

# Ruthenium-hydroxalate (Ru-HT) as an effective heterogeneous catalyst for the selective hydrogenation of CO<sub>2</sub> to formic acid



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## ABSTRACT

The reaction containing CO<sub>2</sub> and H<sub>2</sub> has been investigated for the hydrogenation of CO<sub>2</sub> to formic acid using ruthenium hydroxalate (Ru-HT) catalyst. Ruthenium salt was introduced to the synthesis of hydroxalate as an active metal center to develop ruthenium based heterogeneous catalyst. Hydroxalate not only acted as a support for the active metal but also acted as a soft solid base avoiding the use of the liquid base, which is normally required under homogeneous conditions for the formation of formic acid from the hydrogenation of CO<sub>2</sub>. Reaction temperatures were in the range of 40–100 °C, total pressure 10–100 bar with an ideal 1:1 ratio of pCO<sub>2</sub>:pH<sub>2</sub>. The maximum Turnover Number (TON) of 11389 was obtained for the formic acid formation under the optimized conditions at 60 °C temperature and 60 bar total pressure, using a mixture of methanol:water as a solvent (5:1, v/v). Ru-HT catalyst was synthesised and thoroughly characterized by FT-IR, PXRD, SEM-EDX and surface area analysis. The catalyst was effectively recycled up to 7 times without any loss in catalytic activity.

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## 1. Introduction

The increased emission of carbon dioxide (CO<sub>2</sub>) because of combustion of carbon-rich fossil fuels (i.e. natural gas, oil, and coal) has made a detrimental effect on the environment. Continuous escalation of CO<sub>2</sub> concentration in the atmosphere has reached bizarre levels, which bring apprehension about climate change and rising sea levels [1–5]. Because of the primary position of CO<sub>2</sub> as a greenhouse gas and the consequence of its emissions on the tribulations of environment revolution, CO<sub>2</sub> has become the subject of great environmental concern. Consequently, the transformation of thermodynamically stable CO<sub>2</sub> into the useful fuels and chemicals has attracted much interest towards CO<sub>2</sub> utilization. Hence, the reduction of CO<sub>2</sub> to an energy storage medium is a conceivable and an encouraging solution to the outstretched atmospheric CO<sub>2</sub> level by impersonating the carbon cycle in the environment. In this concern, the use of abundant CO<sub>2</sub> as C1-building block in the pres-

ence of a catalyst is a striking approach for the synthesis of useful chemicals and fuels for the development of a sustainable economy [6,7]. Utilization of CO<sub>2</sub> is the great replacement of toxic chemicals (i.e. phosgene and carbon monoxide) used for the production of value-added compounds [8–10].

The processes based on the CO<sub>2</sub> recycling are attracting the major scientific and technological interest among the feasible approaches to reduce CO<sub>2</sub> emissions [11–15]. The hydrogenation of profuse, nontoxic, renewable and economical viable CO<sub>2</sub> deserves attention for the synthesis of value-added products viz., formic acid/formates, cyclic carbonate, methanol, dimethyl carbonate, etc. [16]. Catalytic transformation of CO<sub>2</sub> to formic acid and its derivatives via the hydrogenation process is one of the best atom inexpensive approaches for the utilization of the abundant C1 feedstock [17].

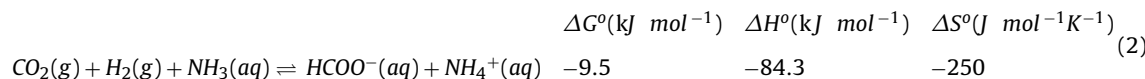
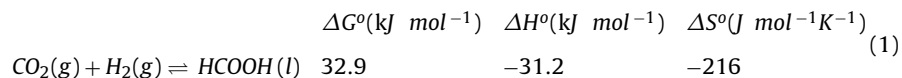
Formic acid is an important chemical amongst the other chemical products procured by CO<sub>2</sub> utilization. It is used as a vital intermediate in many industries viz., dyeing, leather, food, agro-chemical, to promote the fermentation of acetic acid, as coagulants in the rubber synthesis, an antibacterial agent in livestock feed and as a de-icing agent in many manufacturing industries [18,19]. Formic acid has a comparatively small H<sub>2</sub> content in its chemical structure (4.4 wt%), though it is gaining considerable interest

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as a hydrogen storage material in the energy industries because it is easily transportable and storable [20]. The existing commercial process for the production of formic acid involved the use of methanol and toxic carbon monoxide in the presence of a strong base like sodium methoxide, which currently produced 800000 tons of formic acid per year [21,22]. According to a review published in 2014, the production of 1 ton of formic acid via this process release 3076 kg of CO<sub>2</sub>, the same amount of formic acid could be produced by the CO<sub>2</sub> hydrogenation which could release only 100 kg of CO<sub>2</sub> [23]. Therefore, in comparison with the conventional CO-based process, CO<sub>2</sub> utilized production has the vast perspective to reduce the environmental impact. The synthesis of formic acid via the hydrogenation of CO<sub>2</sub> is thermodynamically disfavored, as it comprises the reaction between the gaseous substances to produce a liquid product. Consequently, the reaction is endergonic having  $\Delta G^{\circ}_{298} = 32.9 \text{ kJ mol}^{-1}$  value in the gas phase as well as exergonic having  $\Delta G^{\circ}_{298} = -9.5 \text{ kJ mol}^{-1}$  value in the aqueous phase.

Since Raney-nickel was first used as a catalyst, formic acid has been extensively studied and synthesised in the presence of sundry homogeneous and heterogeneous catalysts which includes transition metals in their structures such as Ti, Fe, Ni, Ru, Rh, Ir, Pd, Mo and Au [24,25]. Transition metal catalyzed hydrogenation of CO<sub>2</sub> is a dynamic area of investigation, as it provides a favorable methodology for the synthesis of formic acid by utilizing CO<sub>2</sub> as a cheap and profuse material for industrial scale chemical synthesis [26]. All these reported methods require the presence of a base or an additive like ammonia, trimethylamine, PPh<sub>3</sub>, NaHCO<sub>3</sub>, etc., because the catalytic activity is considerably reliant on the basic pH of the reaction mixture as it can shift the equilibrium towards the formed product (Eq. (1) and (2)) [27,28].



An impressive digit of Turnover Number (TON) of many heterogeneous catalysts have been reported so far for the direct hydrogenation of CO<sub>2</sub> to formic acid; data are displayed in Table 1. S. K. Kabra et al. have reported polyurea encapsulated ruthenium catalyst, which has given the highest TON of 47600 using an ionic liquid as an additive and scCO<sub>2</sub> as a solvent in only 4 h [29]. The [IrCp\*(N–N)<sub>x</sub>]<sub>y</sub> complex on HBF had given a TON of 6400 when Et<sub>3</sub>N was used as a base/additive and H<sub>2</sub>O as a solvent at 80 bar pressure (1:1, pH<sub>2</sub>/pCO<sub>2</sub>) in 10 h at 120 °C [30]. Palladium on activated carbon was reported by J. Su et al. using NH<sub>4</sub>HCO<sub>3</sub> as a carbon source instead of CO<sub>2</sub> gas giving a TON of 1769 with 27.5 bar hydrogen pressure [31]. A TON of 2254 was reported by Liu and co-workers using Ru-complex supported on TB-MOP and Et<sub>3</sub>N as solvent together with PPh<sub>3</sub> as an additive [32]. A TON of 7088 was achieved using KHCO<sub>3</sub> and H<sub>2</sub> (40 bar) in the presence of Pd/r-GO (1 wt%) catalyst [33]. [Ru(NH–C<sub>4</sub>H<sub>9</sub>)(PPh<sub>3</sub>)<sub>x</sub>Cl<sub>y</sub>] have shown a TON of 1384 with 5 times more concentration of CO<sub>2</sub> than H<sub>2</sub> using PPh<sub>3</sub>/Et<sub>3</sub>N as additive/base [34].

A proficient hydrogen production can be achieved by the decomposition of formic acid, as it is an energy or hydrogen storage compound. At present, the extensively used procedures for the hydrogen production is occurring at the high temperatures (>150° or >200 °C), which are the reverse water–gas shift reaction (RWGS) and the steam reforming of methane gas [35]. High temperature (>150 °C) is useful for catalytic RWGS reaction which is 2.5 times more than the temperature employed in the present work thereby affording to avoid the formation of any side-products (CO formation or methane synthesis) by the RWGS reaction in the gas phase

under the employed reaction conditions in the present investigation [36].

According to the past available reports, there are scarcer results of a heterogeneous catalytic system for the hydrogenation of CO<sub>2</sub> with no additional base or promoter to produce formic acid. The direct and selective synthesis of formic acid via CO<sub>2</sub> hydrogenation over a heterogeneous catalyst without accumulating any base or additive is favorable and needs to be investigated.

Therefore, it is worthwhile to use the ruthenium hydrotalcite as a catalyst that combines the active metal site from ruthenium metal and a basic property from hydrotalcite required for the production of formic acid by CO<sub>2</sub> hydrogenation. It is one of the best auspicious approaches for utilizing CO<sub>2</sub> at moderate temperature. Development of ruthenium-grafted hydrotalcite as a heterogeneous catalyst is desirable because direct ruthenium grafted hydrotalcite by using RuCl<sub>3</sub>·xH<sub>2</sub>O is economically viable, instead of heterogenizing the homogeneous ruthenium complexes. Hydrotalcite is a soft base and this base like property in its structure makes it an important and proficient solid support required during the CO<sub>2</sub> hydrogenation to formic acid. Thus, Ru-HT is reported here considering its advantages as solid, reusable and efficient heterogeneous catalyst for the direct CO<sub>2</sub> hydrogenation to formic acid with a very good TON (11389) at moderate reaction conditions (60 °C and 60 bar (1:1, pCO<sub>2</sub>/pH<sub>2</sub>)) using methanol: H<sub>2</sub>O (5:1, v/v) as a solvent in 24 h without using base.

## 2. Experimental

### 2.1. Materials and methods

Hydrogen gas UHP/Zero grade (99.9%) and carbon dioxide UHP/zero-grade gas cylinders were purchased from Hydro Gas India Pvt. Ruthenium trichloride [RuCl<sub>3</sub>·xH<sub>2</sub>O] was acquired from Sigma–Aldrich, USA. Magnesium chloride [MgCl<sub>2</sub>·6H<sub>2</sub>O; 98%], aluminum chloride [AlCl<sub>3</sub>·9H<sub>2</sub>O; 98%], sodium nitrate [NaNO<sub>3</sub>; 99.9%] and sodium hydroxide [NaOH; 99.9%] were purchased from S.D. Fine Chemicals Ltd., Mumbai, India and used as received. A.R. grade methanol was purchased from Loba Chemie and was used without further purifications. The double distilled milli-Q deionized water was used for the synthesis of catalysts. The FT-IR spectra were recorded on a Perkin–Elmer Spectrum GX FT-IR system using KBr pellets in the mid-IR region. Powder X-ray diffraction (PXRD) patterns were made by Rigaku MINIFLEX-II (FD 41521) Powder X-ray Diffractometer. The samples were scanned in the 2θ range of 10–80° using CuKα (λ = 1.54178 Å) radiation and a Ni filter. The textural analysis of the samples was carried out by nitrogen adsorption at 77.4 K using a Sorptometer (ASAP-2010, Micromeritics). X-ray photoelectron spectroscopy (XPS) analysis was performed using Omicron Nanotechnology system with monochromatic AlKα

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