



# CO<sub>2</sub> hydrogenation to formate over nano-scale zero-valent nickel catalyst under atmospheric pressure

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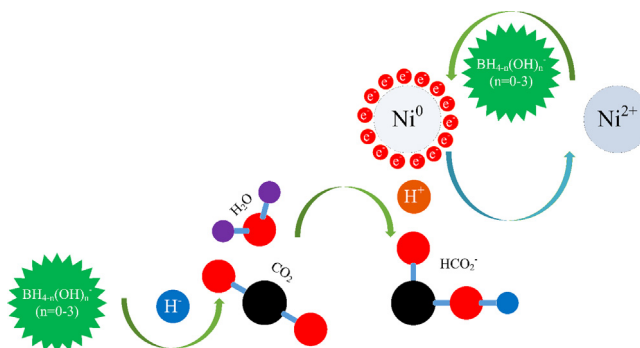
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## HIGHLIGHTS

- Nano-scale zero-valent nickel proved effective for catalyzing CO<sub>2</sub> hydrogenation.
- Cost-effective CO<sub>2</sub> resource utilization was achieved under atmospheric pressure.
- The reaction mechanism was proposed based on the characterizations and references.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

To reduce the energy consumption in the current CO<sub>2</sub> hydrogenation with gaseous H<sub>2</sub>, a novel method of CO<sub>2</sub> hydrogenation with potassium borohydride (KBH<sub>4</sub>) at moderate temperature and ambient pressure under the catalysis of nano-scale zero-valent nickel (nZVN) was developed. Under the optimal experimental conditions where the nZVN dosage was 0.2 g, KBH<sub>4</sub> concentration was 0.28 mol·L<sup>-1</sup>, solution pH was 9.5, reaction temperature was 65 °C and residence time was 24 s, the average highest CO<sub>2</sub> absorption efficiency of 45.88% with formate selectivity of 40.81% was achieved based on the ion chromatograph (IC) analyses of the reaction products. Especially, the physicochemical properties of the fresh and spent catalysts, such as morphological structure, physical structure properties, phase and crystallization and chemical compositions, were characterized systematically by using high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), N<sub>2</sub> adsorption-desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS). In combination with the relevant references, the heterogenetic catalytic transfer hydrogenation reaction mechanism of CO<sub>2</sub> with KBH<sub>4</sub> over nZVN was proposed.

## 1. Introduction

At present, over 85% of global energy demand is offered by thermal power plants fed by fossil fuels, and during the process, 40% of total CO<sub>2</sub> emissions worldwide are emitted into atmosphere [1]. The latest research report of International Energy Outlook 2016 has shown that

the global energy-induced CO<sub>2</sub> emissions will attain about 35.6 billion metric tons in 2020, which will further add up to 43.2 billion metric tons in 2040 [2]. Meanwhile, the data from International Energy Agency have revealed a rapid increase of the proportion of China's CO<sub>2</sub> emissions in the worldwide entire amounts, which is 14.10% in 2000, 26.00% in 2012 and 29.00% in 2013, respectively [3]. In addition, it is

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### Nomenclature

$v_{\text{sfg}}$	Simulated flue gas flow ( $\text{L}\cdot\text{min}^{-1}$ );
$m_{\text{c}}$	catalyst dosage (g);
$c_{\text{pb}}$	$\text{KBH}_4$ concentration ( $\text{mol}\cdot\text{L}^{-1}$ );
$T$	reaction temperature ( $^{\circ}\text{C}$ );
$c_{\text{CO}_2}$	$\text{CO}_2$ concentration (%);
$c_{\text{SO}_2}$	$\text{SO}_2$ concentration ( $\text{mg}\cdot\text{m}^{-3}$ );
$c_{\text{NO}}$	$\text{NO}$ concentration ( $\text{mg}\cdot\text{m}^{-3}$ );
$c_{\text{O}_2}$	$\text{O}_2$ concentration (%);

estimated that the ratio will reach up to approximately 33% by 2035, which can lead to devastating climate crises and threaten our human life [2,3]. Therefore, China is confronted with enormous pressure to reduce domestic  $\text{CO}_2$  emissions.

In fact,  $\text{CO}_2$  is gradually becoming a promising source of carbon, which has the advantages of being abundantly available, cost-free and nontoxic [4]. Thus, considerable work has been emphasized on the resource and utilization of  $\text{CO}_2$ , with a goal to convert  $\text{CO}_2$  into raw industrial materials. For example, N, N-dimethylformamide (DMF) was synthesized from  $\text{CO}_2$  through homogeneous catalytic hydrogenation, in which the yield of 31% DMF was obtained at 40 bar and 413 K [5];  $\text{CO}_2$  hydrogenation into higher hydrocarbons was also achieved under the pressure of 15 bar and 623 K [6];  $\text{CO}_2$  could be converted into methane [7], methanol [8,9] and formic acid [10] effectively as well. However, due to the thermodynamic stability of  $\text{CO}_2$  itself, the above experiments were performed either at higher temperature or higher pressure. In view of industrialized application, the complex operation conditions, high equipment investment and huge energy consumption will become inevitable obstacles. Moreover, as a main reactant in the hydrogenation process, hydrogen is neither stable nor secure especially during continuous operations at high temperature and pressure.

In the previous work [11–14], we have come up with some solutions to the above mentioned problems, but some deficiencies still deserve further improvement. Firstly, in order to restrain the self-hydrolysis of sodium borohydride ( $\text{NaBH}_4$ ) in water, a high dosage of anhydrous ethanol was used as the aprotic solvent because of the smaller autoprotolysis constant [15], which increased the investment costs unavoidably. Besides, for purpose of reducing the dosage of  $\text{NaBH}_4$  and facilitating the conversion of  $\text{CO}_2$ , Ni-P/ $\text{Al}_2\text{O}_3$  was prepared by aging, filtration, drying, calcination and reduction, which will be more convenient if simplified appropriately. Furthermore, the recycling property of the catalyst was not demonstrated adequately. To overcome the

above shortcomings, some meaningful improvements were attempted to be accomplished in this work.

Potassium borohydride ( $\text{KBH}_4$ ), as an excellent hydrogen storage material [16], exhibits much slower self-hydrolysis in protic solvents compared with  $\text{NaBH}_4$  [17]. Moreover, the price of  $\text{KBH}_4$  is lower than that of  $\text{NaBH}_4$ . Consequently, no extra aprotic solvent is required and the investment cost can be decreased obviously. Based on the above advantages,  $\text{KBH}_4$  was selected as the hydrogen donor in this work. It has been proved that nickel-based catalysts are effective for  $\text{CO}_2$  hydrogenation at low temperature [13,18]. In order to simplify the preparation procedure and promote the catalytic activity, a liquid phase reducing method [18] was applied to synthesize nano-scale zero-valent nickel (nZVN) as a catalyst, which is of high purity and easy to be recycled.

There were few relevant reports about  $\text{CO}_2$  hydrogenation with  $\text{KBH}_4$  catalyzed by nZVN under atmospheric pressure and moderate temperature, and therefore, the heterogeneous catalytic transfer hydrogenation reaction was investigated comprehensively in our research. The effects of various factors on  $\text{CO}_2$  absorption efficiency were analyzed, such as the nZVN dosage,  $\text{KBH}_4$  concentration, solution pH, reaction temperature and residence time. Besides, the applicability of the reaction system to different initial concentrations of  $\text{CO}_2$  and other coexistence gases including sulfur dioxide ( $\text{SO}_2$ ), nitric oxide ( $\text{NO}$ ) and oxygen ( $\text{O}_2$ ) was also assessed. To figure out the catalytic mechanism, the physiochemical properties of nZVN were characterized by high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM),  $\text{N}_2$  adsorption-desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS). And the liquid phase reaction products were detected with ion chromatography (IC). Finally, the mechanism of the heterogenetic catalytic transfer hydrogenation reaction was proposed based on the characterization results and relevant literatures.

## 2. Experimental

### 2.1. Materials

All the experimental gases including  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NO}$  and  $\text{O}_2$  were supplied from the compressed gas steel cylinders (North Special Gas Company, Baoding). The chemical reagents (Kermel Company, Tianjin) purchased were of analytical grade and used directly without further purification. The absorption solution was prepared with high purity water with the conductivity higher than  $18.25 \text{ M}\Omega/\text{cm}$ , produced by the laboratory water purification system (Jiaxin Environmental Protection Special Equipment Manufacturing Company, Baoding). The

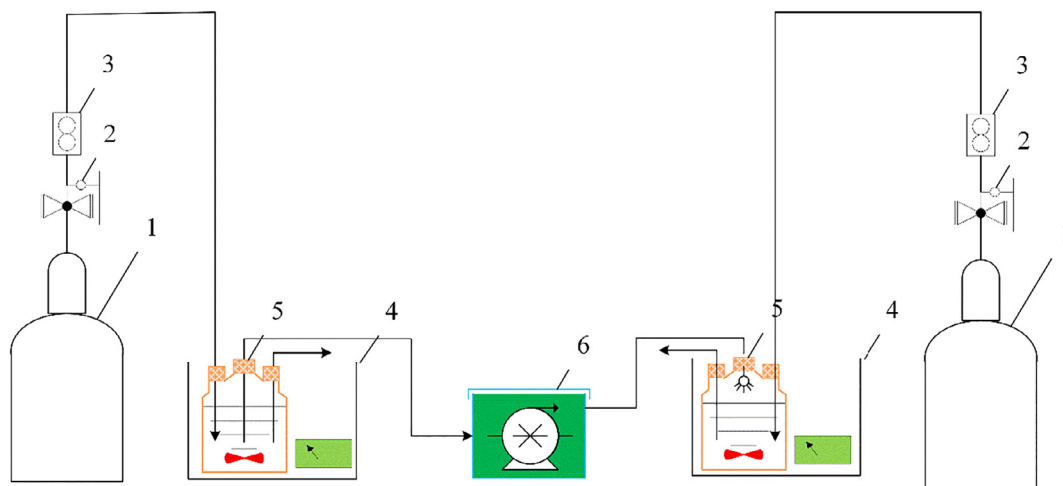


Fig. 1. Catalyst preparation experimental apparatus. 1:  $\text{N}_2$  gas cylinder; 2: pressure relief valve; 3: flow meter; 4: magnetic stirrer; 5: three-necked flask; 6: peristaltic pump.

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