Selective chemical reduction of carbon dioxide to formate using microwave irradiation

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A R T I C L E   I N F O

A B S T R A C T

Selective chemical reduction of carbon dioxide to formate anion under microwave irradiation is reported. No formaldehyde or methanol was generated as by products of the CO$_2$ reduction making the process highly selective. (NH$_4$)$_2$CO$_3$ or dry ice was employed as CO$_2$ source. NaBH$_4$ is used as reducing agent. Aqueous solutions of (NH$_4$)$_2$CO$_3$ or dry ice and NaBH$_4$ were subjected to microwave irradiation for a short duration of 5 min. The formation of formate is unequivocally established from the ^{1}H, ^{13}C and DEPT-135 NMR spectroscopic studies. FT-IR and UV–vis have been employed as auxiliary tools to observe the presence of formate ions. The obtained formate has the potential to be used as fuel in fuel cells or in turn can be converted to alkanes or can be used as a precursor for the production of hydrogen. Thus the current process is highly significant for the energy sector and to the chemical industry as well.

1. Introduction

Conversion of CO$_2$ to formate (yield, 75 wt.%) under microwave irradiation has been the central aspect of this paper. Chemical reduction of carbon dioxide (CO$_2$) to fuels and chemicals is one of the dream reactions of chemists.

Transformation of CO$_2$ is significant from energy (production of fuels like methanol, formate and hydrocarbons) and environmental (climate change due to excessive accumulation of CO$_2$) view points. Chemical reduction of CO$_2$ is a difficult problem owing to the fact that CO$_2$ is a very stable molecule (standard free energy of formation, $\Delta G^\circ = -394.3$ kJ/mol). Chemical reduction methods operating under modest reaction conditions to convert carbon dioxide to formate, selectively are being actively investigated [1–5]. Radiochemical, photochemical, electrochemical and biophotoelectrochemical methods are known to yield formic acid from carbon dioxide [6–8].

But none of the afore mentioned approaches could be employed industrially. Shinjiro Matsuoka et al., have reported the photochemical reduction of CO$_2$ to formate (quantum yield, 0.072) using p-terphenyl as the catalyst. In addition to formate, CO and H$_2$ were also observed as by products [9]. Sato et al., have developed a semiconductor (p-type InP)/complex hybrid (Ru complex polymer) – TiO$_2$, photo catalyst to photoelectrochemically reduce CO$_2$ to formate (HCOO$^-$) with a selectivity of >70% and a conversion efficiency of 0.03–0.04%. Formate ($m/z = 45$) was identified as the main reduction product of CO$_2$ with ion-chromatography time-of-flight mass spectroscopy (IC-TOFMS) [10]. Guoying Zhao and Ferenc Joo have reported a rhodium-phosphine complex [RhCl(mtppms)$_3$] based hydrogenation catalyst for the reduction of CO$_2$ to formic acid (0.13 M) in the presence of sodium formate solutions [11]. Zheng Shen et al., have reported glycerol to be an efficient reducing agent for the conversion of CO$_2$ (either dry ice or NaHCO$_3$) to formate in 90% yield under a hydrothermal method [12].

Formic acid is currently gaining increased attention as a compact hydrogen energy source and is a promising hydrogen storage medium as depicted below [13–15]:

$$HCOOH \leftrightarrow CO_2 + H_2$$
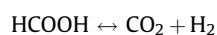
Formic acid was found to be better fuel compared to methanol for fuel cell applications. The electrode showed best tolerance to the surface poisoning when formic acid is used as a fuel compared to methanol [16,17].

Conventionally formic acid is used as reducing agent, coagulating agent, and also as a chemical precursor for the production of several alcohols, acids and esters. The formation of formic acid/formate

anion in the hydrogenation reaction of CO_2 was first reported by Farlow and Adkins in 1935 with Raney Nickel as a catalyst. Subsequently, several heterogeneous and homogeneous catalysts were developed for accelerating the process [18–26]. The reaction between NaOH and CO under pressure and at 210 °C was industrially employed for the production of HCOOH via HCOONa for several years [27]. Currently, a two stage process involving carbonylation of methanol followed by the hydrolysis of methyl formate to formic acid with the net reaction being addition of H_2O to CO is widely exploited [28,29].

Herein we report a new and fast chemical reduction method for the selective conversion of CO_2 to formate under microwave irradiation. $NaBH_4$ is used as reducing agent. Either $(NH_4)_2CO_3$ or dry ice in aqueous medium was used as CO_2 source. Use of $(NH_4)_2CO_3$ as CO_2 precursor is particularly advantageous owing to the fact that the addition of (NH_3, aq.) was found improve the enthalpy (from -31.2 kJ/mol to -84.3 kJ/mol) of the CO_2 hydrogenation reaction [27]. In the current process, NH_3 is generated in situ in addition to CO_2 during the decomposition of $(NH_4)_2CO_3$ and thus eliminating the necessity for the addition of NH_3 ex situ. Moreover, water is the common industrial solvent for the recovery of CO_2 from flue gases [28]. In addition, reduction of CO_2 to liquid fuels like formate rather than gases is desirable owing to the advantages associated with transportation [13]. Thus the current methodology of carrying out the hydrogenation of CO_2 reaction in aqueous solution in the presence of NH_3 (aq.) is particularly attractive for industrial adoption.

2. Experimental

2.1. Materials and methods

$(NH_4)_2CO_3$ and $NaBH_4$ were purchased from Sigma–Aldrich and used as received. THF (99.9%) was procured from Carlo Erba Reagents Ltd. The CO_2 reduction reaction was carried out in a domestic microwave oven (DMWO, SHARP R-390F) operating at 2.45 GHz in a batch mode under atmospheric pressure in the presence of air. The output of the domestic microwave reactor was 1100 W. The microwave oven was operated at 100% power. The microwave oven was modified so as to have provision for a distillation column passing through the MW oven (for enhanced safety of operation) and also stirring facility during the reaction [30–32]. Typical process comprise of placing in the reaction vessel (a round bottom flask, 100 mL), 0.35 g (0.00364 moles) $(NH_4)_2CO_3$ (CO_2 precursor) and 0.35 g (0.0092 moles) $NaBH_4$ in 35 mL water and subsequently subjecting the contents to microwave irradiation for 5 min. In the case of dry ice, 5.0 g dry ice, 1.0 g $NaBH_4$ and 20 mL water were placed in a round bottom flask and subjected to microwave irradiation for different periods of time (1–5 min.). The electricity consumed for the operation of the domestic microwave oven for 5 min was evaluated and was found to be 107 Wh [30]. The reaction temperature attained (90 °C) as a result of microwave irradiation is evaluated using a pyrometer (Fluke, 65 Infrared thermometer). The experimental set up for the microwave assisted CO_2 reduction process is depicted in Fig. S1. For comparison, the CO_2 reduction reaction was also carried out under hydrothermal conditions (at 90 °C) in a cylindrical stainless steel reactor with polytetrafluoroethylene lined inside. Typical batch of the hydro-thermal reaction comprised of taking 0.35 g (0.00364 moles) $(NH_4)_2CO_3$ (CO_2 precursor) and 0.35 g (0.0092 moles) $NaBH_4$ in 35 mL water in the reactor and placing the same in an air oven at the preset temperature. The reaction is quenched after the set reaction time by placing the same in a cold water bath. The reaction products were analyzed by ^1H, ^{13}C, DEPT-135 NMR, FT-IR and UV–vis spectroscopic studies. Quantification of the reaction product, HCOONa, was done with the use of ^1H NMR spectroscopy with D_2O

as solvent and using THF as the internal standard (Figs. S2 and S3). Typical sample for analysis comprise of 400 μL of the analyte and 100 μL of the solvent and 50 μL of internal standard (THF). Spectral analysis was carried out at room temperature. Owing to the ease involved in the sample preparation, NMR analysis was preferred over the regular mass spectrometric analysis [33,34]. UV–vis spectra were recorded on Cary 100 Scan Varian. FT-IR spectra were recorded on Bruker Tensor 27. ^{13}C and ^1H NMR spectra were recorded on Bruker Avance DPX 300.

3. Results and discussion

The reaction product obtained upon microwave irradiation of $(NH_4)_2CO_3$ (0.35 g in 35 mL H_2O) in the presence of $NaBH_4$ (0.35 g) for 5 min. is analyzed by ^1H and ^{13}C NMR spectroscopy. A singlet resonance at 8.3 ppm in the ^1H NMR (Fig. 1a) and a resonance at 171 ppm in ^{13}C NMR (Fig. 1b) establish the presence of formate anion and rule out the presence of formaldehyde or methanol or even carbonic acid.

The yield of HCOONa was found to be 0.186 g (Fig. S4(a)). Theoretically, 1.0 g $(NH_4)_2CO_3$, upon decomposition, is supposed to yield 0.46 g CO_2 and correspondingly 0.71 g HCOONa with appropriate amount of $NaBH_4$ (0.395 g). Calculations for the evaluation of the yield of formate were shown in the supporting material. A wt.% yield of 75 wt.% is obtained from a batch reaction with 0.35 g $(NH_4)_2CO_3$ with an irradiation time of 5 min. This value of yield of HCOONa is also substantiated by the fact that in the ^{13}C NMR spectrum of the reaction product (Fig. 1(b)), in addition to the intense signal at 171.1 ppm corresponding to the HCOONa, an additional signal of relatively lower intensity is observed at 163.1 ppm. Moreover, in the DEPT-135 NMR spectrum of the corresponding sample (Fig. 3(b)), the peak at 163.1 is absent and only the peak at 171.1 ppm is present.

This points to the fact that the peak at 163.1 ppm corresponds to the unreacted traces of $(NH_4)_2CO_3$ as carbonate samples do not show any signal in DEPT NMR. More over, the ^{13}C NMR spectrum of the aqueous solution of $(NH_4)_2CO_3$ (commercial sample) showed sharp singlet signal at 162.3 ppm (Fig. S5) which indeed confirm the presence of traces of unreacted $(NH_4)_2CO_3$. In addition, the positive signal in the DEPT 135 NMR at 171.1 ppm confirm that the reaction product is indeed HCOONa.
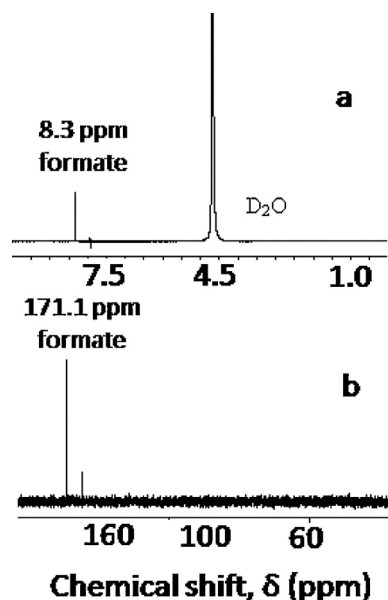

Fig. 1. (a) ^1H and (b) ^{13}C NMR spectra of reaction product from the chemical reduction of CO_2 (from $(NH_4)_2CO_3$).