Generation and Quantification of Formate Ion Produced from Aqueous Sodium Bicarbonate in the Presence of Homogeneous Ruthenium Catalyst

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Supporting Information

ABSTRACT: Formic acid and its salts are an alternative source for hydrogen generation. In this study, we store hydrogen using the formate–bicarbonate cycle. Aqueous sodium bicarbonate is hydrogenated to form sodium formate, which can then be decomposed to release hydrogen and sodium bicarbonate. The hydrogenation step is carried out under mild conditions in the presence of a homogeneous ruthenium catalyst. Hydrogen charge is realized at 70 °C under a hydrogen pressure of 20 bar, achieving yields > 80% and turnover number > 610. The catalyst is stable and robust through numerous cycles of the hydrogenation reaction. The formate ion formed during the bicarbonate hydrogenation is assayed and quantified by ion chromatography.

INTRODUCTION

Formic acid contains only 4.4% w/w of hydrogen; however, it appeals to scientists as a hydrogen carrier due to the simplicity of the decomposition reaction and the potential reversibility of the process to store hydrogen. The process for generating formic acid from hydrogen and carbon dioxide is an uphill reaction and requires a catalyst.

\[
H_2(g) + CO_2(g) \rightarrow HCOOH(l) \quad \Delta G^{\circ} = +32.9 \text{kJ mol}^{-1}
\]  

(1)

The degree of catalyst activity in the reaction is expressed by two indices: turnover number (TON), which describes the moles of desired product per mole of the homogeneous catalyst, and the turnover frequency (TOF), which describes the rate of the catalytic reaction and is dependent on the TON. Actually, TOF is the moles of product per mole of the catalyst per unit time and its value is usually expressed in h⁻¹.

The following summary of the literature begins with hydrogenation processes conducted by ruthenium catalysts on carbon dioxide alone producing formic acid initially, and then be decomposed to release hydrogen and sodium bicarbonate. The hydrogenation step is carried out under mild conditions in the presence of a homogeneous ruthenium catalyst. Hydrogen charge is realized at 70 °C under a hydrogen pressure of 20 bar, achieving yields > 80% and turnover number > 610. The catalyst is stable and robust through numerous cycles of the hydrogenation reaction. The formate ion formed during the bicarbonate hydrogenation is assayed and quantified by ion chromatography.

Several researchers have explored the formation of formic acid with homogeneous catalysts. The prominent metal catalyst for the above homogeneous reaction is ruthenium. Laurenczy and co-workers investigated the ruthenium complex carrying a phosphorous ligand, 1,3,5-triaza-7-phosphaadamantane (PTA), RuCl₂(PTA)₄, and achieved a total TON of 749 for four catalytic cycles at 60 °C. The reaction was run for 120 h under 100 bar of hydrogen and carbon dioxide mixture. The concentration of the formic acid produced was 1.8 M after the first and third cycles, 2.1 M after the second cycle, and 1.9 M after the fourth cycle. Since the reaction described by eq 1 is technically very challenging, most studies prefer to start with formate salts in a basic environment, which was acidified later on to yield formic acid. A ruthenium complex containing a triethylphosphine ligand, RuH₂(P(CH₃)₃)₄, was developed by Jessop et al. for the hydrogenation reaction of supercritical carbon dioxide. Under conditions of a total pressure of 205 bar in the presence of triethyl amine (NET₃) at 50 °C, TOF = 1400 h⁻¹ was realized with this catalyst. Another ruthenium derivative carrying the same phosphine ligand was disclosed by Munshi and co-workers. The catalyst, RuCl(OAc)(PM₃)₄, was active in the hydrogenation of carbon dioxide and achieved a TOF of 95 000 h⁻¹ at 50 °C under a hydrogen pressure of 70 bar and a carbon dioxide pressure of 120 bar. Additives such as NET₃ and C₆F₅OH were also included in the reaction mixture. In another study, Zhang’s team found that the carbon dioxide hydrogenation reaction in the presence of RuCl₃ and triphenylphosphine generated the catalyst form RuH₂(CO)(PPh₃)₂. NET₃ is required for the reaction to occur. The results were TON = 200.1 after 5 h at 60 °C and a pressure of 60 bar of the carbon dioxide and hydrogen mixture. The pyridinyltriazolato catalyst, chlorido[5-(pyridin-2-yl)-1,2,4-triazolato]tris-(trimethylphosphine)ruthenium(II), was synthesized for the same goal by Muller and colleagues. The conditions for the...
The hydrogenation reaction were 20 g of solid carbon dioxide with 70 bar of hydrogen and additives of C6H4OH and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) as a base. The catalyst reached TON = 4800 after 4 h. In another study, it was found by Beller et al. that [RuCl3(benzene)]2+ with phosphorous ligand bis(diphenylphosphino)methane (DPPM) in the presence of NEt3 converts the gases under the same pressure of 60 bar to formate salt with TON = 6442. Another ruthenium complex with a DPPM ligand was investigated by Yap and colleagues. The results of the catalyst [Ru(μ-Cl)(CO)(μ-DPPM)]2+ were TON = 2160 and TOF = 103 h⁻¹. The conditions of the reaction were a total pressure of 70 bar (the ratio of hydrogen to carbon dioxide was 1:1), with a basic medium using NEt3 at room temperature. The meta-trisulfonated triphenylphosphine ligand was found to be active in the presence of ruthenium, NEt3, and an ionic liquid by Leitner. TOF = 1089 h⁻¹. The latter achieved TON = 4800 after 4 h.7 In another study, it was found that the presence of NEt3, generating formate salt with TON = 400 after 10 h at 100 °C.8

Several pincer compounds of ruthenium were also investigated. Ru-PNP pincer was studied by Pidko and colleagues. The latter achieved TON = 1108 after 20 h in the presence of NEt3, generating formate salt in the presence of dimethylformamide and DBU. TOF = 1 100 000 h⁻¹. Another ruthenium pincer complex with a PNN ligand was developed by Sanford’s team. The reaction for generating the inorganic formate salt used hydrogen and carbon dioxide in a pressure ratio of 30:10 (a total pressure of 40 bar) with potassium carbonate achieving TON = 23 000 after 48 h at 200 °C.10 A tetrafluoroborate salt of ruthenium was also studied in the formation of organic formic acid derivatives. The catalyst [(η⁶C₆H₄Pr)²Ru(η³-C₆H₄O)(OH₂)][BF₄] promoted the reaction at 50 bar of carbon dioxide and 50 bar of hydrogen in the presence of NEt3, generating formate salt with TON = 400 after 10 h at 100 °C.11 Finally, a ruthenium complex with a N-heterocyclic carbene ligand was also studied in the carbon dioxide hydrogenation process. The reaction reached TON = 23 000 after 75 h at 200 °C and a hydrogen pressure of 20 bar and the same for carbon dioxide. Potassium hydroxide functioned as a base in this reaction.12 The inorganic formate salts are preferable over the amine-formate compounds as the hydrogen weight capacity of the product is higher and the separation process is simpler.

When decomposing formic acid, as was previously reported by Sanford et al., it is necessary to separate the carbon dioxide from the gas stream for most of the applications of the hydrogen product, such as fuel cells. For separating the carbon dioxide and using it as a storage material, scientists have investigated pathways for converting it to substrates such as bicarbonate salts, which can react with hydrogen. The hydrogenation process of bicarbonate salts instead of carbon dioxide is known as an alternative way for formate generation.13 The reaction is shown in eq 2.

\[
\text{H}_2(\text{g}) + \text{HCO}_3^-(\text{aq}) \rightarrow \text{HCOO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})
\]  

The hydrogenation reaction of sodium bicarbonate at 70 °C under a pressure of 80 bar was performed by Beller and colleagues. The latter achieved TON = 1108 after 20 h in the presence of [RuCl3(benzene)]2+ and the phosphorous ligand DPPM.17 The aforementioned catalyst and ligand achieved TON = 2793 after 20 h at 100 °C in the presence of hydrogen at a pressure of 50 bar and sodium bicarbonate solution. Carbon dioxide at a pressure of 35 bar was also added to the reaction vessel.18 In addition, a ruthenium complex including the sulfonated ligand 3-sulfonyldiphenylphosphine (mTPPMS) aided the generation of formate with a high pressure (95 bar) of hydrogen, achieving TOF > 9600 h⁻¹ at 80 °C.19 A ruthenium complex with a N-heterocyclic carbene ligand was also studied in the bicarbonate hydrogenation process. The reaction reached TON = 1200 after 24 h at 100 °C and a hydrogen pressure of 50 bar. The conversion was 62%.20 Olah et al. discovered the ruthenium compound carbonyldihydro(tetrahydroborato)[bis-(2-diphenylphosphinoethyl) amino] ruthenium(II), which achieved TOF > 2000 h⁻¹ in the potassium bicarbonate hydrogenation process after less than 0.5 h at 70 °C and a pressure of 40 bar of hydrogen. The formate yield was 75%.21 Chatterjee’s team investigated a ruthenium complex with the ethylenediaminetetraacetaete (EDTA) ligand. The hydrogenation of bicarbonate with the Ru(II) catalyst reached a yield of 46% for formate ion and TON = 46. The reaction conditions were a hydrogen pressure of 8 bar and a temperature of 40 °C.22

In most of the above studies, scientists generated organic formic acid salts by using amines such as NEt3, or DBU as a base. The usage of amines has several drawbacks: They reduce the hydrogen weight capacity of the formate salts and the separation from the catalyst solution is complicated. Herein, we report some new findings regarding the ruthenium MACHO (which is a pincer compound)-catalyzed formate generation process via the hydrogenation of sodium bicarbonate under ambient conditions.

**RESULTS AND DISCUSSION**

The catalyst Ru-MACHO (Figure 1) was developed by Kuriyama and co-workers for the hydrogenation of esters.23 The same catalyst was studied by Beller and his team for the hydrogenation process of sodium bicarbonate at a hydrogen pressure of 10 bar achieving TON = 1420 at 100 °C after 20 h.24 We examined the Ru-MACHO complex in the formate generation reaction. The catalyst solution in isopropanol was mixed with an aqueous solution of sodium bicarbonate and was placed in an autoclave. The reaction took place at 70 °C under a hydrogen pressure of 20 bar. The pressure in the autoclave was monitored, and the acquired kinetic graph is shown in Figure 2. The kinetic profile shown in Figure 2 describes a typical second-order behavior.

The yield of the product was 67–79% with a relative standard deviation of 0.16–1.01%.

It was found that both isopropanol and H₂O are crucial for the hydrogenation reaction to take place. The absence of solvent or distilled water prevents the reaction from occurring. The catalyst concentration had a critical effect on the reaction rate, i.e., as the number of moles of the catalyst increases, the yield increases. Nevertheless, the TON and TOF values decrease significantly.
Influence of number of moles of the catalyst, solvent, and additive on the hydrogenation process is presented in Table 1.

We observed that the catalyst starts with a nonclear white solution, which changes during the reaction to a clear pink solution (Figure 3).

One of our objectives in this study is to demonstrate the stability of the catalyst and its ability to function for successive batches without diminishing its activity. Because the concentration of sodium formate that can be quantified by ion chromatography measurement is limited to about 50 ppm, for preparing the same quantities when sampling the product (30 μL of sample was diluted to 100 mL), we investigated the hydrogenation reaction with half of the mass of sodium bicarbonate. The yield of the reaction in one cycle was 78−85% with a relative standard deviation of 0.21−2.14%.

The catalyst was studied for several consecutive runs. In the first cycle, the catalyst, the solvents (isopropanol and distilled water), and sodium bicarbonate were introduced to the autoclave. After washing three times under nitrogen gas and heating to 70 °C, hydrogen was poured into the autoclave. When the hydrogenation process is complete, the autoclave was cooled to room temperature and the hydrogen gas was released. The autoclave was washed with nitrogen and “rested” overnight. The procedure for the other runs consisted of loading the autoclave with isopropanol, distilled water, and the substrate sodium bicarbonate, washing three times under nitrogen gas, and heating to 70 °C. Finally, hydrogen was poured in and the reaction took place until completion. Every cycle was cooled to room temperature, washed with nitrogen, and “rested” overnight. The calculations of the conversions and the TONs included the evidence of the diluting of the catalytic mixture after every cycle. It was found that the conversion achieved in four runs was between 65 and 82% and that the catalytic activity was stable through four cycles (Figure 4).

CONCLUSIONS

A homogeneous ruthenium(II) catalyst was developed for the generation of sodium formate from sodium bicarbonate under mild conditions. The catalytic mixture changes color from a nontransparent white to a clear pink during the process. The catalyst formed in this manner was realized as exceptionally stable even after an overnight rest period at room temperature between the cycles after releasing the hydrogen gas and washing with nitrogen. Its activity was preserved for four cycles under ambient conditions, and it could be reactivated again and again simply by the addition of sodium bicarbonate and heating to 70 °C. At this temperature, TON > 610 was measured for each cycle.

The kinetics of the reaction was measured using an autoclave connected to a computer, and the quantification of the formate anion was done by ion chromatography measurement. Without doubt, the environmentally friendly hydrogenation reaction presented in this paper is appropriate as a hydrogen store in applications such as fuel cells.

EXPERIMENTAL SECTION

Materials. The catalyst Ru-MACHO and sodium bicarbonate (anhydrous, ≥99.7%) were purchased from Sigma-Aldrich. The solvent isopropanol (CMOS grade) was purchased...
Figure 4. Conversion of sodium formate generated during the bicarbonate hydrogenation reaction with Ru-MACHO catalyst. The catalyst 30.48 µmol Ru-MACHO was dissolved in 25 mL of isopropanol, and 24.62 mmol sodium bicarbonate was added with 25 mL of distilled water. The mixture was heated to 70 °C for 1 h, 23 bar of hydrogen was added to the autoclave, and the reaction started immediately. For subsequent batches, 5 mL of isopropanol and 5 mL of distilled water with the new amount of sodium bicarbonate (24.57–24.61 mmol) were added. The hydrogenation process took place under 22.9–23.1 bar of hydrogen.

from J. T. Baker, and the hydrogen cylinder (99.99%) was acquired from Moshalion Jerusalem Oxygen LTD.

**Instruments.** The reaction took place in an autoclave high-pressure Parr 4848 series reactor (290 mL) monitored by the SpecView32 software.

The identification and quantification of the formate ion generated during the hydrogenation process was carried out by ion chromatography-Dionex LC20 Chromatography Enclosure with a precolumn Dionex IonPac AG14, RFIC 4 × 50 mm Guard (Thermo), and a column Dionex IonPac AS14 RFIC 4 × 250 mm Analytical (Thermo).

**Typical Recursive Procedure for the Hydrogenation Process of Sodium Bicarbonate.** A solution of Ru-MACHO (18.5 mg, 30.48 µmol) and isopropanol (25 mL) was placed in an autoclave. Then, sodium bicarbonate (2.0681 g, 24.62 mmol) and distilled water (25 mL) were added. The autoclave was washed with nitrogen three times, and the temperature was raised to 70 °C for 1 h. Afterward, the pressure was released, hydrogen (22.9 bar) was added to the autoclave, and the monitoring system was started. After the system reached equilibrium, the autoclave was cooled to room temperature and the gas was slowly released. A conversion of 65% and TON = 640 after 7.5 h were calculated by ion chromatography apparatus. The system was washed with nitrogen once and stored with 5.3 bar of nitrogen at room temperature overnight.

The third cycle was started by adding isopropanol (5 mL), sodium bicarbonate (2.0675 g, 24.61 mmol), and distilled water (5 mL) to the autoclave. The autoclave was washed with nitrogen three times, and the temperature was raised to 70 °C for 1 h. Afterward, the pressure was released, hydrogen (22.9 bar) was added to the autoclave, and the monitoring system was started. After the system reached equilibrium, the autoclave was cooled to room temperature and the gas was slowly released. A conversion of 65% and TON = 811 after 7.5 h were calculated by ion chromatography apparatus.

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