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COMMUNICATION

A novel method of NaHCO₃ reduction into formic acid with N₂H₄·H₂O over Ni catalyst

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A novel Ni-catalysed CO₂ reduction with N₂H₄·H₂O was proposed. A 50% yield of formic acid with 99% selectivity was achieved by using a commercially available Ni powder catalyst. The proposed method is simple and environmentally friendly because it requires neither elaborately prepared catalysts, nor high-purity, high-pressure hydrogen.

CO₂ reduction into chemicals or fuels has attracted considerable attention as an important method to reduce greenhouse gas emissions and also to alleviate the current dependence on fossil fuels.¹ In the past several decades, many promising methods for CO₂ reduction have been proposed.² Among these methods, the photochemical reduction of CO₂ is regarded as the most promising approach, but its efficiency is very low, and expensive catalysts or complex catalysts are needed.³ The hydrogenation of CO₂ with gaseous hydrogen is currently considered to be the most commercially feasible synthetic route. However, this method requires either elaborately prepared and expensive (or complex) catalysts, such as noble-metal (Ir, Ru, Rh, etc.) complexes, or high-purity, high pressure hydrogen.⁴ Therefore, developing a new method for the hydrogenation of CO₂ with alternative hydrogen sources and simple catalysts is urgently required.

Hydrous hydrazine, N₂H₄·H₂O, might be a promising reductant for the reduction of CO₂. Recently, several studies on hydrogen production by the catalytic decomposition of N₂H₄·H₂O have been reported.⁵ To the best of our knowledge, CO₂ reduction with N₂H₄·H₂O as an in situ, liquid hydrogen source was not yet reported previously.

Hydrothermal reactions have received an increasing attention in organic chemical synthesis because high-temperature water (HTW) is an environmentally benign solvent compared to organic solvents and has suitable properties as a reaction medium.⁶ For example, HTW has a lower dielectric constant, fewer and weaker hydrogen bonds, and a higher isothermal compressibility than ambient liquid water.⁷ Thus, some reactions that can hardly proceed at low temperatures can occur in HTW.⁸ Recently, there is also an increasing interest in CO₂ reduction under hydrothermal conditions. For example, our group and others have demonstrated the reduction of CO₂ into value-added chemicals using metals as the reductant without expensive or complex catalysts in HTW.⁹ As such, it is of

great potential for efficient reduction of CO₂ into chemicals using N₂H₄·H₂O as the reductant together with a simple catalyst in HTW.

In this study, we focused on the use of hydrothermal reactions for the hydrogenation of CO₂ into formic acid by employing N₂H₄·H₂O as an in situ liquid hydrogen source with Ni powder as the catalyst.

Initially, to test the possibility of CO₂ reduction into chemicals with N₂H₄·H₂O, experiments with N₂H₄·H₂O and NaHCO₃, which was used as the CO₂ source in order to simplify the experiments, were conducted at 300 °C. 300 °C was selected because our previous studies have shown that 300 °C was the optimal temperature for CO₂ reduction into chemicals.¹⁰ Analyses of the liquid samples with GC-MS and HPLC showed that the major product was formic acid (see Fig. SI-1 and SI-2). It can be seen from Table 1 that no formation of formic acid was observed in the absence of N₂H₄·H₂O (entry 1). These results indicated that CO₂ was selectively reduced into formic acid and that N₂H₄·H₂O acted as the reductant. Considering that the real product should be formate due to the alkalinity of N₂H₄·H₂O, the formate yield, which was defined as the percentage of formate to the initial amount of NaHCO₃ based on carbon, was used to assess CO₂ reduction in this study. As shown in Table 1, a formate yield of 18% was obtained (entry 2).

Table 1. The yields of formate from CO₂ with N₂H₄·H₂O.^a

Entry	Reductant	Catalyst	Yield (%) ^b
1	-	-	0
2	N ₂ H ₄ ·H ₂ O	-	18
3	-	Ni	1
4	N ₂ H ₄ ·H ₂ O	Ni	23
5	N ₂ H ₄ ·H ₂ O	Cu	9
6	N ₂ H ₄ ·H ₂ O	Fe	13
7	N ₂ H ₄ ·H ₂ O	Co	3
8	N ₂ H ₄ ·H ₂ O	AlNi	4
9	N ₂ H ₄ ·H ₂ O	WC	6

^a Reaction conditions: NaHCO₃: 0.5 M; N₂H₄·H₂O: 2 M; Ni: 4 mmol; water filling: 35%; time: 120 min; temp.: 300 °C. ^b The formate yield is defined as the percentage of formate to initial NaHCO₃ on the carbon basis.

Although CO₂ can be reduced into formic acid without the addition of a catalyst, the formate yield was not high—only 18%. Thus, various metals were screened as the catalyst in order to

enhance the yield of formate. As shown in Table 1, among the metals investigated, only Ni catalyst showed better performance, affording formate with increased yield (entry 4). XRD analyses of the solid residues after the reaction showed that Ni was still in the metallic state (see Fig. SI-3), suggesting that the role of Ni metal was the catalyst in the reduction of CO_2 into formate with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.

Subsequently, a series of experiments were conducted over a wide range of conditions by changing the concentration of reactants, water filling, reaction temperature and time in order to study the reaction characteristics and then design the optimal synthetic conditions for a higher yield of formate. First, the effect of the Ni amount was studied. As shown in Fig. 1, the formate yield increased to 27% with the addition of 2 mmol Ni. However, the formate yield decreased when the amount of Ni further increased to 3 mmol. The decrease in the formate yield with overdose of Ni can be probably ascribed to the decomposition of formate into CH_4 , which was supported by the fact that CH_4 was detected as the side product when using 3 mmol of Ni.

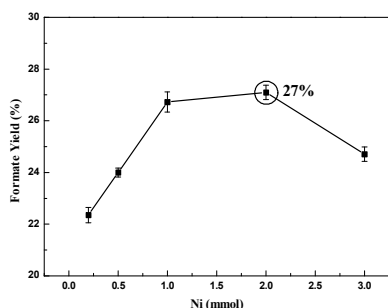


Fig. 1. Effect of the amount of Ni on the yields of formate (NaHCO_3 : 0.5 M; $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$: 2 M; water filling: 35%; time: 120 min; temp.: 300 °C).

The pressure of the reaction system usually has a strong influence on the product yield. The effect of the pressure was then investigated by varying water filling in a batch reactor system. As shown in Fig. 2 (a), the increase in the water filling/pressure facilitated the CO_2 reduction into formate, and the yield of formate significantly increased to 50% as the water filling increased to 60%. A possible reason for the increase in the formate yield with an increase in water filling is that more hydrogen was dissolved in water under a higher pressure. Since similar yields of formate were obtained with 55% and 60% water filling, the following experiments were conducted with 55% water filling. The amount of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ has also been optimized. It is expected that the increase amount of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ could enhance the product yield whereas the capital cost would increase as well. Thus, to obtain the optimal concentration of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (or the ratio of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ to CO_2), the amount of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was varied with a fixed amount of NaHCO_3 (0.5 M). As shown in Fig. 2(a), the yield of formate increased greatly with increased concentration of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, and reached a plateau when the concentration of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ further increased to 6 M.

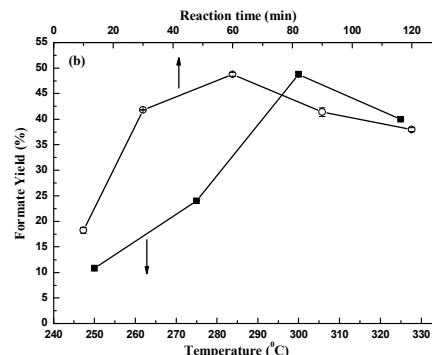
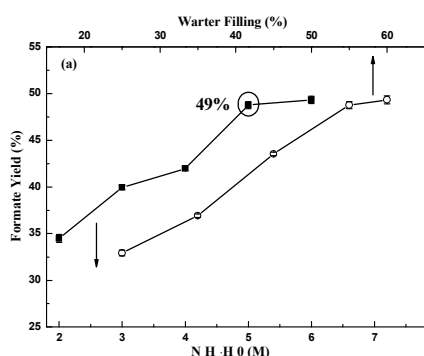


Fig. 2. (a) Effects of water filling and the amount of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ on the yields of formate (time: 60 min; temp.: 300 °C.). (b) Effects of reaction time and temperature on the yields of formate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$: 5 M; water filling: 55%).

The effects of reaction time and temperature on the yield of formate were further investigated under the optimal conditions obtained above. As shown in Fig. 2(b), the formate yield increased first and then decreased with an increase in the reaction time, and the highest yield was obtained after 60 min. The decrease in the formate yield after 60 min indicated that the rate of decomposition of formate was faster than its formation rate. For the effect of temperature, as shown in Fig. 2(b), the formate yield drastically increased as the reaction temperature increased from 250 to 300 °C and reached a maximum at 300 °C. The observed decrease in the formate yield at temperatures above 300 °C could be caused by the decomposition of formate.

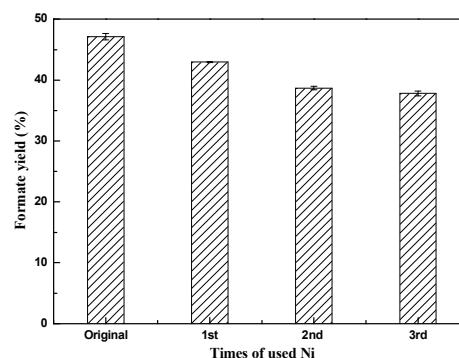


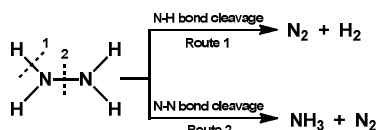
Fig. 3. Effect of reused Ni on the yields of formic acid (NaHCO_3 : 0.5 M; $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$: 5 M; Ni: 3.135 mmol; water filling: 55%; time: 60 min; temp.: 300 °C).

The organic carbon in the liquid samples was also determined by TOC analysis, and the amount of carbon in the formate was comparable to the total carbon in the samples, which indicated that formate was the dominant product in the hydrogenation of CO_2 . The main by-product was acetic acid with a yield of 0.4%, and therefore, the selectivity for the production of formate was approximately 99%.

Finally, the stability of the Ni catalyst was examined, as shown in Fig. 3. Although slight decrease in the yield of formate was observed in the 2nd cycle, further decrease was not observed, indicating that Ni can maintain the activity after 2 cycles. The specific surface area of the Ni powder was measured by BET, which showed that the specific surface area of Ni decreased from 2290 m^2/kg before the reaction to 2196 m^2/kg after the first cycle, which may explain the slight decrease in the formate yield. Moreover, to confirm whether the leaching of the Ni catalyst occurred and the possible contamination of main compositions (Fe, Mn) of the SUS316 reactor wall, the ion concentration of Ni, as well as Fe and Mn, in the solution after the reactions were measured by ICP; small amount of these ions was found in the liquid sample with Ni at 2.126 ppm, Fe at 0.5366 ppm, and Mn at 0.1642 ppm, respectively. The results

indicated that the leaching of these metals was negligible. To further rule out the possible catalytic activity of Fe or Mn from the reactor wall, control experiments were conducted in the absence of Fe or Mn and in the presence of the two with a 10^4 -fold concentration as the values detected by ICP. The results were comparable, indicating that Fe or Mn are not able to catalyse the reaction.

The possible mechanism of CO_2 reduction into formic acid with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ was investigated. It is generally known that the decomposition of N_2H_4 takes place in two typical reaction routes:¹¹ $\text{N}_2\text{H}_4 \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2(\text{g})$ and $3\text{N}_2\text{H}_4 \rightarrow 4\text{NH}_3 + \text{N}_2(\text{g})$, and the ways of decomposition can be explained by Scheme 1.



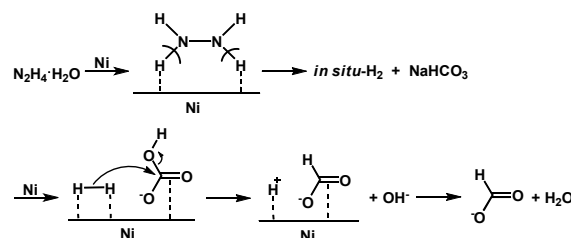
Scheme 1. Decomposition ways of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$.

To investigate the main route of N_2H_4 decomposition in this study, reactions with only $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in the presence and absence of Ni were conducted. Analyses of the gaseous samples with GC-TCD showed that the amounts of both H_2 and total gas were much higher in the presence of Ni compared to those in the absence of Ni. These results indicated that Ni can improve the decomposition of N_2H_4 to H_2 and N_2 by N-H bond cleavage (Route 1), while avoiding the undesired decomposition of N_2H_4 to ammonia (NH_3) (Route 2). Similar results were reported in H_2 production from N_2H_4 , in which Raney Ni and Ni-based bimetallic catalysts, such as Ni-Rh, Ni-Ir and Ni-Pt, were used.¹² Obviously, in this study, the common Ni powder can selectively decompose N_2H_4 into H_2 , which is most likely that HTW can activate the Ni catalyst surface and make the H in N_2H_4 more easily adsorbed onto Ni, leading to N-H bond cleavage and the formation of H_2 . Then, the experiment without Ni under the optimum condition (300 °C, 55% water filling, 5M $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) was conducted and the yield of formate was 15%, which was much lower than that with 3.135 mmol Ni (49% yield). The result further confirmed the catalytic role of Ni. In addition, to study whether the surface of Ni can be oxidised in HTW and then affect the catalyst activity, XPS of the Ni before and after the reaction were measured, and trace amounts of $\text{Ni}(\text{OH})_2$ and NiO before the reaction and $\text{Ni}(\text{OH})_2$ after the reaction were observed (see Fig. SI-4). However, reactions under the catalysis of $\text{Ni}(\text{OH})_2$ or NiO gave low yields of formate yield (8% and 7% respectively), much lower than that even without Ni. These results suggested that Ni, rather NiO or $\text{Ni}(\text{OH})_2$, acted as the catalyst in the CO_2 reduction with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. This phenomenon likely occurred because Ni^{2+} was reduced into Ni(0) by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, which was supported by the fact that Ni(0) was observed in the reaction with NiO or $\text{Ni}(\text{OH})_2$ in the presence of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. Finally, an experiment with NaHCO_3 and ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$) was conducted to examine whether CO_2 can be reduced by ammonia. The result showed that almost no formation of formate was observed, indicating that the formation of formate should be contributed to the hydrogen from N_2H_4 rather than NH_3 .

After understanding the catalytic activity of Ni for decomposing N_2H_4 into H_2 , an important question is whether the formed hydrogen reacts with CO_2 or HCO_3^- . As a result, reactions with gaseous CO_2 instead of NaHCO_3 were conducted. The yield of formate was only 1%, suggesting that the hydrogenation can be considered to occur mainly with HCO_3^- rather than CO_2 . Furthermore, to explore the difference between the activity of the in situ hydrogen from $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and gaseous hydrogen, an experiment with gaseous hydrogen as the hydrogen source instead of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ was performed. Only a 2% yield of formate was obtained. Although

further evidence is needed, from these results it is suggested that in situ hydrogen formed from $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ may act as a higher activity than the gaseous hydrogen in CO_2 reduction into formic acid.

Based on the above results, a possible mechanism was proposed, as shown in Scheme 2. First, the H in $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ is adsorbed onto the Ni surface and the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ prefers the cleavage of the N-H bond, leading to H_2 formation. Subsequently, the in situ generated H_2 is also adsorbed onto the Ni surface and is activated by Ni. Furthermore, the active H attacks the C=O, followed by the leaving of hydroxyl group of HCO_3^- . Finally, formate was obtained together with H_2O , which was formed by the combination of another active H of H_2 and leaving hydroxyl group of HCO_3^- .



Scheme 2. Proposed mechanism of reduction of HCO_3^- into formate with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ over Ni.

Conclusions

We have, for the first time, demonstrated the highly selective reduction of CO_2 into formic acid using $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ over a common Ni powder in HTW. Nearly 99% selectivity and approximately 50% yield of formate were achieved. The recycling of Ni displayed stable activity. This technique provides a simple method for reducing CO_2 into value-added chemicals and also provides an example for a multitude of possible chemical reactions for CO_2 conversion and utilization.

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Notes and references

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