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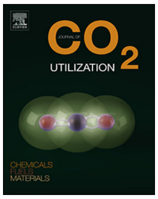

Nitrogen-rich graphitic carbon stabilized cobalt nanoparticles as an effective heterogeneous catalyst for hydrogenation of CO_2 to formate

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ABSTRACT

In this article, we report a catalytic reduction of CO_2 to formate in the presence of metallic cobalt nanoparticles as an elegant heterogeneous catalyst. The aforementioned cobalt nanoparticles was prepared by the pyrolysis of impregnated cobalt precursor on cucurbit[6]uril (CB[6]). During the pyrolysis process, CB[6] framework transform to the nitrogen-rich graphitic carbon support in which cobalt nanoparticles were present in their metallic state. The synthesized catalyst was highly active for the catalytic hydrogenation of CO_2 with 1 M KOH solution at 120 °C by applying 1:1 partial pressure of pCO_2/pH_2 to obtain a high TON of 82,265 in 24 h. Moreover, the influence of all the catalytic parameters was investigated with the reusability of the catalyst. In sort, the catalytic protocol shows excellent activity and robust nature for the CO_2 utilization reaction with economical/ abundant metal source, in aqueous media and with molecular hydrogen.

1. Introduction

Carbon dioxide (CO_2) is an astonishing raw material for the synthesis of numerous value-added chemicals and is mounting attention steadily due to the public, legal and environmental apprehensions [1–3]. The global warming and greenhouse effect is essentially credited to the growing concentration of CO_2 (~400 ppm) in the atmosphere, which is due to rapid and wide consumption of carbon-opulent fossil fuels and natural gas [4,5]. Further, the viable solution to reduce the CO_2 level on the environment is, through the proper carbon management i.e. CO_2 should be captured, preserved and utilize for the diverse production of carbon-based products [2–6]. The commercially available most of the organic chemicals are achieved from crude oil, which is an unsustainable feedstock and would be ceasing in the future [1–3,7]. Alternatively, biomass a substitute, and sustainable source of organic chemicals. In the present scenario, CO_2 is an imperative biomass, because of its inexpensive, efficient, safe, abundant, renewable and non-toxic nature. CO_2 as the C_1 source is present in a massive amount on our environment and has to be converted into organic chemicals by various possible methods [6,8]. The fixation of CO_2 was first discovered by the *Prof. Calvin* and his group in the year 1956, commonly known as Calvin cycle [9]. Since then, the various CO_2 utilized products such as urea, formic acid, cyclic carbonates, methanol, amides etc. are manufactured in significant scale [6,10].

Formic acid is one of the crucial [13,14], and important C1 feedstock, used as a fuel, hydrogen storage material, insecticide, preservative, a leather tanning, an antibacterial and de-icing agent in many industries [12–15]. Hence, all these promising potentials of formic acid or formates via CO_2 hydrogenation are eye-catching to the scientific and technological societies on the way to success [16–19]. Presently, formic acid is manufactured ~800 KT per annum by using toxic methanol and carbon monoxide in the presence of a homogeneous catalyst [20]. However, carbon monoxide is known as a highly poisonous gas, which is perilous and hazardous to humans for its use on an industrial scale. Apart from this, CO_2 is very safe, but due to high thermodynamic and kinetic stability in the gas phase ($\Delta G^\circ = +32.9$ kJ/mol), its utilization is challenging, but favorable in the presence of base [21,22]. Also, in literature, reports are available with homogeneous [5,23] as well as with heterogeneous [24] catalytic systems for the production of formic acid/ formate salts by hydrogenation of CO_2 in organic or

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aqueous solvents. Further, the heterogeneous systems are mostly reported with the precious metal complexes (like iridium, ruthenium, and rhodium), these are not only expensive but with ligands makes it more uneconomical. Hence, the development of alternative catalysts which based on abundant, lucrative and sustainable metal (cobalt, iron, nickel) catalysts are needed to be explored. Among the sustainable metals, cobalt catalysts were very efficient for hydrogenation reaction, since its first report on 1938 for the Fischer-Tropsch process by *Prof. Otto Roelen*. Ever since only a few reports are available with cobalt as a heterogeneous and homogeneous catalyst for the synthesis of formic acid by CO_2 reduction [25–27]. Yet again, most of the articles were based on electrochemical methods for CO_2 hydrogenation.

Recently, nitrogen doped heterogeneous supports were extensively used because of several benefits like cheaper than phosphorous ligands, stabilizes the metal particles with uniform dispersion etc. [28]. We have also reported the nitrogen-rich framework with cucurbit[6]uril (CB[6]), and exploited for the hydrogenation reaction [29,30]. The beauty of CB [6] is that it contains a high number of carbon and nitrogen atoms in its framework which easily stabilizes the metal nanoparticles [29] and also used for the formation of nitrogen-rich graphitic carbon by simple pyrolysis, which enhances its catalytic activity [30]. So, after reviewing the literature reports and our previous experience in hydrogenation reactions and CO_2 utilization [29–33], herein we report the catalytic reduction of CO_2 for the synthesis of formate salt in an aqueous medium. The high efficiency of the catalytic protocol reported here is because of metallic cobalt and nitrogen-rich surface. Further, the catalyst was reused for four consecutive cycles without significant loss in catalytic activity with the highest turnover number (TON) of 82,265. In addition, reaction pathway was proposed based on the results obtained from characterization and catalytic experiments.

2. Experimental

2.1. Materials and methods

Carbon dioxide UHP/zero-grade gas and hydrogen gas UHP/Zero grade (99.9%) cylinders were purchased from Hydro Gas India Pvt. Cobalt acetate hydrated $[Co(OAc)_2{\cdot}4H_2O]$ was acquired from Sigma Aldrich, USA. Glyoxal, urea, potassium hydroxide and hydrochloric acid were purchased from S. D. Fine Chemicals Ltd., Mumbai, India and used as received. Ethanol (96%) was purchased from Merck, Mumbai, India and used without further purification. The UHPLC analysis was done using a Nexera UHPLC instrument system SHIMADZU instrument. Preceding to HPLC analysis, all samples and standards were filtered using Axiva SFNY25XB Nylon HPLC Syringe Filter (25 mm filter diameter/0.45 μm pore size) and left undiluted. Formic acid was separated on a HiQSilC18HS HPLC Column (4.6 mm × 250 mm) operated at ambient temperature with an overall flow rate of 0.5 mL per minute of a 0.1% phosphoric acid mobile phase and detected using an SPD-M20A, Prominence, Diode Array UV detector set to 190 nm wavelength. The sample injection volume was 20 μL. Analysis was completed within 30 min, and data were recorded using Lab solution Chromatography software.

2.2. Catalyst preparation and characterization

The synthetic steps for catalyst preparation (see ESI, Scheme S1) and its characterization (see ESI) are reported in our previous research work [30].

2.3. Catalytic hydrogenation of CO_2

Stainless steel high-pressure 100 mL reactor vessel was charged with metallic cobalt catalyst (100 mg) and 1 M KOH solution (20–50 mL). The reactor vessel was first flushed with 3 cycles of nitrogen gas to remove air from the vessel. Then, the reactor vessel was pressurized with hydrogen gas and carbon dioxide gas (1:1, H_2/CO_2) at room temperature. The reactor vessel was heated to reach the temperature at 30–150 °C and stirring was maintained at 800 rpm. The pressure drop was observed at the reaction temperature, which indicated that the reaction proceeded well with the formation of the product within 24 h. After completion of the reaction, the heating mantle was removed and the reactor was allowed to cool at room temperature. After attaining ambient temperature, the reactor was depressurized and the reaction mass was collected into the sample vial, which was then centrifuged to remove the catalyst. The aqueous layer was separated for HPLC analysis and the solid catalyst was washed several times with water, dried in an oven for next catalytic hydrogenation reaction. The reproducibility of the catalytic results was confirmed by repeated experiments under equal reaction conditions and the results were in the range of 3–5% product variation.

N.B- The hydrogenation reactions were performed in the high-pressure laboratory taking all safety provisions for hydrogen gas using at high temperature and pressure. All processes concerning gas pressurizing were done in a ventilated fume hood.

3. Results and discussion

The aforementioned catalyst was prepared by the chelation of Co $(OAc)_2$ with CB[6] and pyrolyzed in an argon atmosphere at 800 °C for 2 h (see ESI) [30]. After careful characterization of the catalyst by various analytical methods (see ESI, Figs. S1–S6), 30 we observed that cobalt is present in its metallic state (PXRD, TEM, and XPS) with particle size in between 5–15 nm, stabilized by nitrogen atoms present with the graphitic layer (TEM, RAMAN, and XPS). The synthesized catalyst has a surface area of 184.3 m^2/g with an average pore diameter of 2.4 nm (From N_2 adsorption and desorption). The ICP analysis states that ~0.7% of cobalt is present in the catalyst with 64.3 and 8.5% of carbon and nitrogen respectively (from CHNS analysis). Further, the cobalt dispersion was 7% with 48% metallic surface area presents as calculated from the pulse chemisorption analysis. Additionally, we also carried out the CO_2-TPD (temperature programmed desorption) analysis for understanding the role of catalyst/ support for the activation of CO_2. In TPD spectra, we observe two intense peaks at a temperature range of 100–400 °C which suggests the catalyst/ support has a basic nitrogen atom and strong ability to adsorb/ interact with CO_2 (adsorption value of 0.273 mmol/g). Hence, we started our catalytic reactions with cobalt nanoparticle by using KOH for the synthesis of formate using molecular CO_2 and H_2. The selectivity and TON of formate were confirmed by the HPLC analysis using 0.1% phosphoric acid as a mobile phase with a flow rate of 0.5 mL/minute (see ESI, Fig. S9) and ^1H and ^{13}C NMR spectra (see ESI, Fig. S10). Initially, the catalytic reaction was carried out at 120 °C using 30 mL KOH solution (1 M) and total 62 bar pressure of pCO_2/pH_2 (1:1, p/p) with 100 mg Co catalyst for 24 h. Inspiring results with a TON of 77,060 with 100% selectivity of formate (Fig. 1a) prompted us for further optimization to achieve maximum TON with excellent selectivity. Further, to confirm our results and understand the role of catalyst and nitrogen-rich surface we have carried out series of control experiments with only nitrogen-rich graphitic carbon and cobalt nanoparticles on graphitic support. Interestingly, the control experiments demonstrate inferior results with TONs of nil and 4674 respectively (see ESI, Fig. S7), suggesting the cobalt nanoparticles with nitrogen-rich graphitic carbon facilitate the CO_2 reduction reaction with a high TON value.

Subsequently, we have varied various parameters like temperature, selection of base, the concentration of the optimized base, catalyst amount, pressure and solvent to understand the effects on the formate formation. The catalyst was screened at different temperatures (150, 90, 60 and 30 °C) with other parameters constant as above to acquire respective TONs i.e. 37,880, 39,373, 1036 and 60 (Fig. 1a). The outcomes suggest that the reduction of CO_2 increase gradually with temperature from 30–120 °C and decrease at 150 °C. The decrease in TON