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## Nanoporous Nickel catalyst for selective hydrogenation of carbonates into formic acid in water

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An efficient unsupported nanoporous nickel (NiNPore) material for the hydrogenation of carbonates to formic acid (FA) in water was firstly investigated. NiNPore represented an environmentally benign catalyst and exhibited remarkable catalytic activity in the reduction of a wide range of carbonates to afford formic acid in excellent yields with high selectivity, and the maximum values of 86.6% from NaHCO<sub>3</sub> and even up to 92.1% from KHCO<sub>3</sub> were obtained, respectively. Hydrogen pressure and pKa of carbonates showed significant influence on the formation of FA. The catalyst was easily recovered and could be recycled at least five times without leaching and loss of activity. The present study provided a potential application for the synthesis of FA from CO<sub>2</sub> or carbonate compounds.

### 1. Introduction

As is known to all, CO<sub>2</sub> is the main greenhouse gas that causes global warming which has a series of bad influence on both environment and ecology, such as temperature growth, forests degradation, glaciers melt, sea level rise, etc., which may destroy the natural balance<sup>1</sup>. To reduce CO<sub>2</sub> in the atmosphere is one of the most important and difficult challenges that requires scientific and technological methods<sup>2,3</sup>. CO<sub>2</sub> is often considered as a renewable C1 source to be converted into useful chemicals and fuels such as formic acid (FA) due to its abundant, nontoxic and readily available<sup>3,4</sup>.

FA is a very important organic chemical feedstock because of its numerous applications which has often been found as acid and reductant and widely used as a precursor in the leather and textile in chemical industries and agriculture<sup>5</sup>. Besides, FA has the potential to power fuel cells for electricity generation and automobiles<sup>6-9</sup>. Moreover, from the aspect of energy storage, FA is considered as a hydrogen storage media or carrier while hydrogen is difficult to handle and transfer due to its low density and easily explosive nature<sup>10</sup>. The catalytic hydrogenation of CO<sub>2</sub> to FA is greener and safer as an attractive route. Advantageous and desirable the way is, it deserves exploration. The researches focused on different

catalysts for the hydrogenation of CO<sub>2</sub> to FA have been reported, such as homogeneous metal catalysts (M: Rh, Ir, Ru, Co, Fe, etc.)<sup>11-21</sup> and heterogeneous supported metal catalysts<sup>22-24</sup>. However, most of those reactions still have considerable drawbacks. For example, due to the high kinetic and thermodynamic stability of CO<sub>2</sub>, the reaction requires high-energy starting materials<sup>25-29</sup>, thus inorganic or organic bases are always added into the reaction in order to make the thermodynamics favourable<sup>23, 30</sup>. The reactions using homogeneous catalysts were hardly applied in industries because of two main obstacles: the cleavage of FA from corresponding salts as bases that are required in the hydrogenation; the recycling and separation of the bases and the noble catalysts<sup>23, 24, 31</sup>. Therefore, to avoid that, the development of an efficient and green reaction process with a highly active and selective heterogeneous catalyst for hydrogenation of CO<sub>2</sub> to FA is highly desirable.

Recently, unsupported nanoporous nickel (NiNPore) material has attracted much attention because of their large surface-to-volume ratios, distinguished electronic property, nontoxic nature, high recyclability and simple recovery. NiNPore can be prepared by selective leaching of Mn from an alloy foil of Ni<sub>30</sub>Mn<sub>70</sub> at electrochemical conditions<sup>32, 33</sup>. It behoves us to think that NiNPore as a catalyst for hydrogenation of CO<sub>2</sub> to FA should be ideal from environmental and industrial viewpoints. Besides, there has not been reported for the transformation using NiNPore catalyst so far.

Herein, we first report a safer and greener route for hydrogenation of carbonates (as CO<sub>2</sub> sources) to FA by unsupported nanoporous nickel in aqueous phase, NiNPore exhibits significant catalytic activity in the reduction of a wide range of carbonates to afford formates in excellent yields with high selectivity (Scheme 1).

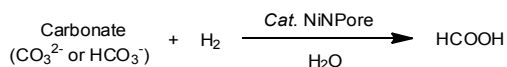
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**Scheme 1.** Hydrogenation of carbonates to FA over NiNPore in water.

## 2. Experimental

### 2.1 Experimental materials

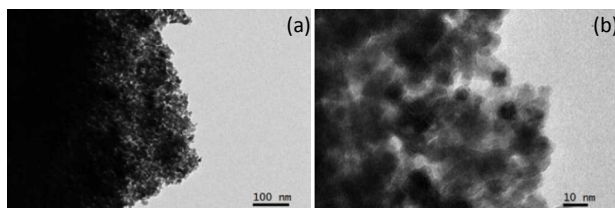
NaHCO<sub>3</sub> as the initial reactant was purchased from Sinopharm Chemical Reagent Co., Ltd, as well were KHCO<sub>3</sub>, NH<sub>4</sub>HCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>. Hydrogen (99.999%) was obtained from Shanghai Wetry Standard Reference Gas Analytical Technology Co., LTD. Ni power, NiO, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Al-Ni alloy were also purchased from Sinopharm Chemical Reagent Co., Ltd. And Ru/C (5 wt.%, Aladdin) was as well used in our experiments. Raney Ni was prepared by ourselves according to the previous literatures<sup>34</sup>. Formic Acid (Sigma–Aldrich, >98%) was used in the quantitative analysis of liquid samples.

### 2.2 Preparation and characterization of catalyst

Ni nanoporous catalyst was prepared according to previous literatures<sup>32,33</sup>. First, pure Ni and Mn (purity >99.9%) were melted using an Ar-protected arc melting furnace to form Ni<sub>30</sub>Mn<sub>70</sub> ingots. Then the ingots were cold-rolled to thin sheets whose thickness was around 50 μm at room temperature after annealing at 900 °C for 24 hours for homogenizing microstructure and composition. Next, Ni nanoporous was prepared by dealloying in 1.0 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aqueous solution at 50 °C. Final, the already prepared samples were washed thoroughly with water and ethanol and dried in vacuum. The prepared microstructure of dealloyed material NiNPore by transmission electron microscopy (TEM) is shown in Figure 1. The structure of NiNPore with bright nano-pores and dark-contrast ligaments<sup>33</sup> can be observed clearly (Figure 1 (a)) and the pore size is around 7 nm (Figure 1 (b)). The specific surface area of NiNPore is around 62 m<sup>2</sup>/g (calculated by the Brunauer–Emmett–Teller (BET) method). The pore size distributions were also determined from the adsorption branch of the isotherms based on the density functional theory (DFT), and calculative pore size is 7.1 nm (Figure SI-2), which is in good agreement with the TEM observation.

### 2.3 Experimental procedure

NaHCO<sub>3</sub> was selected as a source of CO<sub>2</sub> for the optimization of reaction conditions in all reactions. All the reactions were



**Figure 1.** TEM images of NiNPore.

carried out in a Parr reactor whose internal volume is 100 mL. The procedure of hydrogenation of NaHCO<sub>3</sub> was as follows. Firstly, NaHCO<sub>3</sub> (1 mmol, 0.084 g), 10 mL deionized water and desired catalysts were loaded into the reactor. Then, desired pressure of hydrogen at ambient temperature was introduced into the reactor from hydrogen cylinder though the intake of Parr after purified the reactor three times with 1 MPa H<sub>2</sub>. And then we began heating and kept stirring at 800 rpm. Once the temperature inside Parr reactor was heated to the setting temperature, we started to time. After reaction, we stopped heating and cooled Parr by an electric fan. Finally, liquid and gaseous samples were collected for analysis. Solutions were filtered with 0.45 μm Syringe Filter and solid samples were washed with deionized water several times and then saved in ethanol.

### 2.4 Products analysis

Liquid samples were analysed by GC-MS, HPLC and GC-FID qualitatively and quantitatively. Products were confirmed by GC-MS (Agilent7890A GC system, 5975C inert MSD with Triple-AxisDetector) equipped with a HP Innovax polyethylene glycol capillary column whose dimensions are 30 m × 250 μm × 0.5 μm. The quantitative calculation of FA and byproducts was conducted by HPLC (Agilent1200 system, equipped with RI and VW detectors) and GC-FID (Agilent7890A GC system, 5975C inert MSD with Triple-Axis Detector) equipped with the same column as GC-MS. The solid samples were analysed by XRD (Shimadzu, Lab-XRD-6100, scanning rate: 6°min<sup>-1</sup>, 2θ ranges: 10–80°). Gaseous samples were detected by TCD (thermal conductivity detector, Agilent Technologies). And a TOC Analyzer (Shimadzu TOC-V) was used to measure the total organic carbon concentration. The yields of products (formic acid, acetic acid and methanol) were calculated as the following equations:

$$\text{Yield}_{\text{product}} (\%) = \frac{n_{\text{product}} \text{ after reaction, mmol}}{n_{\text{NaHCO}_3} \text{ in the initial time, mmol}} \times 100\%$$

## 3. Results and discussion

A series of experiments were conducted systematically in order to investigate the optimum reaction parameters for the hydrogenation of NaHCO<sub>3</sub> to FA. The influences of different catalysts, amounts of catalyst, temperatures, hydrogen pressures and reaction times on FA yields were investigated. Details are showed as follows.

### 3.1 Catalyst screening

Table 1 showed that the effect of different catalysts on FA yield. To examine the feasibility of hydrogenation of NaHCO<sub>3</sub> to FA, we tried the reaction with 1 mmol NaHCO<sub>3</sub> and 3 MPa H<sub>2</sub> in the presence of 10 mg (17 mol%) NiNPore catalyst in H<sub>2</sub>O at 200 °C for 2 h. The results indicated that the main product FA was obtained in 63.2% yield with trace amount of methanol (MA) and acetic acid (AA) (entry 7). These products were identified by GC-MS as shown in Figure SI-3. The absence of catalyst only afforded trace amount of FA (entry 1). Among the

## Journal Name

## ARTICLE

**Table 1.** Effect of catalysts on the hydrogenation of NaHCO<sub>3</sub> to FA.<sup>a</sup>

Entry	Catalyst	Catalyst loading	Yield (%)		
			FA <sup>b</sup>	MA <sup>b</sup>	AA <sup>b</sup>
1	none	0	0.5	0	0
2	Ni power	17 mol%	1.8	trace	trace
3	NiO	13 mol%	3.5	trace	0.1
4	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	10 mg	2.2	trace	trace
5	Al-Ni alloy	10 mg	56.5	trace	trace
6	Raney Ni	17 mol%	60.0	trace	0.1
7	NiNPore	17 mol%	63.2	trace	trace
8	Ru/C	10 mg	20.9	trace	trace
9	NiNPore	15 mol%	62.2	trace	0.3
10	NiNPore	22 mol%	72.6	trace	0.3
11	NiNPore	25 mol%	70.8	trace	0.4
12 <sup>c</sup>	NiNPore	22 mol%	54.7	trace	0.3

<sup>a</sup> Reaction conditions: 1 mmol NaHCO<sub>3</sub>, 3 MPa H<sub>2</sub>, H<sub>2</sub>O 10 mL, 200 °C, 2 h. <sup>b</sup> FA: Formic acid; MA: Methanol; AA: Acetic acid.

<sup>c</sup> Temperature was 150 °C.

various nicks investigated, nickel power, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and NiO catalysts were proved to be not effective for this transformation (entries 2-4). The use of Al-Ni alloy and Raney Ni gave good results, but yields were lower relative to NiNPore catalyst (entries 5 and 6). This might be because big specific surface area of NiNPore contributed to the hydrogenation of NaHCO<sub>3</sub> to FA (see Table SI-1). The use of Ru/C afforded 20.9% yield (entry 8). The effect of NiNPore loadings on FA yield was investigated (also see Figure SI-4). Decreasing the NiNPore loading gave low yield (entry 9). When NiNPore loading was increased to 22 mol%, the yield of FA increased from 63.2% to 72.6%, further up to 25 mol% gave a low 70.8% yield (entries 10 and 11). Decreasing yield might be because increasing NiNPore loading could cause the formed FA to decompose into CO<sub>2</sub> and H<sub>2</sub> more easily, which was a reversible reaction competing with hydrogenation process. To confirm this hypothesis, reactions were conducted with formed FA as starting material at 3 MPa H<sub>2</sub> for 2 h at 200 °C in water using different NiNPore loadings. The results showed that the concentration of FA was decreased from 62.4 mmol/L to 57.3 mmol/L as catalyst loading increasing from 15 mol% to 22 mol% (Table SI-2) and CO<sub>2</sub> was also detected by GC-MS (Figure SI-5), which supported our assumption. Besides, low temperature was completely ineffective for the hydrogenation of NaHCO<sub>3</sub> to FA (entry 12). However, due to the safety factor of Teflon material inside Parr, more than 200 °C was not inspected.

### 3.2 Effect of hydrogen pressure

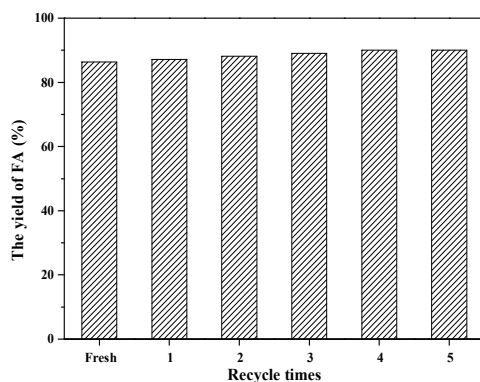
Normally, hydrogen pressure has great influence on FA yield. Further studies on the effect of hydrogen pressure were conducted for hydrogenation of NaHCO<sub>3</sub> using NiNPore catalyst. The results are summarized in Table 2 and Figure SI-6.

It can be seen obviously that the yield of FA increased significantly with the hydrogen pressure increasing from 2 MPa to 6 MPa (entries 1-4), and the maximum value of 86.6% was achieved (TOF of 1738 h<sup>-1</sup>, TON of 3476) as hydrogen pressure reached to 6 MPa. FA yield remained unchanged when hydrogen pressure increased to 7 MPa (entry 7). It indicated that high hydrogen pressure contributed to the hydrogenation of NaHCO<sub>3</sub> to FA. To promote the hydrogenation of FA, some attempts by adding an alkaline additive (NEt<sub>3</sub>), decreasing temperature and changing reaction time were also tested, but the yields were not improved (entries 5-6 and 8-9, also see Figure SI-7). To understand the effect of additive for the reaction, the experiments was conducted with 2 mmol NEt<sub>3</sub> under the standard conditions. Results showed that residual FA (68.7 mmol/L) with 2 mmol NEt<sub>3</sub> was lower than the without NEt<sub>3</sub> (78.7 mmol/L) (see Table SI-3). Moreover, CO<sub>2</sub>

**Table 2.** Effect of hydrogen pressure on FA yield.<sup>a</sup>

Entry	H <sub>2</sub> Pressure (MPa)	Time (h)	Yield (%)		
			FA	MA	AA
1	2	2	57.9	trace	0.3
2	3	2	72.6	trace	0.3
3	5	2	80.5	trace	0.3
4	6	2	86.6	trace	0.3
5 <sup>b</sup>	6	2	84.2	trace	0.3
6 <sup>c</sup>	6	2	67.7	trace	0.4
7	7	2	86.1	trace	0.3
8	6	1	83.3	0.4	0.3
9	6	3.5	84.7	0.5	0.3

<sup>a</sup> Reaction conditions: 1 mmol NaHCO<sub>3</sub>, 22 mol% NiNPore, H<sub>2</sub>O 10 mL, 200 °C. <sup>b</sup> 2 mmol NEt<sub>3</sub> was used. <sup>c</sup> Temperature was 150 °C.

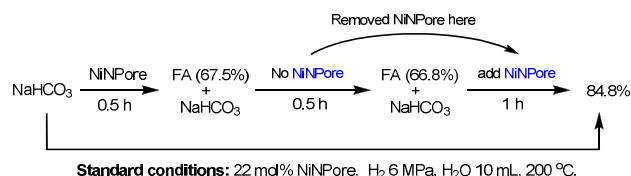


**Figure 2.** Recycling tests for the hydrogenation of NaHCO<sub>3</sub> (NaHCO<sub>3</sub> 1 mmol, H<sub>2</sub> 6 MPa, Catalyst 22 mol%, H<sub>2</sub>O 10 mL, 200 °C, 2 h).

was also detected (see Figure SI-8). We thus concluded that NEt<sub>3</sub> can promote FA decomposition, which can explain the decreasing yield of FA with NEt<sub>3</sub> in the reaction.

### 3.3 Reusability test

Recycling tests of NiNPore catalyst were performed under the optimal conditions. Results were shown in Figure 2. After each recycle, the NiNPore catalyst was simply washed by deionized water for several times to remove the surface substances and then reused in the next run without further purification. After five recycles, high FA yields were still obtained, indicating that the activity of NiNPore was not lost. Interestingly, the FA yield was further increased in the first four recycles and then remained unchanged. It is supposed that NiNPore catalyst had a little oxidation before the reaction, and was reduced step by step by hydrogen during the reaction leading to the increasing yield of FA. To confirm the hypothesis, XPS measurements of fresh, 1st cycle and 5th cycle catalysts were provided to investigate the change of nickel and nickel oxide on the surface. The states of nickel on the surface can be determined from the binding energies (BE). Previous literatures<sup>35,36</sup> had supported information of BEs of 852.6 eV, 854.9 eV and 860.9 eV to Ni 2p<sub>3/2</sub> XPS spectra corresponding to Ni, Ni(OH)<sub>2</sub> and NiO, respectively. From Figure 3 and Table SI-4, we can see that the ratio of Ni increased from 9.8% to 25.6% while the ratio of NiO decreased from 24.3% to 17.7% and Ni(OH)<sub>2</sub> decreased from 65.9% to 56.7% as recycle-times increased. Results showed that FA yield increased from 86.6%

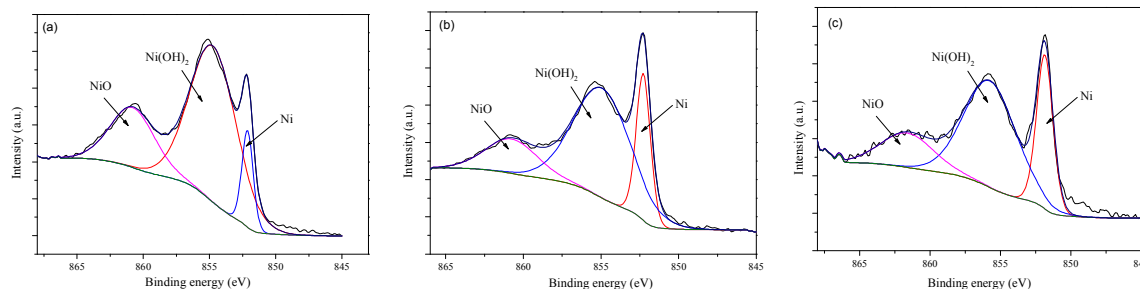


to 90.5% as the ratio of Ni increased, which is consistent with our assumption. Besides, XRD patterns of fresh NiNPore in Figure SI-9 indicated that fresh NiNPore was oxidized partly as a broad peak associated with a Ni oxide (located between 60° and 65°) can be observed<sup>33</sup>.

Next, we checked the possibility whether the dissolved nickel species in water played a catalytic role in the hydrogenation of NaHCO<sub>3</sub> to FA under the optimal conditions. After 0.5 h, we stopped the reaction and filtered to remove the NiNPore catalyst, and then continued the reaction without NiNPore for 0.5 h, the result showed that FA yield almost kept unchanged. Finally, NiNPore was put back to solution and hydrogenation of NaHCO<sub>3</sub> reacted completely to give the FA in 84.8% yield after 1 h. As an evidence, NiNPore was an efficient catalyst for the hydrogenation of NaHCO<sub>3</sub>, and no nickel species was found in water by inductively coupled plasma (ICP).

### 3.4 Catalytic hydrogenation of various carbonates

Further expanding the scope of the feedstock was carried out with various bicarbonates and carbonates as CO<sub>2</sub> sources, and the results were summarized in Table 3. As the results showed, KHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> were also good CO<sub>2</sub> sources and afforded 92.1%, 76.6% and 71.2% yields, respectively (entries 2, 5 and 6). It is worth noting that bicarbonates can give much better yields than corresponding carbonates, and KHCO<sub>3</sub> afforded higher FA yield of 92.1% than NaHCO<sub>3</sub> (entries 1 and 2). In aqueous solutions, hydrogenation of carbonates is difficult than that of bicarbonates because the protonation of carbonate ions was considered to be inferior<sup>37,38</sup>, thus bicarbonates can give much better yields compared to the carbonates. Cations of bicarbonates can affect the equilibrium between HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. The concentration of HCO<sub>3</sub><sup>-</sup> in KHCO<sub>3</sub> solution is higher than that in NaHCO<sub>3</sub> solution: NaHCO<sub>3</sub> (0.61M) < KHCO<sub>3</sub> (0.89M)<sup>37,38</sup>, which can explain the higher FA yield of KHCO<sub>3</sub>. Bicarbonate with an ammonium cation (NH<sub>4</sub><sup>+</sup>) is not effective and only gave 7.2% yield (entry 3). That's because HCOONH<sub>4</sub> is more easily to decompose into NH<sub>3</sub>, CO<sub>2</sub> and H<sub>2</sub><sup>39</sup> compared to formed HCOONa. The results were shown in Table SI-5. However, the hydrogenation of



**Figure 3.** X-ray photoelectron spectra (XPS) of fresh, 1st cycle and 5th cycle catalyst. (a) fresh catalyst, (b) 1st cycle catalyst, (c) 5th cycle catalyst

## Journal Name

## ARTICLE

**Table 3.** Hydrogenation of various feedstocks as CO<sub>2</sub> source.<sup>a</sup>

Entry	Feedstock	Yield (%)		
		FA	MA	AA
1	NaHCO <sub>3</sub>	86.6	0.4	0.3
2	KHCO <sub>3</sub>	92.1	trace	0.3
3	NH <sub>4</sub> HCO <sub>3</sub>	7.2	0	0
4	(NH <sub>4</sub> ) <sub>2</sub> HCO <sub>3</sub>	6.5	0	0
5	K <sub>2</sub> CO <sub>3</sub>	76.6	trace	0
6	Na <sub>2</sub> CO <sub>3</sub>	71.2	trace	0
7	CaCO <sub>3</sub>	0	trace	0
8 <sup>b</sup>	NaH <sup>13</sup> CO <sub>3</sub> + Na <sub>2</sub> CO <sub>3</sub>	84.1 (1.2 : 1)	trace	0.2

<sup>a</sup> Reaction conditions: 1 mmol Feedstock, 6 MPa H<sub>2</sub>, 22 mol% NiNPore, H<sub>2</sub>O 10 mL, 200 °C, 2 h. <sup>b</sup> 0.5 mM NaH<sup>13</sup>CO<sub>3</sub> and 0.5 mM Na<sub>2</sub>CO<sub>3</sub> were used.

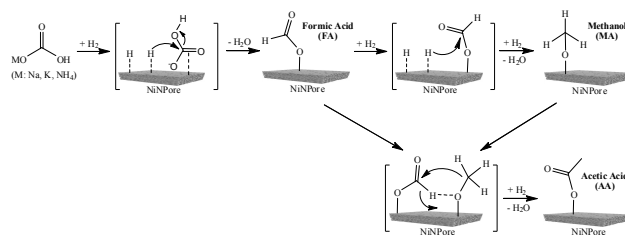
calcium carbonate as CO<sub>2</sub> source didn't take place under optimal conditions due to poor solubility of calcium carbonate in water (entry 7). In addition, the reactivity was investigated simultaneously in hydrogenation of labelled NaH<sup>13</sup>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> under the optimal conditions, and we found that the reactivity of NaH<sup>13</sup>CO<sub>3</sub> was better than that of Na<sub>2</sub>CO<sub>3</sub> with the ratio of 1.2 to 1 (entry 8). The observation indicated it is consistent well with the results in entries 1 and 5.

#### 4. Mechanistic Studies

Based on the present findings and previous literatures<sup>40,41</sup>, a plausible mechanism for the hydrogenation of bicarbonates to FA over NiNPore in water is proposed in Scheme 2. Firstly, hydrogen is absorbed on the surface of NiNPore catalyst though the formation of hydrogen bonds between NiNPore and hydrogen. Additionally, bicarbonate is adsorbed on the surface of NiNPore by the combination of NiNPore with carboxylic C and O atoms. When the hydrogen reacts with bicarbonate molecule, formate is obtained along with the formation of water. Next, Methanol is produced by the further hydrogenation of formed formate. In addition, pathway for acetic acid production is as follows: formed formic acid and methanol are adsorbed on the surface of NiNPore, and then reacts to afford acetic acid.

#### Conclusions

In summary, we developed an efficient and green process for the hydrogenation of CO<sub>2</sub> to FA over NiNPore catalyst in water. With optimized conditions in hand, NiNPore exhibited high catalytic activity and gave the yield of 86.6% in the presence of 22 mol% NiNPore with 6 MPa hydrogen in



**Scheme 2.** Plausible pathway for the hydrogenation of HCO<sub>3</sub><sup>-</sup> into FA over NiNPore.

aqueous phase at 200 °C for 2 h. Extending the scope of the feedstock showed that the hydrogenation of a wide range of carbonates can also be catalyzed to formic acid in excellent yields over NiNPore without any additives. Recycling tests of NiNPore catalyst indicated that no catalytic activity and capability lost obviously after recycling five times. The present study proposed a promising and green method of FA formation by the hydrogenation of carbonates or CO<sub>2</sub> in water. Further research is underway and to develop efficient methods for the conversion of CO<sub>2</sub> to value-added chemicals.

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#### Notes and references

- M. Aresta, in *Carbon Dioxide as Chemical Feedstock*, ed. M. Aresta, Wiley-VCH, Weinheim, Germany, 2010, ch. 1, pp. 1-13.
- J. Meléndez, M. North and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, **2007**, 3323-3326.
- H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults and W. Tumas, *Chem. Rev.*, 2001, **101**, 953-996.
- S. Bontemps and S. Sabo-Etienne, *Angew. Chem. Int. Ed.*, 2013, **52**, 10253-10255.

## ARTICLE

## Journal Name

5. W. Reutemann and H. Kieczka, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2011, vol. 16, pp. 13-33.
6. N. Akiya and P. E. Savage, *AIChE J.*, 1998, **44**, 405-415.
7. J. Yu and P. E. Savage, *Ind. Eng. Chem. Res.*, 1998, **37**, 2-10.
8. C. Rice, S. Ha, R. I. Masel, P. Waszczuk, A. Wieckowski and T. Barnard, *J. Power Sources*, 2002, **111**, 83-89.
9. S. Uhm, S. T. Chung and J. Lee, *J. Power Sources*, 2008, **178**, 34-43.
10. T. C. Johnson, D. J. Morris and M. Wills, *Chem. Soc. Rev.*, 2010, **39**, 81-88.
11. C. Federsel, C. Ziebart, R. Jackstell, W. Baumann and M. Beller, *Chemistry*, 2012, **18**, 72-75.
12. P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1995, **95**, 259-272.
13. T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365-2387.
14. R. Tanaka, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2009, **131**, 14168-14169.
15. G. A. Filonenko, R. van Putten, E. N. Schulpen, E. J. M. Hensen and E. A. Pidko, *ChemCatChem*, 2014, **6**, 1526-1530.
16. C. A. Huff and M. S. Sanford, *ACS Catal.*, 2013, **3**, 2412-2416.
17. P. G. Jessop, T. Ikariya and R. Noyori, *Nature*, 1994, **368**, 231-233.
18. J. C. Tsai and K. M. Nicholas, *J. Am. Chem. Soc.*, 1992, **114**, 5117-5124.
19. Y. Inoue, H. Izumida, Y. Sasaki and H. Hashimoto, *Chemistry Letters*, 1976, DOI: 10.1246/cl.1976.863, 863-864.
20. C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy and M. Beller, *Angew. Chem. Int. Ed.*, 2010, **49**, 9777-9780.
21. C. Ziebart, C. Federsel, P. Anbarasan, R. Jackstell, W. Baumann, A. Spannenberg and M. Beller, *J. Am. Chem. Soc.*, 2012, **134**, 20701-20704.
22. Z. Xu, N. D. McNamara, G. T. Neumann, W. F. Schneider and J. C. Hicks, *ChemCatChem*, 2013, **5**, 1769-1771.
23. Z. Zhang, Y. Xie, W. Li, S. Hu, J. Song, T. Jiang and B. Han, *Angew. Chem. Int. Ed.*, 2008, **47**, 1127-1129.
24. S. Wesselbaum, U. Hintermair and W. Leitner, *Angew. Chem. Int. Ed.*, 2012, **51**, 8585-8588.
25. N. Eghbali and C.-J. Li, *Green Chem.*, 2007, **9**, 213-215.
26. G. A. Olah, *Angew. Chem. Int. Ed.*, 2005, **117**, 2692-2696.
27. D. H. Gibson, *Chem. Rev.*, 1996, **96**, 2063-2096.
28. T. Aida and S. Inoue, *Acc. Chem. Res.*, 1996, **29**, 39-48.
29. T. Ohishi, M. Nishiura and Z. Hou, *Angew. Chem. Int. Ed.*, 2008, **120**, 5876-5879.
30. P. G. Jessop, in *Handbook of Homogeneous Hydrogenation*, ed. J. G. De Vries, Elsevier, C. J., Wiley-VCH, Weinheim, Germany, 2007, ch. 17, pp. 489-511.
31. T. Schaub and R. A. Paciello, *Angew. Chem. Int. Ed.*, 2011, **50**, 7278-7282.
32. Y. Ito, Y. Tanabe, H. J. Qiu, K. Sugawara, S. Heguri, N. H. Tu, K. K. Huynh, T. Fujita, T. Takahashi, K. Tanigaki and M. Chen, *Angew. Chem. Int. Ed.*, 2014, **53**, 4822-4826.
33. H. J. Qiu, J. L. Kang, P. Liu, A. Hirata, T. Fujita and M. W. Chen, *J. Power Sources*, 2014, **247**, 896-905.
34. Z.-B. Huo, J.-K. Liu, G.-D. Yao, X. Zeng, J. Luo and F.-M. Jin, *Appl. Catal. A: Gen.*, 2015, **490**, 36-41.
35. M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2011, **257**, 2717-2730.
36. A. P. Grosvenor, M. C. Biesinger, R. S. C. Smart and N. S. McIntyre, *Surf. Sci.*, 2006, **600**, 1771-1779.
37. J. Su, M. Lu and H. Lin, *Green Chem.*, 2015, **17**, 2769-2773.
38. J. Su, L. Yang, M. Lu and H. Lin, *ChemSusChem*, 2015, **8**, 813-816.
39. Z. Shen, Y. Zhang and F. Jin, *Green Chem.*, 2011, **13**, 820.
40. C. He, G. Tian, Z. Liu and S. Feng, *Org. Lett.*, 2010, **12**, 649-651.
41. J. Duo, F. Jin, Y. Wang, H. Zhong, L. Lyu, G. Yao and Z. Huo, *Chem. Commun.*, 2016, **52**, 3316-3319.

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# Nanoporous Nickel catalyst for selective hydrogenation of carbonates into formic acid in water

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## Graphic abstract

