

Supporting Information

A novel method of NaHCO_3 reduction into formic acid with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ over Ni catalyst

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1. General Information. NaHCO₃ was used as the source of CO₂ to simplify the experiments. NaHCO₃, N₂H₄·H₂O (85%), and Ni (200 mesh) were purchased from Sinopharm Chemical Reagent Co., Ltd. Formic acid (98%) was ordered from Sigma-Aldrich. Gaseous H₂ (≥99.999%) was obtained from Shanghai Poly-Gas Technology Co., Ltd. All reagents were used as test materials without further purification. Formic acid and gaseous H₂ were employed for the quantitative analysis of liquid and gaseous products, respectively.

2. Product analysis. The HPLC analysis of liquid products was performed on Agilent 1260 series equipped with UV-vis detector. Two Shodex RSpak KC-811 columns were used in series. The solvent was 2 mM HClO₄ with a flow rate of 1.0 mL·min⁻¹. Liquid samples also were analyzed by GC-MS on an Agilent 7890 AGC system equipped with a 5975C inert MSD. The samples were separated by an HP-Innowax capillary column (dimension: 30 m × 250 μm × 0.25 μm) using helium as a carrier gas. Gaseous samples were analyzed using HP-5890 Series II GC-TCD system equipped with an HP-Innowax packing column. Solid samples were characterized by XRD on Shimadzu XRD-6100 equipment.

The yields are mean value of three times experiments. The relative errors of these data are less than 5% and standard deviations are less than 0.9.

$$Yield, mmol\% = \frac{C \text{ in formate, } mmol}{C \text{ in initial NaHCO}_3, mmol} \times 100\%$$

3. General Procedure for the Synthesis of formate from NaHCO₃. All experiments were conducted in a batch reactor (3/8 in. diameter, 1 mm wall thickness, and 120 mm length) made of SUS 316 alloys with an internal volume of 5.7 mL. In a typical procedure, the 2235 μL water mixture of test materials with 0.5 M NaHCO₃, 5 M N₂H₄·H₂O (85%, 900 μL), and 3.135 mmol Ni were added into the reactor, and then the sealed reactor was put into the salt bath that had been preheated to desired temperature. The salt bath can offer a fast heat-up time of about 15 s from 20 °C to 300 °C. The reactor was shaken horizontally in the salt bath until the desired reaction time was complete. After the reaction, the reactor was taken out of the salt bath and put into a cold water bath to quench the reaction. The reaction time was defined as the time that the reactor was kept in the salt bath. Water filling was defined as the ratio of the volume of the solution, including

added $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and deionized water, to the inner volume (5.7 mL) of the reactor. After cooling off, liquid sample was collected and filtered with 0.45 μm filter membrane. Solid sample washed with deionized water and ethanol several times and dried in air for analysis.

4. GC-MS chromatograms of liquid products

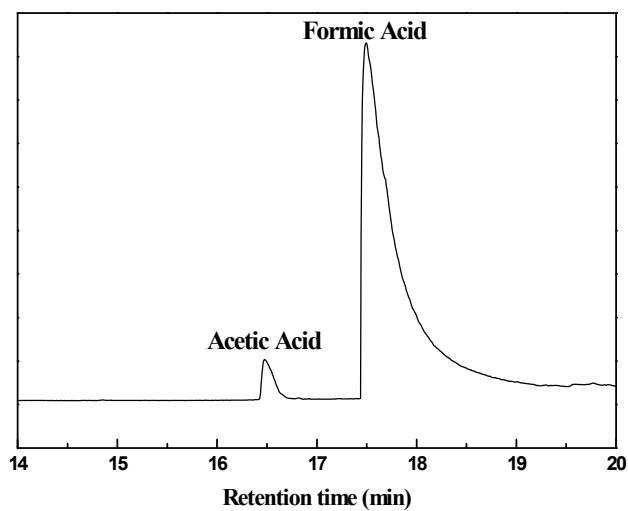


Fig. SI-1. GC-MS chromatograms of liquid products

5. HPLC chromatograms of liquid products

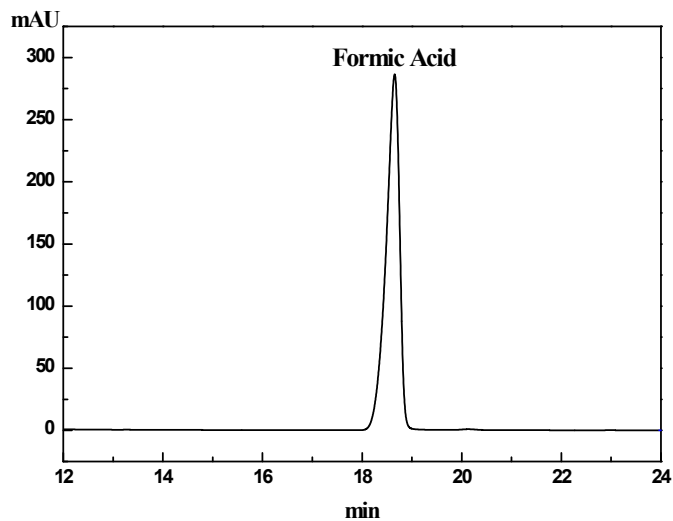


Fig. SI-2. HPLC chromatograms of liquid products

6. XRD patterns of solid products after the reaction of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ with Ni.

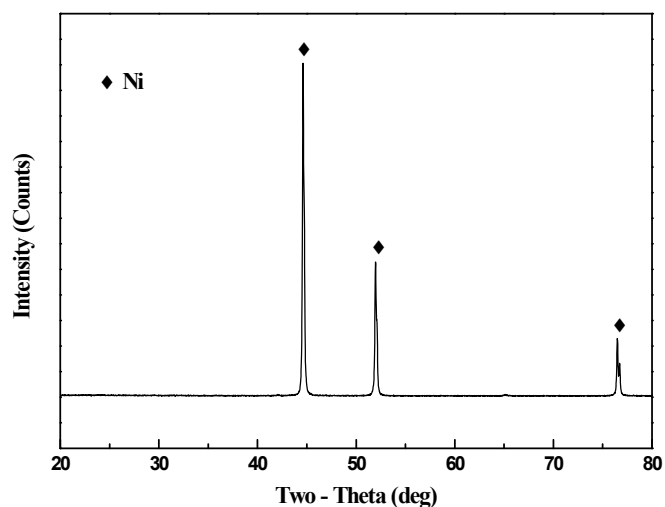


Fig.SI-3. XRD patterns of solid products after reaction (NaHCO_3 : 0.5 M; $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$: 2 M; Ni: 4 mmol; water filling: 35%; time: 120 min; temp.: 300 °C.).

7. XPS patterns of nickel metal. To study whether the surface of Ni used can be oxidized, and then affect the catalyst activity of Ni, XPS analysis of Ni before and after the reaction was performed on ESCALab 250Xi. As shown in Fig. SI-4(a), peak 1 at 852.6 eV, peak 2 at 853.58 eV and peak 3 at 855.38 are characteristic peaks of metallic Ni $2p_{3/2}$, $\text{Ni}^{2+} 2p_{3/2}$ in NiO and $\text{Ni}^{2+} 2p_{3/2}$ in $\text{Ni}(\text{OH})_2$, respectively. Peaks 4, 5, 6, 7 and 8 are accompanying peaks. The results showed that a trace of $\text{Ni}(\text{OH})_2$ and NiO on Ni surface before the reaction. As shown in Fig. SI-4(b), peak 1 at 852.6 eV and peak 2 at 855.78 eV are characteristic peaks of metallic Ni $2p_{3/2}$ and $\text{Ni}^{2+} 2p_{3/2}$ in $\text{Ni}(\text{OH})_2$, respectively. Peaks 3, 4, 5, 6, 7 are accompanying peaks. The results showed that a trace of $\text{Ni}(\text{OH})_2$ on Ni surface after the reaction.

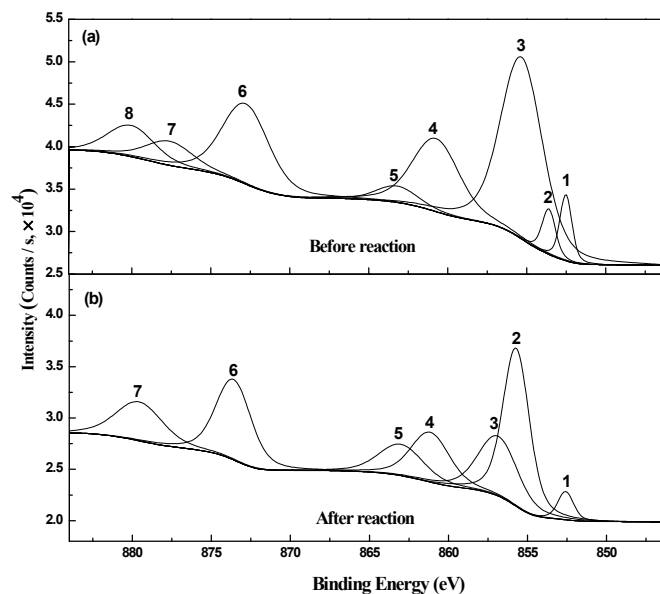


Fig.SI-4. XPS spectra of Ni $2p_{3/2}$ from Ni metal before (a) and after (b) the reaction.

8. XRD patterns of solid samples after reactions of $N_2H_4 \cdot H_2O$ with NiO or $Ni(OH)_2$.

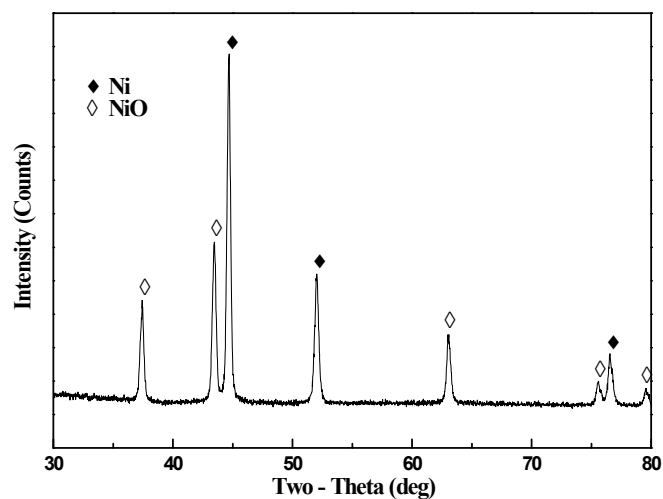


Fig. SI-5. XRD patterns of solid products after the reaction ($NaHCO_3$: 0.5 M; $N_2H_4 \cdot H_2O$: 5 M; NiO: 3.135 mmol; water filling: 55%; time: 60 min; temp.: 300 °C.).

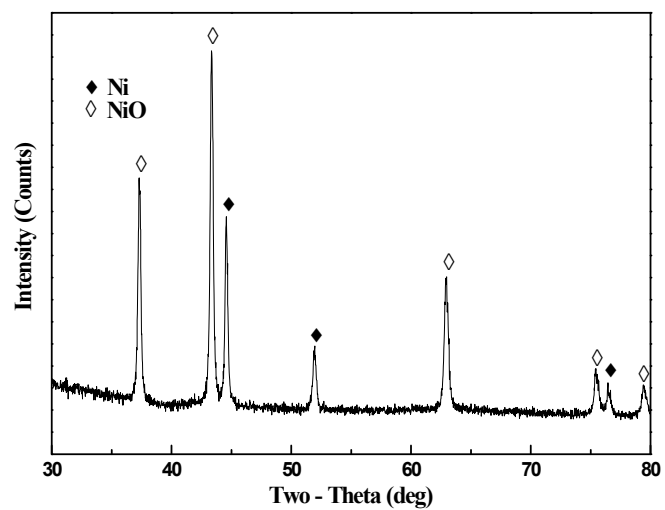


Fig. SI-6. XRD patterns of solid products after the reaction (NaHCO_3 : 0.5 M; $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$: 5 M; $\text{Ni}(\text{OH})_2$: 3.135 mmol; water filling: 55%; time: 60 min; temp.: 300 °C.).