Low temperature hydrogenation of carbon dioxide into formaldehyde in liquid media

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ABSTRACT

There is a growing demand for formaldehyde (HCHO) in various industrial applications, however, current industrial processes cannot be considered as green. There is an urgent need to develop an environmentally friendly and efficient method to produce this chemical. Our previous work introduced a novel HCHO production method via catalytic hydrogenation of CO in liquid media. This work demonstrates for the first time that HCHO can be synthesized via catalytic hydrogenation of CO_2 in liquid media. Unlike CO conversion however, CO_2 conversion is not believed to be a single step conversion. The conversion may proceed via two possible pathways: Route A − CO_2 hydrogenation into formic acid (HCOOH) followed by dehydration-hydrogenation into HCHO; and Route B − CO_2 conversion into CO via reverse water gas shift reaction, followed by direct hydrogenation of CO into HCHO similar to our previous report. To study feasibility of Route A, HCOOH conversion into HCHO was tested in methanol solvent and Pt-Cu/alumina showed the best conversion and highest yield. This partly confirmed our hypothesis that dehydration-hydrogenation of HCOOH into HCHO is feasible and hence HCOOH may act as an intermediate. However, the rate of HCHO production was substantially lower than the rate of HCOOH consumption, which suggests that there may be other competing reactions, such as decomposition of HCOOH. No intermediates could be detected in one-pot conversion of CO_2 into HCHO in our investigation, which may be due to their low concentration and/or rapid consumption to form the products. Therefore, this study concludes that both the routes are likely for the conversion of CO_2 into HCHO in a liquid phase reaction.

1. Introduction

Formaldehyde (HCHO) is one of the most important bulk chemicals in the world. It is used as a feedstock in over 50 industries including resins (with urea, phenol, melamine, etc), adhesives, plastics, foam, polyurethane paints, and disinfectants. Due to its high demand in various industrial applications, HCHO was manufactured in excess of 30 million tonnes in 2011 and has been growing at a rate of 5.4% per annum worldwide [1,2]. However, current industrial methods of HCHO production uses a series of high temperature reactions, starting from steam reforming of natural gas to form syngas, followed by methanol synthesis, and finally partial oxidation into HCHO. This process results in high exergy loss [3]. Therefore, a more environmental friendly and efficient method is crucially needed to replace the current energy intensive method.
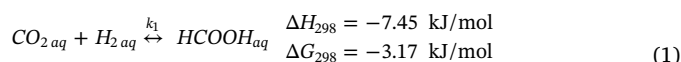
Our previous works have demonstrated that HCHO can be synthesized directly from CO and H_2 in a liquid-phase reaction at low temperature with 100% selectivity (353–403 K) [4,5]. Syngas may obtained from gasification of renewable feedstock like lignocellulose [6,7]. However, syngas also contains CO_2 and hence this manuscript explores conversion of CO_2 into formaldehyde using our earlier approach. Moreover, CO_2 is a more attractive feedstock to produce platform chemicals, since it may reduce the rate of CO_2 emission which may be helpful in climate change mitigation. In this report, hydrogenation of CO_2 into HCHO in a slurry reactor is presented.

The reaction pathway of CO_2 hydrogenation into HCHO in liquid phase is unclear. We hypothesise it to be a two-step reaction, which involves the formation of intermediate product(s). Two possible routes are considered in this study − Route A: formic acid as an intermediate and Route B: carbon monoxide as an intermediate.

Route A: Formic acid as intermediate product (Formate-mediated)

In this reaction pathway, CO_2 is first hydrogenated into HCOOH, which in turn goes through dehydration-hydrogenated into HCHO. The mechanism for Route A is illustrated below:
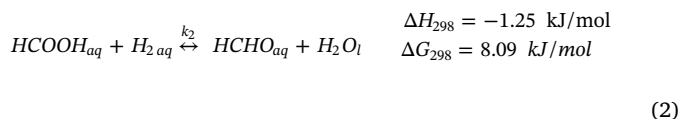
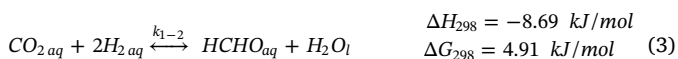$$CO_{2\,aq} + H_{2\,aq} \overset{k_1}{\leftrightarrow} HCOOH_{aq} \quad \begin{aligned} \Delta H_{298} &= -7.45 \ \text{kJ/mol} \\ \Delta G_{298} &= -3.17 \ \text{kJ/mol} \end{aligned} \tag{1}$$

$$HCOOH_{aq} + H_{2\,aq} \overset{k_2}{\leftrightarrow} HCHO_{aq} + H_2O_l \qquad \begin{array}{l} \Delta H_{298} = -1.25 \ kJ/mol \\ \Delta G_{298} = 8.09 \ kJ/mol \end{array}$$

(2)

Overall Reaction:

$$CO_{2\,aq} + 2H_{2\,aq} \overset{k_{1-2}}{\longleftrightarrow} HCHO_{aq} + H_2O_l \qquad \begin{array}{l} \Delta H_{298} = -8.69 \ kJ/mol \\ \Delta G_{298} = 4.91 \ kJ/mol \end{array} \quad (3)$$
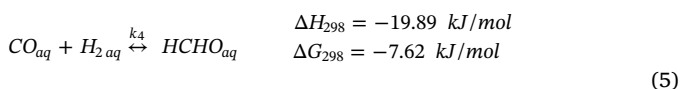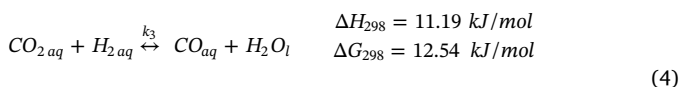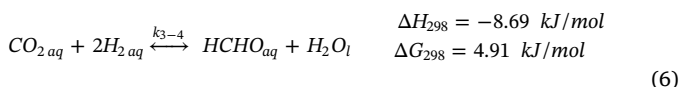
Conversion of CO_2 into HCOOH (Reaction (1)) is thermodynamically favourable and has been experimentally investigated in the recent years [8–10]. However, Reaction (2) has positive Gibbs free energy change, which suggests that the reaction is non-spontaneous. To the best of our knowledge, Reaction (2) has not been investigated in liquid media. In order to verify the feasibility of formate-mediated pathway, Reaction (2) must be investigated. In this work we used HCOOH as a feedstock, in methanol media, to investigate HCHO production via Reaction (2). The effects of temperature and catalysts on the rate of HCOOH conversion and HCHO production were also studied.

Route B: Carbon monoxide as intermediate product (Carbonyl-mediated)

An alternative reaction pathway for CO_2 hydrogenation in HCHO is through the production of CO via reverse water-gas shift (RWGS) reaction, followed by hydrogenation of CO into HCHO, as illustrated by Reactions 4–6.

$$CO_{2\,aq} + H_{2\,aq} \overset{k_3}{\leftrightarrow} CO_{aq} + H_2O_l \qquad \begin{array}{l} \Delta H_{298} = 11.19 \ kJ/mol \\ \Delta G_{298} = 12.54 \ kJ/mol \end{array}$$

(4)

$$CO_{aq} + H_{2\,aq} \overset{k_4}{\leftrightarrow} HCHO_{aq} \qquad \begin{array}{l} \Delta H_{298} = -19.89 \ kJ/mol \\ \Delta G_{298} = -7.62 \ kJ/mol \end{array}$$

(5)

Overall reaction:

$$CO_{2\,aq} + 2H_{2\,aq} \overset{k_{3-4}}{\longleftrightarrow} HCHO_{aq} + H_2O_l \qquad \begin{array}{l} \Delta H_{298} = -8.69 \ kJ/mol \\ \Delta G_{298} = 4.91 \ kJ/mol \end{array}$$

(6)

RWGS reaction is a well-researched gas phase reaction and is considered to be of significant importance for the production of transportation fuels via catalytic CO_2 hydrogenation [11]. However, this route has not been investigated in detail for chemicals production. As can be seen, in Route B the first step (Reaction (4)) is non-spontaneous, whereas the second step (Reaction (5)) is thermodynamically favourable and has been experimentally proven in our previous works [4,5]. In this manuscript catalytic hydrogenation of CO_2 into HCHO was investigated with different H_2/CO_2 ratios to study its effects in HCHO production. Attempts were made identify the intermediates of the reaction by sampling both liquid and gas phases at periodic intervals. Alumina supported Ni and Cu catalysts promoted by Pt and Ru were used in this study. Ni and Cu have been used as hydrogenation catalysts in industry and academic research, however, at low temperatures they are not sufficiently active. Therefore, Pt and Ru were used as promoters in this study. Moreover, Ru-Ni was shown as the best catalyst in our previous study on CO hydrogenation into formaldehyde [5].

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared via wet impregnation method using γ-alumina (Sigma-Aldrich) as the support for all catalysts. Nickel nitrate (Ni $(NO_3)_2·6H_2O$), copper nitrate (Cu$(NO_3)_2·3H_2O$), chloroplatinic acid (H_2PtCl_6) and ruthenium chloride (RuCl$_3$), all sourced from Sigma-Aldrich, were used as the chemical precursors for the synthesis. Pt-Ni

and Pt-Cu supported catalysts had 10 wt% Ni or Cu content and 1 wt% Pt content. Ru-Ni and Ru-Cu supported catalysts had 10 wt% Ni or Cu content and 4 wt% Ru content. Detailed synthesis procedures the catalyst can be found in our previous publication [6].

2.2. Catalyst characterisation

2.2.1. X-Ray fluorescence spectroscopy

The elemental composition of Ni, Cu and alumina of the prepared catalysts were determined by using an Ametek Spectro iQ II XRF. Pt and Ru loading were calculated using mass balance from the XRF results.

2.2.2. Carbon dioxide temperature programmed desorption (CO_2-TPD)

CO_2-TPD on Pt promoted Ni catalyst were carried out in a custom built flow instrument. Detailed description of this flow instrument can be found in our previous publication [6]. For each experiment, 500 mg of catalyst was loaded into a quartz reactor and heated up to 673 K at a heating rate of 10 K/min under 5% H_2/N_2 gas flow. The catalyst was reduced *in-situ* at the set temperature for 4 h, followed by purge for 1 h under Ar flow. The catalyst sample was cooled to the desired CO_2-adsorption temperature (298–373 K) under Ar flow. During the CO_2 adsorption step, the catalyst was exposed to pure CO_2 at the adsorption temperature for 1 h, then cooled to room temperature under CO_2 gas flow. The saturated catalyst was flushed with Ar gas at 100 ml/min for 1 h to remove any excess CO_2. Once the CO_2 partial pressure readings, as measured by the quadrupole mass spectrometer was stable, desorption step was initiated by heating the sample from room temperature to 973 K at 10 K/min. CO_2 and CO desorption data were recorded using RGA300 (Stanford Research Systems) quadrupole mass spectrometer (Table 1).

2.3. Catalytic activity evaluation

All catalytic studies were carried out in a set of four 100 ml high pressure stirred batch reactors (M4 reactor system, Amar Equipment Pty. Ltd.). In the formate-mediated reaction pathway study, 500 mg of the desired catalyst was reduced *ex-situ* prior to adding it into the reactor along with 50 ml of 99.99% methanol as solvent and 0.0343 ml of HCOOH, to make a 1000 ppm or 17.2 µM solution. The reactor was subsequently assembled and pressurised to 70 bar using ultra-high purity H_2 (Coregas). The reactor was then heated to the desired temperature (298 K, 323 K, 343 K, or 363 K) with continuously stirring at 400 rpm. Liquid samples were periodically collected through a dip-tube for further analysis.

In the carbonyl-mediated reaction pathway study, 500 mg of *ex-situ* reduced catalyst was loaded into the reactor along with 50 ml of methanol. The reactor was first pressurised with high-purity CO_2 (Coregas) and then H_2 up to a total pressure of 70 bar. The partial pressures of CO_2 and H_2 were varied to adjust the H_2:CO_2 ratio. Experiments were conducted at 298 K with continuously stirring at 400 rpm for 22 h while liquid samples were collected periodically.

The collected liquid samples were analysed with several different analytical instruments. HCOOH in the sample was quantified by first derivatising it into methyl formate by heating the sample for 2 h at

Table 1
Comparison of the amount of CO_2 adsorbed and reduced at different adsorption temperature.

Adsorption Temperature (K)	Total CO_2 adsorbed[a] ($\mu mol·g_{cat}^{-1}$)	% of CO_2 Reduced (CO evolved/Total CO_2 adsorbed)
323	32.6	2.3
353	41.8	28.0
373	67.6	43.8

[a] Sum of CO_2 desorbed and CO evolved.