ammonia, no formamide was obtained. Therefore, the coupling of *CHO and dissolved lattice N can generate formamide, which can occur even under ambient conditions. Furthermore, acetamide was observed in some reactions together with acetate. The formation of acetamide from acetate can follow a similar pathway to formamide, in which the −OH group is substituted with NH$_2$.

**CONCLUSIONS**

We have shown that nickel–iron nitride heterostructures can act as catalysts and substrates to convert CO$_2$ and water to oxygenates and amides under mild hydrothermal conditions, without using any synthetic hydrogen and nitrogen. While monometallic Ni and Fe nitrides did not yield any formamide, bimetallic Ni–Fe nitride heterostructures yield formate, formamide, acetate, and acetamide. The formation of formate and amides was found to be very sensitive to the reaction conditions including temperature, pressure, pH, and reaction time. Postcharacterization analyses indicated the alteration of catalyst, dissolution of nitrogen from the lattice structure, and formation of metal carbonate phase. The outcome of this study showed that CO$_2$ and water could be fixed to formamide, which is an important building block for the synthesis of prebiotic organics. Since the direct incorporation of N$_2$ gas into the carbon fixation system is demanding, using a metal-based solid catalyst with chemisorbed nitrogen for the direct synthesis of formamide from CO$_2$ and H$_2$O can provide a different perspective for the possible formation scenario of formamide under hydrothermal vent conditions.

**EXPERIMENTAL METHODS**

**Reagents and Materials.** Fe(NO$_3$)$_3$·9H$_2$O (≥98%) and Ni(NO$_3$)$_2$·6H$_2$O (≥97%) and all of the standards were obtained from Merck. Tea leaves were purchased from Goran-Tee.

**Synthesis of Nickel–Iron Nitrides.** Nickel–Iron oxide nanoparticles were prepared through a hard-templating route by using...
spent tea leaves as a carbon-based template. Briefly, tea leaves were washed with distilled H$_2$O at 80 °C several times and dried at 80 °C overnight. For the synthesis of NiO, 0.1 M of aqueous solution of Ni(NO$_3$)$_2$·6H$_2$O was prepared and dried tea leaves were added to this solution. The mass ratio of tea leaves to total metal precursor was adjusted to 2:1. After continuously stirring at room temperature for 2 h, the tea leaves were dried at 80 °C overnight and calcined at 550 °C (with a heating rate of 2 °C/min) under air for 4 h. For the synthesis of Fe$_3$O$_4$, the same procedure was implemented by using an aqueous solution of Fe(NO$_3$)$_2$·9H$_2$O. Ni$_2$Fe nanoparticles were prepared by setting the molar ratio between Ni and Fe salt precursors to 3:1. After the drying process at 80 °C, the composite material was calcined at 550 °C for 2 h to remove the remaining metal oxide nanoparticles (ramping rate is 2 °C/min). The diluted acid leaching method was used to remove possible residues, such as Ca and Mg, after the calcination of spent tea leaves. For that, the synthesized metal oxides were washed with 40 mL of 0.1 M HCl for 2 h (4 h for Fe) and centrifuged three times with H$_2$O. Upon acid treatment and leaching, samples were dried at 80 °C overnight. The reduction of synthesized metal oxides was performed with 10% H$_2$/Ar gas flow (total flow rate: 100 mL/min) at 300 °C for 2 h to obtain reduced metal nanoparticles (ramping rate is 2 °C/min). In order to prevent the complete oxidation of metal nanoparticles after H$_2$ reduction, the surface passivation process with air/Ar gas flow (100 mL/min, 2% air) was performed at room temperature for 1 h.\textsuperscript{38} Ni–Fe nitrides were obtained via the ammonolysis method. After H$_2$ reduction, metal powders were subjected to ammonia treatment in the tube furnace. The samples were prepared according to the following procedures: the Ni$_2$Fe/Ni$_2$Fe heterostructure was prepared by the reaction of reduced Ni$_2$Fe and ammonia in a tube furnace at the temperature range of 300–400 °C for 1 or 2 h. The heating rate was 10 °C/min, and the flow rate of ammonia gas was 100 mL/min. The samples were labeled as follows: Ni$_2$Fe sample treated at 350 °C for 2 h; Ni$_2$Fe/Ni$_2$Fe-Ni$_2$Fe-350-2h, Ni$_2$Fe sample treated at 300 °C for 2 h; Ni$_2$Fe/Ni$_2$Fe-Ni$_2$Fe-300-2h, Ni$_2$Fe sample treated at 350 °C for 2 h; Ni$_2$Fe/Ni$_2$Fe-Ni$_2$Fe-350-1h, Ni$_2$Fe sample treated at 300 °C for 2 h; Ni$_2$Fe/Ni$_2$Fe-Ni$_2$Fe-300-2h. Ni$_2$N/Ni sample was prepared by treating metallic Ni with an ammonia flow at 300 °C for 2 h with a flow rate of 100 mL/min. The Fe$_2$N/Fe heterostructure was obtained by treating metallic Fe with ammonia at 350 °C for 2 h. After ammonia treatment, the furnace was cooled down under ammonia flow to prevent the decomposition of nitrides at high temperatures. Upon reaching room temperature, the system was purged with an Ar flow (100 mL/min) for 2 h and the samples were left in the quartz tube overnight under ambient conditions in order to naturally passivate the surface of nitride samples in order to prevent the exchange of nitrogen with oxygen when the samples interact with air.

**Structural Characterization.** Crystal structures of synthesized materials were analyzed by powder X-ray diffraction (XRD) using Stoe theta/theta diffractometer with the Bragg–Brentano geometry using Cu Kα1/2 radiation. In situ high-temperature X-ray diffraction data were collected on a Rigaku SmartLab with a rotating anode (9 kW, 45 kV, 200 mA) in the Bragg–Brentano geometry (Cu Kα1/2: 1.541862 Å). Data were collected with a HyPix-3000 multidimensional detector in 1D mode. A reaction chamber (XRR9000, Anton Paar) was mounted on the diffractometer for the heating experiments. Heating was performed from room temperature to 30 °C and from 200 to 400 °C (10 K/min) in 20 °C steps where the sample was kept for 30 min each under a constant flow of 20 mL/min NH$_3$. Data were collected continuously in the range of 35–80° 2θ in steps of 0.01° and a scan speed of 6°/min. For each temperature, three scans were collected and then merged. N$_2$ sorption analysis was used to determine the textural parameters of synthesized Ni–Fe nitride heterostructures. Ni$_2$-physiosorption isotherms were measured with a 3Flex Micromeritics setup at ~196 °C. Before each measurement, samples were degassed at 150 °C for 10 h. Specific surface areas were determined by applying the Brunauer–Emmett–Teller (BET) method in the relative pressure range between 0.06 and 0.2. The morphology of samples was investigated by the transmission electron microscopy (TEM) imaging of powder samples using a Hitachi H-7100 (100 kV). Lattice fringes are obtained with high-resolution TEM micrographs collected with a Hitachi HF2000. Scanning electron microscopy/scanning transmission electron microscopy–energy-dispersive X-ray spectroscopy (SEM/STEM–EDX) mapping was performed with a Hitachi S-3500N electron microscope. The alteration of the catalyst after the reaction was analyzed by XRD. The postreaction catalyst was washed with 40 mL of distilled water and dried in the vacuum furnace at 50 °C prior to the measurement. Dry powder was directly measured with XRD.

**CO$_2$ Reduction Experiments.** CO$_2$ reduction reactions were performed by using an in-house built autoclave made of Mo–Ni alloy, which provides stability for high-pressure and high-temperature conditions. Poly(tetrafluoroethylene) (PTFE) inlet with a volume of 28 mL was utilized in order to prevent possible contaminations and catalytic effects coming from the metallic reactor. The reaction temperature and pressure were monitored by the thermocouple and the pressure transmitter, respectively. For a typical reaction, the reactor was loaded with 2 mmol (1 M) of the metal catalyst in 2 mL of H$_2$O. Therefore, 0.5 mmol of Ni$_2$Fe/Ni$_2$Fe, 2 mmol of Ni$_2$Ni/Ni$_2$Fe, and Fe$_2$N/Fe were used. Then, the reactor was pressurized with 25 bar of CO$_2$ gas at different reaction temperatures (25–100 °C) and different initial pH values in the range of 6–11. For high-pressure reactions, the reactor was filled with 50 or 100 bar of CO$_2$ and reactions were conducted at 100 °C for 16 h. The pH of alkaline reactions was adjusted by the addition of KOH solution (0.1 M) and verified with pH indicator strips (Merck, 1.09526.0003, Universal indicator, 376). Reactions under alkaline conditions were performed with 25 bar CO$_2$ at 100 °C for 16 h.

Several control reactions were performed. First, the possible catalytic effect of the reactor was checked in the absence of the metal catalyst with 25 bar of CO$_2$ in H$_2$O at 100 °C. Furthermore, possible contamination from the catalyst (selected sample: Ni$_2$Fe/Ni$_2$Fe-Ni$_2$Fe-350-2h) was checked by performing a reaction under 25 bar of Ar at 100 °C for 16 h. Additional experiments were performed by using either formic acid as a carbon source or NH$_3$OH as a nitrogen source. For the formic acid conversion reaction, 10 mM formic acid solution and Fe$_2$N/Ni$_2$Fe-350-2h heterostructure as a nitrogen source. After purging with Ar, the reaction was performed at 25 °C for 16 h. Then, the nitrogen source was changed to NH$_3$OH solution and CO$_2$ gas was used as a carbon source. For the ammonia reaction, 0.5 mmol of Ni$_2$Fe metal was used with 1 mM of NH$_3$OH solution under 25 bar of CO$_2$ at 100 °C for 16 h.

After the reaction, the reactor was cooled down to room temperature for 2 h. The solid catalyst was removed after the reaction by centrifugation at 9000 rpm for 10 min. The liquid was then filtrated with a syringe and a filter (MULTOCLEAR-13 PTFE membrane, 0.45 μm) and washed with distilled H$_2$O at 80 °C several times and dried at 80 °C overnight. For the analysis of liquid product, 10 mM of formic acid solution and centrifuged at 13 500 rpm for 15 min to minimize the paramagnetic effect coming from possibly leached metal species as it is described in our previous study.\textsuperscript{65} NMR spectra were obtained on either a Bruker Avance Neo spectrometer operating at a field of 14.1 T (3H Larmor frequency of 600 MHz) with a cryogenically cooled TCI probe for the highest sensitivity on the direct observation of 1H. All spectra were collected at 25 °C in standard 5 mm tubes containing sample volumes of about 700 μL with the addition of 10% D$_2$O (70 μL) as it was described previously.\textsuperscript{47} In $^1$H spectra, water suppression at 4.68 ppm was achieved using “excitation sculpting” together with “perfect echo”
using the Bruker standard pulse program “zgesgppe”. Concentrations of amides (formamide and acetamide) were calculated with $^1$H NMR by using pentaerythritol (100 μM) as an internal standard.

A Shimadzu LC-2030 equipped with a refractive index (RI) detector was used for HPLC measurements. The column was Metacarb 67H with a 6.5 mm inner diameter and 300 mm length. The mobile phase is 0.1% of trifluoroacetic acid (TFA) at a flow rate of 0.8 mL/min, and the temperature was constant at 50 °C during the measurements. HPLC was used for the analysis of carboxylic acids including formic acid and acetic acid.

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