



# Properties of carbon dioxide absorption and reduction by sodium borohydride under atmospheric pressure



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## HIGHLIGHTS

- An innovative method for CO<sub>2</sub> conversion by sodium borohydride was developed.
- 41.5% of CO<sub>2</sub> was reduced into formate under atmospheric pressure.
- The mechanism of CO<sub>2</sub> reaction with sodium borohydride was proposed.
- Thermodynamics and kinetics of the reaction CO<sub>2</sub> between were investigated.

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## ABSTRACT

An innovative method has been developed to reduce carbon dioxide into formate under atmospheric pressure and ambient temperature, in which, sodium borohydride solution was used as a reducing agent. The effects of various factors on carbon dioxide reduction were investigated experimentally, from which, the optimal experimental conditions were obtained with 80% of ethanol content, 0.44 mol L<sup>-1</sup> of sodium borohydride concentration, 318 K of reaction temperature and 9.0 of solution pH. And the average absorption efficiency of carbon dioxide was achieved at about 54.1%. According to the analysis results of products, the comparison of electrode potentials and the relevant references, formate was determined as the main reduction product; [BH<sub>i</sub>(OH)<sub>4-i</sub>]<sup>-1</sup> (i = 4, 3, 2, 1) and [BH<sub>j</sub>(HCO<sub>2</sub>)(OH)<sub>3-j</sub>]<sup>-1</sup> (j = 3, 2, 1, 0) were considered as the vital active intermediates for carbon dioxide reduction. The thermodynamic parameters such as enthalpy, Gibbs free energy and equilibrium constant were calculated at about -7.84 × 10<sup>2</sup> kJ mol<sup>-1</sup>, -5.78 × 10<sup>2</sup> kJ mol<sup>-1</sup> and 95.0, respectively, indicating that this reduction was feasible in thermodynamics. Meanwhile, the kinetics of carbon dioxide reduction was investigated, from which, the reaction order of 1.03 and the apparent activation energy of 11.1 kJ mol<sup>-1</sup> were obtained, respectively.

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## 1. Introduction

Among the major greenhouse gases (GHGs), carbon dioxide (CO<sub>2</sub>) has the most important impact on climatic changes because of its greatest emissions, and power plants may account for at least one quarter of its total emissions every year [1]. By the middle of this century, the atmospheric concentration of CO<sub>2</sub> will reach up to 550 ppm [2], resulting in more and more serious greenhouse effects [3].

With the increasing concern on energy saving and emission reduction in thermal power industry, developing more effective technologies of CO<sub>2</sub> capture, storage and utilization at low cost has become an urgent issue. Under atmospheric pressure, the rapid

absorption of CO<sub>2</sub> by ammonia or alkanolamine solutions has been widely studied and partially applied to industry engineering [4–6]. However, this process is energy-intensive for the regeneration of solvent and is also plagued by corrosion problems. Currently, more attention has been focused on CO<sub>2</sub> absorption by ionic liquids (ILs) [7]. Nevertheless, the complicated design and synthesis for highly effective ILs and poor economics may be major obstacles to industrial applications and future developments [8].

As one of methods for CO<sub>2</sub> utilizations, the hydrogenation of CO<sub>2</sub> into formate (HCOO<sup>-</sup>) by CO<sub>2</sub>-expanded solvent was carried out under 4–20 MPa [9]. Through homogeneously catalyzed hydrogenation, Himeda developed a process for CO<sub>2</sub> reduction into HCOO<sup>-</sup>, and pressures of CO<sub>2</sub> and hydrogen gas (H<sub>2</sub>) were kept in the range of 1–6 MPa [10]. Under 1.01 MPa, Pérez-Alonso tested the performance of CO<sub>2</sub> reaction with H<sub>2</sub> [11]. Apart from H<sub>2</sub>, other hydrogen donors such as isopropyl alcohol, dimethylamine-borane,

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and ammonia-borane were also applied to CO<sub>2</sub> hydrogenation under dozens of atmospheric pressure [12–17]. Apparently, high pressure may bring two vital issues in consideration of industrializations. One is that the investment cost will be raised due to the need of large amounts of pressure-resistant metal materials. Secondly, the energy consumption of operating processes will be significantly increased. Thus the development of technologies with high efficiency at mild conditions is greatly meaningful to CO<sub>2</sub> utilization. For years, as a hydrogen donor, sodium borohydride (NaBH<sub>4</sub>) has been utilized in chemical synthesis [18,19]. The boron-doped porous carbon was produced from CO<sub>2</sub> reaction with NaBH<sub>4</sub> under ambient pressure and 500 °C [20,21]. Nevertheless, the absorption reaction between CO<sub>2</sub> and NaBH<sub>4</sub> at low temperature and atmospheric pressure has not been reported yet. In this study, the effects of ethanol content, NaBH<sub>4</sub> concentration, reaction temperature, solution pH and coexisting gases such as sulfur dioxide (SO<sub>2</sub>), nitric oxide (NO) and oxygen (O<sub>2</sub>) in flue gas on CO<sub>2</sub> absorption were investigated to obtain the optimal experimental conditions. The results of product analyses and the comparison of electrode potentials were used to deduce the mechanism of HCOO<sup>−</sup> production from CO<sub>2</sub> absorption. The reaction characteristics were examined on the basis of thermodynamic and kinetic theories.

Although cost is an issue for using NaBH<sub>4</sub> to CO<sub>2</sub> absorption, this process has the following advantages: (1) both the energy consumption in operation and the investment on devices are decreased, because of the operating conditions of atmospheric pressure and moderate temperature; (2) the building of hydrogen storage facilities is avoided and the security in operation is improved, compared with the usage of H<sub>2</sub> as a reducing agent for CO<sub>2</sub> hydrogenation.

## 2. Experimental

### 2.1. Materials

All gases in experiments were supplied by compressed gas steel cylinders (North Special Gas Co., Ltd., China), with the purity of >99.8%. All chemicals with analytical reagent (AR) were used as received without further purification (Tianjin Chemical Reagents Company). The high purity water that was applied to prepare the absorption solutions was produced by the lab water purification system (Changfeng Co., Ltd., Beijing), with the specific resistance of >18.25 MΩ/cm.

The absorption solution of NaBH<sub>4</sub> was prepared as follows: (I) putting ethanol and water with an appropriate ratio into a beaker to form a mixture solution; (II) adjusting the solution pH from 8 to 13 by sodium hydroxide (1 mol L<sup>−1</sup>) to inhibit the self-hydrolysis of NaBH<sub>4</sub>; (III) adding certain amounts of NaBH<sub>4</sub> and making it dissolve completely by magnetic stirring at ambient temperature before applying.

### 2.2. Experimental procedure

The key part of experimental system is a bubble reactor (self-made) with 250 mL of effective volume and 15.5 cm of height, and a gas blanket of micron porous core fabric is located at 1.5 cm far from the bottom of reactor to evenly distribute gas flow, as shown in Fig. 1.

During the experiments, N<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, SO<sub>2</sub> and NO were metered through mass flow controllers (LZB, Tianjin Flow Meter Co., Ltd., China) and mixed in a buffer bottle, in which CO<sub>2</sub>, O<sub>2</sub>, SO<sub>2</sub> and NO were diluted by N<sub>2</sub> to desired concentrations, and then the simulated flue gas with 1 atm was formed. The total gas flow was kept around 400–750 mL min<sup>−1</sup>. The gas temperature was controlled in

the range of 288–338 K by an electrical heater device in accordance with the temperature of actual flue gas after desulphurization processes. The absorption reaction occurred when simulated flue gas entered into the bubbling reactor containing NaBH<sub>4</sub> solution. The reaction temperature was adjusted from 288 K to 338 K by an electric-heated thermostatic water bath. The solution pH was regulated by mixed acid and alkali (phosphoric acid, acetic acid, boric acid and sodium hydroxide) buffer, and measured by a pH meter (PHSJ-5, Shanghai Leici Instrument Company, China). The stirrer speed was controlled in the range of 20–30 rpm. After passing through the tail gas treatment part, the spent simulated flue gas was discharged into atmosphere.

In order to improve the validity of experimental results, the effects of influencing factors such as ethanol content, NaBH<sub>4</sub> concentration, reaction temperature and solution pH on CO<sub>2</sub> absorption were investigated consecutively, in which, the experiments were implemented by increasing the numerical values of each influencing factor, and then by decreasing these values. The experimental data were obtained by averaging the two measurements.

### 2.3. Analysis methods

An infrared gas analyzer (Xibi GXH510, China) was used to determine the inlet and outlet concentrations of CO<sub>2</sub>, from which, the absorption efficiency can be calculated according to Eq. (1).

$$\eta_{ce} = (1 - \varphi_0/\varphi_i) \times 100\% \quad (1)$$

where  $\eta_{ce}$  represents the absorption efficiency of CO<sub>2</sub>, %;  $\varphi_i$  and  $\varphi_0$  are the inlet and outlet CO<sub>2</sub> concentrations, respectively, %.

An ion chromatograph (IC, Metrohm 792, Switzerland) and a Fourier Transform Infrared Spectroscopy (FT-IR, NICOLET 380, USA) were applied to characterize reaction products. A multifunctional flue gas analyzer (MRU95/3 CD, Germany) was used to detect the concentrations of SO<sub>2</sub>, NO and O<sub>2</sub>.

## 3. Results and discussion

### 3.1. Effect of influencing factors on CO<sub>2</sub> absorption

In protic solvents, for example water, NaBH<sub>4</sub> can undergo the self-hydrolysis process [22]. Nonetheless, the process will be weakened in organic solvents because of their smaller autoprotolysis constants [23]. Generally, the solubilities of NaBH<sub>4</sub> in organic solvents such as ethanol, acetonitrile, pyridine and tetrahydrofuran are 0.04 g g<sup>−1</sup> at 298 K, 0.01 g g<sup>−1</sup> at 301 K, 0.03 g g<sup>−1</sup> at 298 K and 0.001 g g<sup>−1</sup> at 293 K, respectively. By comparison, ethanol was selected as the suitable solvent in the views of the solubility and economics for the preparation of NaBH<sub>4</sub> solution [22,23].

The effect of ethanol content ( $r_0$ , %) on CO<sub>2</sub> absorption was studied, as shown in Fig. 2a. The absorption efficiency is about 6% when water is used alone as the solvent, possibly owing to the self-hydrolysis of NaBH<sub>4</sub> and the slight dissolution of CO<sub>2</sub> in weak alkalinity [23]. As ethanol content ranges from 0% to 80%, the absorption efficiency is enhanced rapidly and the highest absorption efficiency appears at 80%, which can be interpreted as that the inhibition of self-hydrolysis of NaBH<sub>4</sub> is increased with an increase of ethanol content, which will make more NaBH<sub>4</sub> participate in CO<sub>2</sub> absorption. However, the absorption efficiency decreases slightly when ethanol content exceeds 80%, mainly due to the decreasing solubilities of NaBH<sub>4</sub> and CO<sub>2</sub> in the high concentrations of ethanol [24]. Hence, the optimal ethanol content was set at 80%.

In order to verify the absorption characteristics of NaBH<sub>4</sub> in the mixture of ethanol and water ( $r_0 = 80\%$ ), the experiments were carried out by using NaBH<sub>4</sub> solution as the absorbent and then, also

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