



# Pd/C-catalyzed reduction of NaHCO<sub>3</sub> into CH<sub>3</sub>COOH with water as a hydrogen source



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## ABSTRACT

In this paper, a simple method of NaHCO<sub>3</sub> reduction to CH<sub>3</sub>COOH in water with Al powder as a reductant on a commercially available Pd/C catalyst is described that producing CH<sub>3</sub>COOH with a good yield of 8% from NaHCO<sub>3</sub> on a carbon basis at 300 °C under hydrothermal conditions. A high adsorption enthalpy of C<sub>1</sub> intermediates on the Pd catalyst may act as an important role in the reduction of NaHCO<sub>3</sub> into CH<sub>3</sub>COOH on Pd/C catalyst. This research provides a simple way to convert the CO<sub>2</sub> into a C<sub>2</sub> compound.

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## 1. Introduction

Global warming caused due to the increase in atmospheric CO<sub>2</sub> concentration is one of the most serious problems faced by human beings in the 21st century [1,2]. A great deal of efforts has been expended to reduce the CO<sub>2</sub> concentration in the atmosphere [3–7]. The hydrogenation of CO<sub>2</sub> into organic chemicals with gaseous hydrogen is one of the most developed methods to reduce CO<sub>2</sub> [8–11]. However, high-purity of gaseous hydrogen and/or noble metal catalysts is needed, which increase the cost. Recently, photocatalytic, photoelectrochemical and electrochemical methods for CO<sub>2</sub> reductions have been widely reported because renewable energies can be used [12–14]. However, their CO<sub>2</sub> conversion rates and efficiencies are still very low, and a highly efficient conversion still remains a great challenge.

Hydrothermal reactions have played an important role in the abiotic conversion of CO<sub>2</sub> into hydrocarbons in the Earth crust [15,16]. Previous research have demonstrated that CO<sub>2</sub> or NaHCO<sub>3</sub>

can be reduced into organic chemicals such as CH<sub>4</sub>, HCOOH and CH<sub>3</sub>OH effectively and efficiently under hydrothermal condition with earth abundant metallic materials such as Fe, Al, and Zn [17–20]. In such hydrothermal CO<sub>2</sub> reduction, the required hydrogen source comes from the *in-situ* reaction of high temperature water (HTW). Therefore, the disadvantages of hydrogen gas preparation, transportation and storage in traditional hydrogenation of CO<sub>2</sub> reactions can be avoided. Although the metal reductants are oxidized during the reaction in HTW, these metal oxides can be reduced into its zero-valent state by using solar energy, renewable energies derived electricity or biomass (for example: glycerol) [17,21,22]. Therefore, the metal reductants can be recycled with renewable energies. Although hydrothermal reactions are usually operated under high temperatures (200–350 °C), the reactions of CO<sub>2</sub> reduction are exothermic with a metal reductant [18], which means they can be potentially self-supported. Thus, the hydrothermal reduction of CO<sub>2</sub> into organic chemicals could be one promising and efficient method to help alleviating the problem of global warming and provide alternative and potentially sustainable chemical feedstock instead of the traditional fossil fuel-based feedstock.

In previous research of hydrothermal reduction of CO<sub>2</sub>, the products were mainly C<sub>1</sub> compounds such as HCOOH and CH<sub>3</sub>OH [18–20]. Although there have been reports of synthesis of long carbon-chain organics from CO<sub>2</sub> for hydrogenation and electro-

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chemical reduction [23–25], synthesis of C<sub>2</sub> compounds using hydrothermal methods has not been well studied. He et al. reported that CO<sub>2</sub> can be reduced into CH<sub>3</sub>COOH under hydrothermal conditions, however, a very long reaction time (ca. 72 h) is required [26]. Therefore, more efficient methods and higher active catalysts are needed to be developed. Unlike production of C<sub>1</sub> compound, the synthesis of C<sub>2</sub> compounds requires C–C bond formation which is usually difficult to realize in CO<sub>2</sub> reduction. The reduction of CO<sub>2</sub> into C<sub>2</sub> compounds is a key step for further synthesizing long-chain organics [24,27]. It has been reported that palladium (Pd) based catalysts have the activity to catalyze C–C bond formation in the hydrogenation of CO<sub>2</sub> [28,29]. However, the activity of Pd catalyst for CO<sub>2</sub> reduction under hydrothermal conditions is still unknown. In the present article, we report the hydrothermal reduction of CO<sub>2</sub> into CH<sub>3</sub>COOH by using commercially available Pd/C catalyst and Al (powder) reductant. In the process, water acts not only as an excellent solvent, but also as a source of hydrogen generated by reduction of metal Al. The proposed system is simple and efficient for C<sub>2</sub> compound (CH<sub>3</sub>COOH) formation from CO<sub>2</sub>. Based on the experimental results and thermodynamic data of the reaction intermediates, a reaction mechanism for HCO<sub>3</sub><sup>-</sup> reduction into CH<sub>3</sub>COOH is proposed.

## 2. Experimental

Since CO<sub>2</sub> can be effectively absorbed in NaOH solutions to form NaHCO<sub>3</sub> [30], NaHCO<sub>3</sub> was used as the source of CO<sub>2</sub> in this research to simplify the operation and to allow for quantification of CO<sub>2</sub>. Chemicals of NaHCO<sub>3</sub> (99.5%, Sinopharm Chemical Reagent Co. Ltd, China), Al powder (200-mesh, 99%, Sinopharm Chemical Reagent Co. Ltd, China) and Pd/C powder (200-mesh, 5% Pd, Sinopharm Chemical Reagent Co. Ltd, China) were used directly without any further purification. Standard reagents of HCOOH (puriss. p.a., ~98%, Fluka) and CH<sub>3</sub>COOH (99.7%, Sigma-Aldrich Co. LLC.) were used for HPLC quantitative analysis. A stainless steel (SUS316) tube with a Swagelok cap and a gas valve (Autoclave Engineering Inc.) with a reducing union at each end was used as the hydrothermal reactor. The inner volume of the reactor was 5.7 mL. The schematic drawing of the hydrothermal reactor can be found elsewhere [31]. Experimental procedures were employed and described as follows. The reaction chemicals (Pd/C: 0–0.3 g; Al: 1–6 mmol; NaHCO<sub>3</sub>: 0.5–4 mmol) and deionized water (1.4–3.1 mL) were first added to the reactor, and then the reactor was sealed. Next, the reactor was put into a salt bath (mixture of NaNO<sub>3</sub> and KNO<sub>3</sub>) which was pre-heated to target reaction temperature (260–320 °C). At the desired reaction time (0.5–3 h), the reactor was taken out from the salt bath and was put into a cold-water bath (20 °C) immediately to quench the reaction. The reaction time is defined as the duration of the reactor remaining in the salt bath. A water filling ratio, which is defined as the ratio of the volume of water added into the reactor to the total inner volume of the reactor, is used to describe the used amount of water. At the reaction temperature of 260–320 °C, the water exists in a mixture of liquid and vapor state. The pressure of the water vapor is 4.7, 8.6 and 11.3 MPa at 260, 300 and 320 °C, respectively [32].

After the reactions, gas samples were collected through the gas valve and analyzed by a Hewlett-Packard model 5890 Series II gas chromatograph equipped with a thermal conductivity detector (GC/TCD). The liquid samples were filtered (0.22 μm filter film) and analyzed by an Agilent 1200 high-performance liquid chromatography (HPLC) with a UV-detector (210 nm), one Shodex RSpak KC-G and two RSpak KC-811 columns using 2 mmol L<sup>-1</sup> HClO<sub>4</sub> as flowing solvent. An Agilent 7890 gas chromatography-mass spectrometry (GC-MS) equipped with 5985C inert mass selective detector (MSD) with triple-axis detector was also used to investigate other possi-

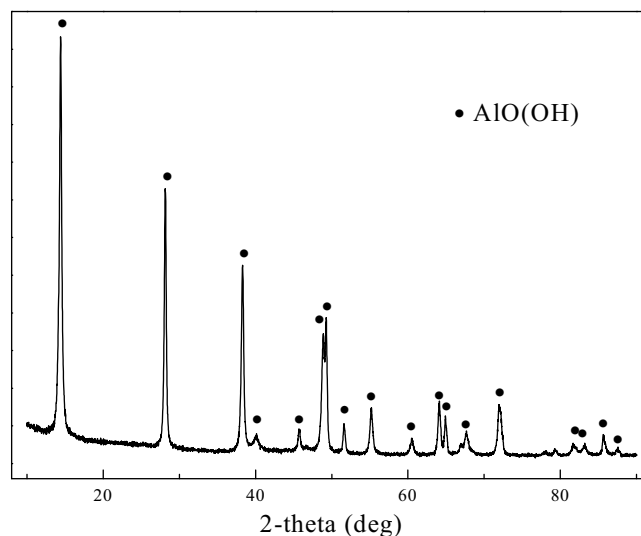


Fig. 1. XRD pattern of solid precipitate after the reaction catalyzed by Pd/C (reaction conditions: 1.0 mmol NaHCO<sub>3</sub>, 6.0 mmol Al, 0.1 g Pd/C, water filling ratio: 35%, 300 °C, 2 h).

ble chemicals in liquid phase. The solid samples were dried in an isothermal oven (50 °C) for 24 h after washing with distilled water. Then it was examined by X-ray diffractometer (XRD) using a Bruker D8 Advance X-ray Diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å, scanning rate: 0.02° s<sup>-1</sup>, 2θ ranges: 10–90°).

The Pd/C catalyst was analyzed by a high-resolution scanning transmission electron microscopy (HRSTEM) with a JEM-2100F field-emission electron microscope equipped with a high-angle annular dark field (HAADF) detector. Samples for HRSTEM analysis were ultrasonically dispersed in ethanol and then suspended on a copper grid before the analysis. Surface area of the Pd/C catalyst was also determined by nitrogen sorption experiments on an ASAP2010 instrument (Micromeritics, USA). The samples were degassed at 160 °C for 2 h under vacuum prior to the adsorption measurements. Thermal stability of Pd/C was examined on a SII Exstar 6000 (TG-DTA 6200) system between RT and 500 °C in N<sub>2</sub> at a heating rate of 5 °C/min.

The yields of organic acids were defined as:

$$\text{Yield, mol\%} = \frac{\text{Carbon in the produced organic acids, mol}}{\text{Carbon in the initial NaHCO}_3, \text{ mol}} \times 100\% \quad (1)$$

Each experiment in this study was repeated at least three times and the average of the experimental data with a deviation less than 10% was used in this report.

## 3. Results and discussion

### 3.1. Investigation of the catalytic activity of Pd/C in the CO<sub>2</sub> reduction into CH<sub>3</sub>COOH

Firstly, the effect of Pd/C catalyst on the CO<sub>2</sub> reduction was investigated by reacting NaHCO<sub>3</sub> (1.0 mmol) with Al (6.0 mmol), Pd/C (0.1 g) and H<sub>2</sub>O (2 mL) at 300 °C for 2 h. Results showed that CH<sub>3</sub>COOH and HCOOH were produced. The XRD analysis of the solid precipitate after the reaction showed that only Al(OH)<sub>3</sub> was detected in the solid precipitate (See Fig. 1), demonstrating a reductant role of Al. However, Pd was not observed in the XRD pattern, which is probably because the particle size of Pd is very small and is well distributed in the activated carbon support. To verify the catalytic activity of Pd, reactions with activated carbon support instead of Pd/C or in the absence of Pd/C were further conducted, and the results showed that no formation of CH<sub>3</sub>COOH in both cases, suggesting that the Pd/C acts as a catalyst in the reduction of

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