



Highly selective hydrogenation of CO₂ into formic acid on a nano-Ni catalyst at ambient temperature: Process, mechanisms and catalyst stability



Chuan-Shu He, Li Gong, Jie Zhang, Pan-Pan He, Yang Mu*

CAS Key Laboratory of Urban Pollutant Conversion, Collaborative Innovation Centre of Suzhou Nano Science and Technology, Department of Chemistry, University of Science and Technology of China, Hefei, China

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ABSTRACT

The hydrogenation of CO₂ with gaseous hydrogen is currently believed to be the most commercially feasible synthetic method to resolve the serious worldwide greenhouse gas effects. However it is suffering from several disadvantages, such as expensive complex catalysts, and high energy consumption. In this study, a novel method for the hydrogenation of CO₂ into formic acid with nano-Ni catalyst is developed. The effects of various parameters on the capability of the catalyst for CO₂ conversion were investigated. Furthermore, the HCO₃⁻ reduction process on the catalyst was rationalized theoretically with density functional theory simulations. The prepared nano-Ni was demonstrated to be an available catalyst for CO₂ conversion into formic acid by employing H₂ as a hydrogen source at ambient temperature and almost constant pressure. Moreover, the nano-Ni catalyst displayed good tolerance with pH variations in CO₂ reduction. The formation of formic acid from CO₂ reduction on nano-Ni particles was enhanced with an increase NaHCO₃ concentration and catalyst dosage. Additionally, theoretical analysis elucidated that the hydrogenation of CO₂ into formic acid on nano-Ni catalyst was favorable over attacking the C of HCO₃⁻ by the active H and hydroxyl group.

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1. Introduction

While offering the majority of the current energy supply, fossil fuels also emit alarming levels of CO₂, leading to serious worldwide greenhouse gas effects. CO₂ is a thermodynamically and chemically stable compound [1], and thus, noticeable energy input and catalysis are necessary for its reduction [2,3]. To overcome this problem, many promising methods have already been previously proposed [4,5]. Catalytic conversion of CO₂ into desired products combined with solar energy is regarded as the most promising approach. Although researchers have achieved obvious advancement in photocatalytic CO₂ conversion, a low efficiency and expensive or complex catalyst make satisfying practical applications an elusive goal.

The hydrogenation of CO₂ with gaseous hydrogen is currently believed to be the most commercially feasible synthetic method [6,7]. Fischer–Tropsch (F–T) synthesis is an attractive alternative

approach for the conversion of CO₂ and H₂ into high quality hydrocarbons [8]. Fe- and Co-based catalysts are good choices for the F–T synthesis due to their good activities and selectivity [9]. In the Fe-based catalyst systems, Pt, an important promoter, could improve the CO₂ uptake and selectivity towards olefins and long-chain hydrocarbons [10]. When Al₂O₃ was added as a structural promoter in this system, enhancement of CO₂ conversion as well as high selectivity to C₂+ hydrocarbons were also observed [10]. It has been reported that Cu-based heterogeneous materials were able to successfully catalyze CO₂ hydrogenation into CH₃OH [1,2]. Moreover, many noble metals such as Pd, Ru and Rh could also be adopted as catalysts for formic acid production from CO₂ conversion [11,12] as summarized in Table S1 in the supporting information (SI). Precious metals (Rh, Ru, Ir, Pd) are the most commonly used catalysts for CO₂ conversion into formic acid as they contain homogeneous materials predominating with the water soluble ligands, such as phosphine ligands, pincer ligands, N-heterocyclic carbene ligands, proton-responsive ligands [13]. However, besides for the application of noble metals and non-cheap organic ligands, the synthesis of these homogenous catalysts was complicated along with high energy consumption [14]. Special

* Corresponding author.

E-mail address: yangmu@ustc.edu.cn (Y. Mu).

solvents such as DMSO and MeOH were often used to stabilize the catalytic intermediate or exert and influence the entropy value [13]. Additionally, in order to achieve reasonable rates and conversions, many of these reactions should be conducted at elevated temperatures and/or pressures, leading to dramatic increase in energy consumption.

In recent years, Ni-based catalysts have attracted intense attention because nickel is comparatively inexpensive and readily available, which is suitable for large scale industrial applications. It has been proven to efficiently break down the C–C bond and dissociate the hydrogen molecules [15,16]. It also has efficient activity close to the noble metals [4,17]. Recently, commercially available Ni powder catalyst was adopted for CO₂ reduction with N₂H₄·H₂O as a hydrogen source, achieving a 50% yield of formic acid with 99% selectivity [18]. However, extra heat energy is required in order to maintain the reaction temperature at 300 °C for the Ni powder catalyst. Compared to the powder catalyst, nanoparticles have higher specific surface area and better catalytic activity, which might be able to compensate for the extra heat required during the hydrogenation of CO₂. However, to the best of our knowledge, there are no reported studies on CO₂ hydrogenation into formic acid with nano-Ni particles as the catalyst.

In this study, we have successfully demonstrated the prepared nano-Ni to be a highly efficient catalyst for the hydrogenation of CO₂ into formic acid, a raw chemical that has the potential to compensate for the cost of the reaction, at ambient temperature and almost constant pressure. The effects of various parameters on the capability of the catalyst for CO₂ conversion were investigated. Furthermore, the CO₂ reduction process on Ni nanoclusters was rationalized theoretically by employing density functional theory (DFT) calculations. Additionally, the stability of nano-Ni catalyst as well as its recovery was also evaluated in this study.

2. Experimental

2.1. Chemicals

The chemical reagents (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) used in this study were of analytical grade, including formic acid, ethanol, N₂H₄·H₂O, NiCl₂·6H₂O, NaOH, NaHCO₃, H₂SO₄ and HCl, except for 96% NaBH₄. Nano-Ni and nano-NiO were purchased from Aldrich (Sigma–Aldrich Chemical Co., China). The reagents were used directly without any pretreatment. High purity compressed H₂, N₂, and CO₂ gases were obtained from the Shangyuan Gas Products Co., Ltd (Nanjing, China). All chemical stock solutions were prepared using purified water and stored at 4 °C.

2.2. Catalyst synthesis and characterization

Nano-Ni particles were freshly prepared by using the liquid phase reducing method, similar to the synthesis of nano-zero valent iron [19]. In brief, the reductant was prepared by dissolving 14.16 g of NaBH₄ and 1 g of NaOH into 500 mL of purified water, which was sparged with N₂ for 20 min in advance. Additionally, nickel chloride solution was prepared by adding 38.64 g of NiCl₂·6H₂O into a 400 mL mixture of ethanol and water ($V_{\text{ethanol}}/V_{\text{water}} = 4:1$), and then, it was transferred into a three-necked bottle for titration. A NaBH₄ reducing agent solution was added drop-wise and slowly into a nickel chloride solution under the protection of highly purified N₂ with magnetic stirring at 800 rpm at room temperature. The vigorous stirring was continued for an extra 30 min after the reductant titration was finished, and then, the products were washed 5 times with water and dried

overnight at 65 °C under vacuum. The characterization of the synthesized nano-Ni particles is shown in the SI.

2.3. Batch tests for CO₂ reduction

Since the preliminary experiments showed that the major product was the same for hydrogenation of CO₂ and NaHCO₃ with nano-Ni catalysts, NaHCO₃ was adopted as the CO₂ source for simplification in this study. After purging with N₂ in advance for approximately 10 min to remove the dissolved oxygen, 35 mL of NaHCO₃ solution was added into a 75 mL serum bottle first. Then, the reaction vial was flushed with high purity N₂ for approximately 10 min to remove dissolved oxygen, followed by transferring it into the anaerobic chamber for the addition of Ni nanoparticles. When 5 min of aeration with high purity H₂ was completed, the serum bottles were sealed with rubber stoppers and aluminum caps. For insurance, additional H₂ was supplied into the bottles to confirm that enough H₂ was added using an injector. Finally, the initial H₂ pressure was 1.2–1.5 times the atmospheric pressure.

In the typical reduction experiment of aqueous CO₂, the reaction conditions were controlled at 10 mM NaHCO₃, 0.5 M Ni and a pH of 6 with continuous H₂ aeration, where the H₂ was continuously added into the bottle until the initial pressure was achieved every 24 h. Then, the tests were conducted in the shaker at 35 °C with a shaking speed of 220 rpm and shielded from light. To probe the differences of formic acid production caused by various parameters and attain the optimized parameters, pH values, catalysts and reactants were separately evaluated as variables, and the other conditions were controlled at the typical experiment conditions. The initial pH value in a range of 3.8–9.8 was adjusted by using HCl or NaOH solution after adding NaHCO₃ into the solution in this study. To choose an optimum catalyst dosage, 0.05, 0.25, 0.5, 1.0, and 1.5 M Ni NPs were evaluated. In the tests of the catalyst stability, after each cycle, 0.5 M used Ni particles were collected through centrifugation and further used directly after 3-min of ultrasonic pretreatment. Concentrations of 1, 10, 25, 50, 100, 200, 300, 400, and 500 mM were separately set up as the initial NaHCO₃ concentrations to explore the reduction capacity of Ni nanoparticles. The H₂ aerated initial experiments were compared with continuous H₂ aeration to estimate the effect of the reductant, where the H₂ was aerated initially to 1.2–1.5 times the atmospheric pressure and no further H₂ aeration was carried out. As for the test without H₂, no H₂ aeration was carried out after the addition of nano-Ni. In the H₂ and CO₂ adsorption tests, 1 g targeted nanoparticles were added into 35 mL deoxygenated water with keeping pH at around 8.5, following with initial H₂ or CO₂ aeration for about 5 min and then sealed operation. All tests were administered at least three times.

2.4. Analysis and calculations

The liquid products of CO₂ reduction were determined by using high-performance liquid chromatography (HPLC) equipped with a UV detector and a 300 × 7.7 mm Hi-Plex H column at 55 °C (Agilent Technologies, USA). The mobile phase was 5 mM H₂SO₄ at a flow rate of 0.6 mL/min, and the detection wavelength was 210 nm. H₂ and CO₂ were measured by a gas chromatograph (GC) (Model SP-6800A, Lunan Co., China) using a gas-tight syringe according to Sheng and Yu [20]. An Agilent 6890 N GC equipped with a flame ionization detector and Plot Q-19095P-Q04 column (Agilent Technologies, USA) was used to detect the generation of hydrocarbons in the headspace [21]. Both the total carbon (TC) and total organic carbon (TOC) were measured with a TOC analyzer (MultiN/C 2100, Analytik Jena, Germany). The simulation of NaHCO₃ consumption and the determination of formic acid yield (FAY, %) are provided in the SI. In order to demonstrate the state of

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