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Pd/C-catalyzed reduction of $NaHCO_3$ into CH_3COOH with water as a hydrogen source

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ABSTRACT

In this paper, a simple method of $NaHCO_3$ reduction to CH_3COOH in water with Al powder as a reductant on a commercially available Pd/C catalyst is described that producing CH_3COOH with a good yield of 8% from $NaHCO_3$ on a carbon basis at 300 °C under hydrothermal conditions. A high adsorption enthalpy of C_1 intermediates on the Pd catalyst may act as an important role in the reduction of $NaHCO_3$ into CH_3COOH on Pd/C catalyst. This research provides a simple way to convert the CO_2 into a C_2 compound.

1. Introduction

Global warming caused due to the increase in atmospheric CO_2 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_2 concentration in the atmosphere [3–7]. The hydrogenation of CO_2 into organic chemicals with gaseous hydrogen is one of the most developed methods to reduce CO_2 [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_2 reductions have been widely reported because renewable energies can be used [12–14]. However, their CO_2 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_2 into hydrocarbons in the Earth crust [15,16]. Previous research have demonstrated that CO_2 or $NaHCO_3$ can be reduced into organic chemicals such as CH_4, HCOOH and CH_3OH effectively and efficiently under hydrothermal condition with earth abundant metallic materials such as Fe, Al, and Zn [17–20]. In such hydrothermal CO_2 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_2 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_2 reduction are exothermic with a metal reductant [18], which means they can be potentially self-supported. Thus, the hydrothermal reduction of CO_2 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_2, the products were mainly C_1 compounds such as HCOOH and CH_3OH [18–20]. Although there have been reports of synthesis of long carbon-chain organics from CO_2 for hydrogenation and electro-

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chemical reduction [23–25], synthesis of C_2 compounds using hydrothermal methods has not been well studied. He et al. reported that CO_2 can be reduced into CH_3COOH 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_1 compound, the synthesis of C_2 compounds requires C—C bond formation which is usually difficult to realize in CO_2 reduction. The reduction of CO_2 into C_2 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_2 [28,29]. However, the activity of Pd catalyst for CO_2 reduction under hydrothermal conditions is still unknown. In the present article, we report the hydrothermal reduction of CO_2 into CH_3COOH 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_2 compound (CH_3COOH) formation from CO_2. Based on the experimental results and thermodynamic data of the reaction intermediates, a reaction mechanism for $HCO_3{}^-$ reduction into CH_3COOH is proposed.

2. Experimental

Since CO_2 can be effectively absorbed in NaOH solutions to form $NaHCO_3$ [30], $NaHCO_3$ was used as the source of CO_2 in this research to simplify the operation and to allow for quantification of CO_2. Chemicals of $NaHCO_3$ (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_3COOH (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; $NaHCO_3$: 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 $NaNO_3$ and KNO_3) which was preheated 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^{-1} $HClO_4$ 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 possible 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^{-1}, 2θ ranges: 10–90°).

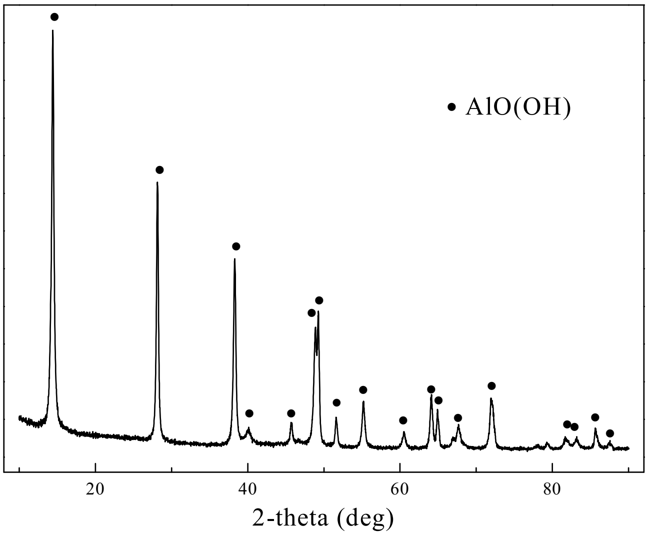


Fig. 1. XRD pattern of solid precipitate after the reaction catalyzed by Pd/C (reaction conditions: 1.0 mmol $NaHCO_3$, 6.0 mmol Al, 0.1 g Pd/C, water filling ratio: 35%, 300 °C, 2 h).

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_2 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_2 reduction into CH_3COOH

Firstly, the effect of Pd/C catalyst on the CO_2 reduction was investigated by reacting $NaHCO_3$ (1.0 mmol) with Al (6.0 mmol), Pd/C (0.1 g) and H_2O (2 mL) at 300 °C for 2 h. Results showed that CH_3COOH and HCOOH were produced. The XRD analysis of the solid precipitate after the reaction showed that only AlO(OH) 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_3COOH in both cases, suggesting that the Pd/C acts as a catalyst in the reduction of

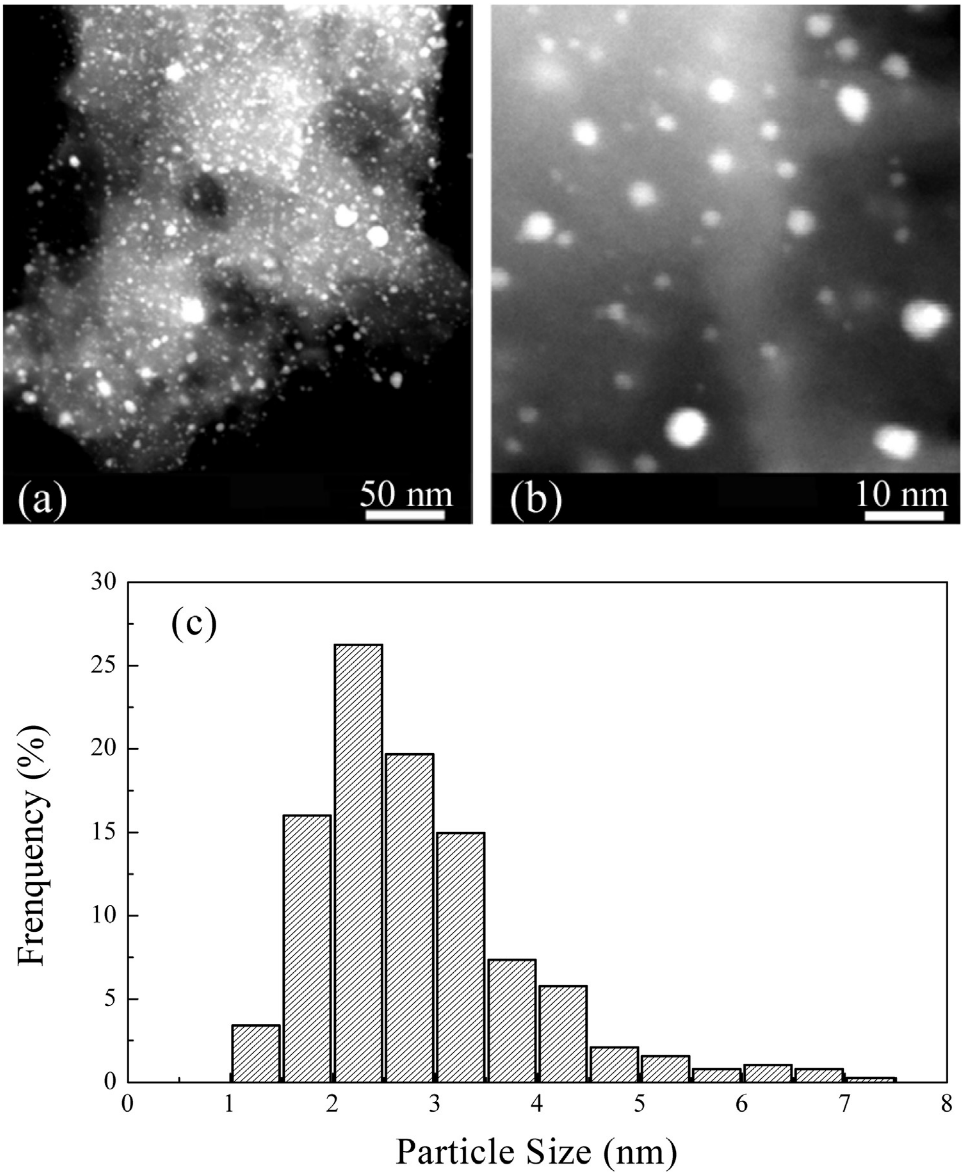


Fig. 2. High-resolution scanning transmission electron microscopy (HRSTEM) images of Pd/C catalyst ((a) and (b)) and particle size distribution of Pd (c) (average particle size: 2.82 ± 1.03 nm).

$NaHCO_3$ into CH_3COOH. These results can be evident that the Pd/C can catalyze the C—C bond formation in the CO_2 reduction under hydrothermal condition.

To check whether a pre-reduction of the Pd/C catalyst was needed or not, experiments of first reducing 0.1 g Pd/C at 320 °C with 1.5 MPa H_2 for 3 h, and then reaction at 300 °C for 2 h after further addition of 1.0 mmol $NaHCO_3$, 6.0 mmol Al and 2 mL H_2O in the same reactor was conducted. No obvious difference was observed in the liquid products obtained with H_2-reduced Pd/C or as-obtained Pd/C, suggesting that a pre-reduction of the Pd/C catalyst is not necessary in this reaction. Thermal stability of the Pd/C catalyst was then investigated with thermogravimetric analysis (TGA) in N_2 atmosphere, and the result (Fig. S1, Supporting Information) showed that the Pd/C was stable at temperatures of about 300 °C. Subsequently, the surface area of the Pd/C was determined by BET analysis, and the result showed that the surface area of Pd/C was 983 m^2/g. Fig. 2 shows the HRSTEM images and particle size distribution of Pd/C, and the average particle size of Pd was determined to be 2.82 ± 1.03 nm.

The effect of the Pd/C amount on the CH_3COOH production was investigated with 1.0 mmol $NaHCO_3$, 6.0 mmol Al and 0–0.3 g Pd/C at 300 °C for 2 h. As shown in Fig. 3a, an increase in the Pd/C amount could promote the formation of CH_3COOH, and the CH_3COOH production rate increased from 5.8 $\mu mol \cdot g^{-1}(Pd) \cdot min^{-1}$ to 9.7 $\mu mol \cdot g^{-1}(Pd) \cdot min^{-1}$ when the Pd/C amount increased from 0.05 to 0.3 g. This is probably because the increase in the amount of catalyst causes the increase in the formation of reaction intermediates that were adsorbed on the Pd/C as discussed in Section 3.3. Although the details are unclear, it is reasonable to assume that the CH_3COOH formation from the intermediates adsorbed on the Pd/C has a reaction order higher than 0. Therefore, an increase in the amount of Pd/C catalyst leads to an increase in the concentration of adsorbed reaction intermediates, which then promotes the reaction rate of CH_3COOH formation. Fig. 3b shows the yield of the liquid products after the reaction at the same condition. Only HCOOH was produced with a yield of *ca.* 60% when Pd/C was not used, suggesting that Al has the ability to reduce HCO_3^- into HCOOH, which is in accordance with our previous research [34]. However, the yield

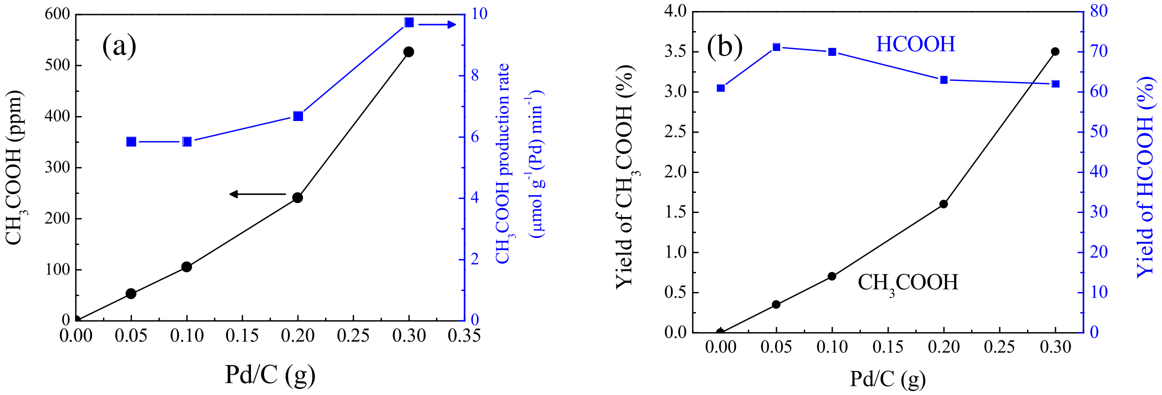


Fig. 3. Effect of the Pd/C amount on the (a) concentration of CH_3COOH and its production rate; (b) yields of CH_3COOH and HCOOH after the reduction of 1.0 mmol $NaHCO_3$ with 6.0 mmol Al and 35% water filling ratio at 300 °C for 2 h.

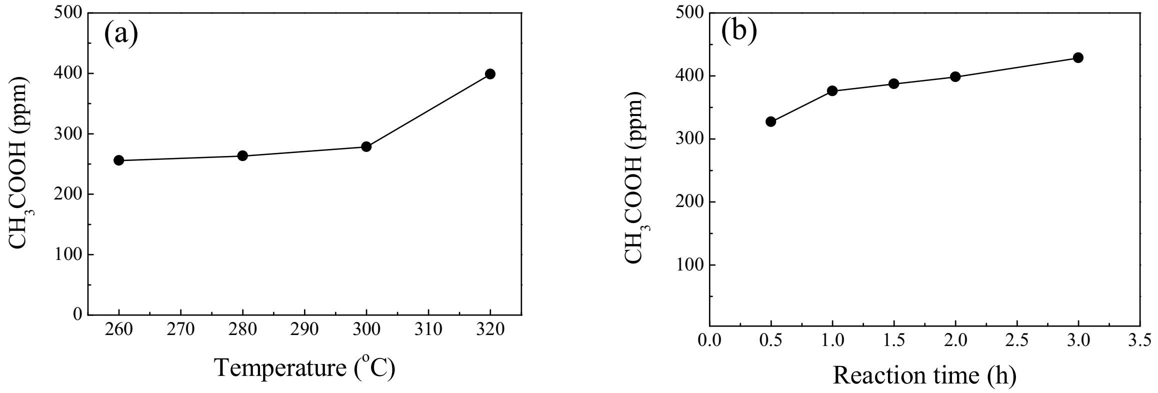


Fig. 4. Effects of (a) reaction temperature from 260 to 320 °C at a constant reaction time of 2 h and (b) reaction time from 0.5 to 3.0 h at a constant reaction temperature of 320 °C on the concentration of produced CH_3COOH after the reactions with 0.5 mmol $NaHCO_3$, 1.0 mmol Al, 0.3 g Pd/C and 35% water filling ratio.

of HCOOH was not obviously affected by gradually increasing the amount of Pd/C, indicating that Pd/C mainly catalyzes the CH_3COOH formation.

3.2. Effect of various reaction conditions on the CH_3COOH production

3.2.1. Effect of reaction temperature and time

The effect of reaction temperature and time on CH_3COOH production was investigated by varying the temperature from 260 to 320 °C and reaction time from 0.5 to 3.0 h, and the results are shown in Fig. 4. As the reaction temperature increased from 260 to 300 °C, the concentration of produced CH_3COOH slightly increased from 255 to 278 ppm (Fig. 4a). When the reaction temperature further increased to 320 °C, the CH_3COOH concentration increased to 398 ppm. The reduction of HCO_3^- into CH_3COOH is exothermic (Section 3.3), suggesting that increasing temperature should be adverse to the CH_3COOH formation. One possible explanation for the increase in CH_3COOH production with the increase in the reaction temperature could be that the reduction of HCO_3^- into CH_3COOH has high activation energy, and then increasing the temperature is advantageous to overcome the high activation energy. Considering the pressure limitation of the used reactor, experiments with temperatures over 320 °C were not conducted. As illustrated in Fig. 4b, when the temperature was maintained at 320 °C, increasing the reaction time from 0.5 to 3.0 h promoted the CH_3COOH production from 327 to 428 ppm, which suggests that a longer reaction time is effective to enhance the CH_3COOH production.

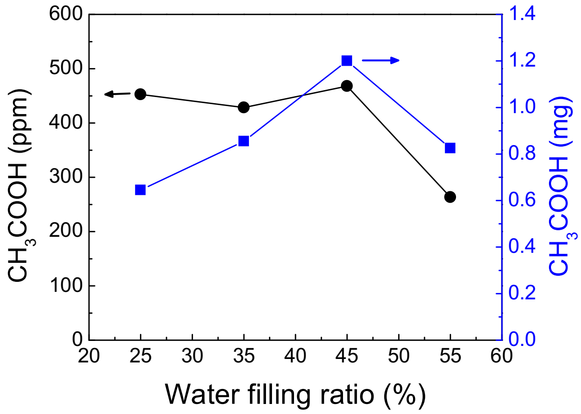
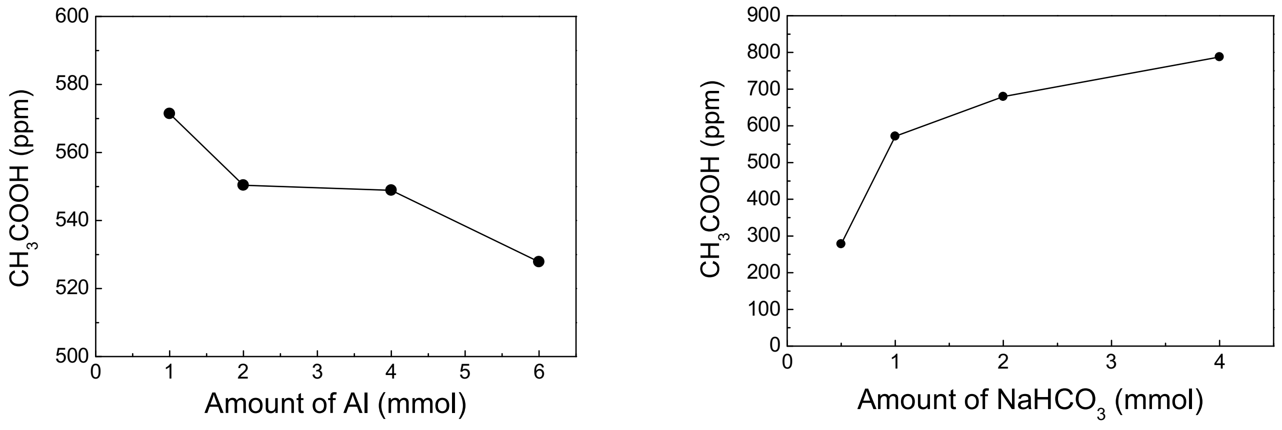


Fig. 5. Concentrations (●) and absolute amounts (■) of the CH_3COOH obtained at various water filling ratios after the reduction of 0.5 mmol $NaHCO_3$ with 1.0 mmol Al and 0.3 g Pd/C at 320 °C for 2 h.

3.2.2. Effect of water filling ratio

Since water is used not only as the reaction media, but also as the reactant to provide hydrogen source in the hydrothermal CO_2 reduction, the effect of water filling ratio on the CH_3COOH production were investigated. The concentrations of CH_3COOH obtained at various water filling ratios after the reduction of $NaHCO_3$ at 320 °C for 2 h are illustrated in Fig. 5. When the water filling ratio increased from 25% to 45%, no significant change in the concentration of CH_3COOH was observed. However, a further increase in the water filling ratio up to 55% led to a remarkable decrease in the CH_3COOH



(a) (b)

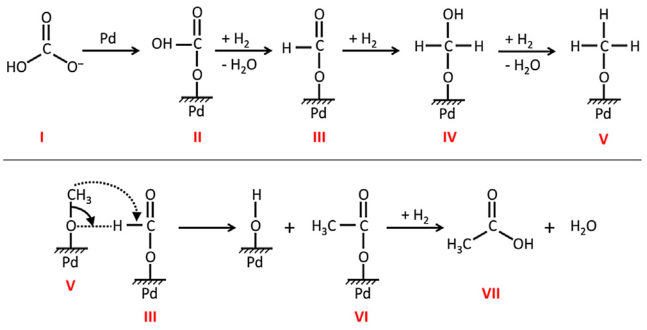
Fig. 6. Concentrations of produced CH_3COOH as functions of (a) Al amount and (b) $NaHCO_3$ amount after the reactions at 300 °C for 2 h (Pd/C: 0.3 g, water filling ratio: 35%, (a): $NaHCO_3$: 1.0 mmol; (b): Al: 1.0 mmol).

concentration. Since the initial amount of $NaHCO_3$ was unchanged in these experiments, increasing the water filling ratio should dilute the produced CH_3COOH and then affect the CH_3COOH concentration. Therefore, the real effects of the water filling ratio cannot be distinguished from the CH_3COOH concentration. Then, the absolute amounts of CH_3COOH production with different water filling ratios were investigated. As shown in Fig. 5, the absolute amount of the produced CH_3COOH first increased with the water filling ratio from 0.65 to 1.2 mg and then decreased when the water filling ratio exceeded 45%. This suggests that the water filling ratio has a positive effect on the CH_3COOH production at low water filling ratios; however, it becomes adverse to the CH_3COOH formation when the water filling ratio is higher than 45%. This is probably because a high water filling ratio will reduce the empty space in the reactor, which leads to an increase in the partial pressure of produced H_2. Then, the increased H_2 partial pressure becomes unfavorable to the H_2 gas generation from the water according to the Le Chatelier's principle. As a result, the CH_3COOH production decreased at high water filling ratios. The yield of CH_3COOH from $NaHCO_3$ was also examined, and the results showed that the highest yield of CH_3COOH was *ca.* 8%, which was obtained with the water filling ratio of 45%.

3.2.3. *Effect of the amount of reactants*

The effect of the amount of Al and $NaHCO_3$ on the CH_3COOH formation was studied by changing the amount of $NaHCO_3$ (0.5–4.0 mmol) and Al (1.0–6.0 mmol) at 300 °C for 2 h with 0.3 g Pd/C and a water filling of 35%. As shown in Fig. 6a, when the amount of $NaHCO_3$ was fixed at 1.0 mmol, increasing the amount of Al from 1.0 mmol to 6.0 mmol caused a slight decrease in the CH_3COOH concentration from 571 to 527 ppm. This is probably because the excess amount of Al promotes the conversion of CO_2 into HCOOH, which has been studied in our previous researches [34]. On the other hand, when the amount of Al was fixed at 1.0 mmol, the CH_3COOH production ascended dramatically from 278 to 788 ppm when the $NaHCO_3$ amount increased from 0.5 to 4.0 mmol as illustrated in Fig. 6b. The CH_3COOH increased clearly with the $NaHCO_3$ amount when the amount of $NaHCO_3$ was less than 1.0 mmol. However, the increase in CH_3COOH concentration became slow when the amount of $NaHCO_3$ further increased. This is probably caused by the insufficient amount of Pd/C catalyst.

Based on the results above, the highest CH_3COOH production in this research was 788 ppm, which was obtained at 300 °C for 2 h with 4.0 mmol $NaHCO_3$, 1.0 mmol Al, 0.3 g Pd/C, and 35% water filling. Combined with the reaction time and amount of Pd (5% of 0.3 g Pd/C), the highest production rate of CH_3COOH is 14.6 $\mu mol \cdot g^{-1}(Pd) \cdot min^{-1}$. Compared to the previous report, in which 210 ppm CH_3COOH was produced after a 72 h hydrothermal reaction catalyzed by nano-Fe, giving an average reaction rate of 0.017 $\mu mol \cdot g^{-1}(Fe) \cdot min^{-1}$ [26], our results significantly reduced the reaction time and promoted the CH_3COOH production.



Scheme 1. Proposed reaction mechanism of the hydrothermal reduction of HCO_3^- into CH_3COOH catalyzed by Pd/C.

3.3. *Reaction mechanism of the CH_3COOH formation*

Our previous research has showed that the Al has the ability to produce H_2 from H_2O based on Reaction (2) and catalyze the reduction of $NaHCO_3$ into HCOOH under hydrothermal conditions, in which the HCO_3^- is considered to be a reactant for HCOOH formation [34].

$$2Al + 4H_2O \rightleftarrows 2AlO(OH) + 3H_2 \tag{2}$$

When Pd/C catalyst is added, not only HCOOH but also CH_3COOH and trace amount of CH_4 are formed, suggesting that the Pd/C can catalyze the CH_3COOH formation from HCO_3^-. Based on our experimental results and the reported adsorption enthalpies of various CO_2 reduction intermediates on the Pd catalyst [28], a possible reaction mechanism of the hydrothermal reduction of HCO_3^- into CH_3COOH was proposed as shown in Scheme 1. At the beginning of the reaction, HCO_3^- is adsorbed onto the Pd catalyst to form intermediate **II**, which is then transformed into intermediate **III** by reacting with the *in-situ* formed H_2 from H_2O. Since the adsorption enthalpy of the intermediate **III** on Pd is relatively high (56.4 kcal/mol) [28], the intermediate **III** is not easy to desorb from Pd to form formate, which then leads to a further hydrogenation of the intermediate **III** into the intermediates **IV** and **V** on Pd. The adsorption enthalpy of the intermediate **V** on Pd is also relatively high (42.7 kcal/mol) [28], and then the desorption of the intermediate **V** from Pd to form CH_3OH is unfavorable. As a result, the firm adsorptions of the intermediates **III** and **V** on Pd make the reaction of the intermediate **III** with the **V** to form the intermediate **VI** available. The adsorption enthalpy of the intermediate **VI** on Pd is reported to be only 12.8 kcal/mol [28], which is much smaller than those of the intermediates **III** and **V** on Pd. Therefore, the intermediate **VI** is easy to desorb from Pd to produce CH_3COOH.

To further examine the above proposed reaction mechanism, the adsorption enthalpies of the intermediate of formate on the Pd, Cu and Ni were compared by referring the data from literature, and our previous research, in which the HCO_3^- was mainly reduced into C_1 products when Cu or Ni as the catalyst [18,20,33]. It has been reported that the formate adsorption enthalpy on the Pd, Cu and Ni follows the order of Cu (110) < Pd (110) < Ni (110) [35], which suggest that the formate adsorption enthalpy on Cu is the lowest, that is Cu can catalyze the HCOOH formation effectively. This is in accordance with our previous research, in which a HCOOH yield of 76% was obtained with the catalyst Cu [18]. On the other hand, Ni has the largest formate adsorption enthalpy among Cu, Pd and Ni, suggesting that more reduced products than HCOOH can be obtained on the Ni catalyst according to the proposed mechanism (Scheme 1). Ni has been reported to be a high active catalyst in the formation of CH_4 from CO_2 [36], which requires a firm adsorption of the intermediate of formate on Ni, and this is in accordance with the above formate adsorption enthalpy sequence and the proposed mechanism. Thus, the proposed mechanism in Scheme 1 is reasonable. However, no C_2 compounds were produced in our previous research when Ni was used as the catalyst even Ni has a higher formate adsorption enthalpy than Pd. One possible explanation could be that although relatively firm adsorption of formate can be achieved on Ni, further reaction of the intermediates to form CH_3COOH or other C_2 compounds was not favorable on Ni. The exact mechanism of CO_2 reduction into CH_3COOH is still not clear at this stage and is under further investigation.

Considering that the reaction system is slightly basic due to the existence of HCO_3^-, the produced CH_3COOH should convert to CH_3COO^- finally. Therefore, the reaction equation of the hydrothermal reduction of HCO_3^- into CH_3COO^- by H_2 can be given as:

$$2HCO_3^-(aq) + 4H_2(g) \rightleftarrows CH_3COO^-(aq) + 3H_2O(l) + OH^-(aq)$$

$$\Delta H_r^{\ominus}(298.15\,K) = -193.6\,kJ/mol \tag{3}$$

The calculated standard enthalpy (ΔH_r^{θ}) of Reaction (3) at 298.15 K is −193.6 kJ/mol, indicating that the reaction is exothermic. Since the Al was used as the reductant for H_2 production (Reaction (2)), the overall reaction equation of the hydrothermal reduction of HCO_3^- into CH_3COO^- with Al and H_2O can be expressed as follows by combing Reactions (2) and (3) together.

$$6HCO_3^-(aq) + 8Al(cr) + 7H_2O(l) \rightleftarrows 3CH_3COO^- (aq) + 3OH^-(aq) + 8AlO(OH)(cr) \tag{4}$$

$$\Delta H_r^{\ominus}(298.15\,K) = -4029.3\,kJ/mol$$

The calculated standard enthalpy of Reaction (4) at 298.15 K is −4029.3 kJ/mol, which is also an exothermic process. Therefore, these hydrothermal reactions can be potentially self-supported. All the thermodynamic data used for the calculation of the standard enthalpies of Reactions (3) and (4) were referred from the Lange's Handbook of Chemistry [37], except the thermodynamic data of AlO(OH) which was referred from Chen's report [38].

4. Conclusions

In this work, the production of CH_3COOH, a C_2 compound, was achieved through a highly exothermic reaction of hydrothermal reduction of HCO_3^- catalyzed by a commercial Pd/C catalyst with Al powder as a reductant. The Pd/C acted as a good catalyst in the C—C bond formation and CH_3COOH generation. The highest production rate of CH_3COOH from HCO_3^- was 14.6 μmol·g^{-1}(Pd)·min^{-1}, which was obtained at 300 °C for 2 h. High adsorption enthalpies of the C_1 intermediates on the Pd catalyst may be a key factor in C—C bond formation and CH_3COOH production.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2016.05.010.

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