

a. Rationale

Climate change and fossil fuel depletion are expected to cause significant economic damage worldwide [1], [2]. Carbon dioxide hydrogenation is a method that could be used to mitigate the effects of climate change and address fossil fuel depletion by recycling waste CO₂ and providing renewable routes of production for value-added chemicals such as light olefins [3]. One reaction pathway of CO₂ hydrogenation uses the reverse water-gas shift (RWGS) reactions and Fischer-Tropsch synthesis (FTS) process to produce hydrocarbons from CO₂ and H₂ [4]. Transition metal carbides have been identified as promising catalyst materials for CO₂ hydrogenation due to their CO₂ adsorption and also their ability to dissociate carboxyl bonds [5], [6]. In particular, Fe-Co carbides have been shown to have good performance for CO₂ hydrogenation [7]. However, challenges remain in synthesizing effective catalysts for CO₂ hydrogenation, especially with regard to light olefin selectivity [8]. Guanidine has been previously shown to have catalytic properties, with guanidine-based catalysts being synthesized for various reactions, such as the production of biodiesel [9], [10]. Guanidine could improve the performance of Fe-Co catalysts by providing a carbon source to induce carburization. Guanidine's properties as a reducing agent could also improve the performance of Fe-Co catalysts [11]. The aim of this study is to determine the effects of guanidine treatment on CO₂ hydrogenation activity over Fe-Co catalysts.

b. Research Questions, Hypotheses, Goals, Expected Outcomes

Research Question: To what degree does guanidine treatment increase CO₂ hydrogenation activity over Fe-Co catalysts?

Hypothesis: Guanidine treatment will increase the CO₂ hydrogenation activity of Fe-Co catalysts by promoting the reverse water-gas shift (RWGS) reaction and Fischer-Tropsch synthesis (FTS) process.

Goals:

1. Assess to what degree CO₂ hydrogenation activity is increased by guanidine treatment over Fe-Co catalysts.
2. Determine possible reaction intermediates of the CO₂ hydrogenation process over the guanidine-treated Fe-Co catalyst.

Expected outcomes: The guanidine-treated Fe-Co catalyst will show higher light-olefin product yields compared to the untreated Fe-Co catalyst. CO and H₂O will be observed indicating RWGS activity.

c. Procedures

A. Catalyst synthesis

a. Polymeric complex synthesis

i. Iron polymeric complex (IPC)

1. 28 g iron powder and 96.5 g citric acid will be mixed into 2.5 L deionized water.
2. Solution will be vigorously mixed and air-purged.
3. After 24 hours, excess solvent will be evaporated to produce solid IPC powder.

ii. Cobalt polymeric complex (CPC)

1. 29 g cobalt powder and 96.5 g citric acid will be mixed into 2.5 L deionized water.
2. Solution will be vigorously mixed and air-purged.
3. After 24 hours, excess solvent will be evaporated to produce solid CPC powder.

b. $\text{Fe}_2\text{-Co}_6\text{-CeO}_2$ synthesis

- i. 0.0627 g of IPC and 0.01910 g of CPC will be physically mixed and ground together.
- ii. 1.4546 g CeO_2 will be grounded into IPC and CPC mixture.
- iii. Mixture will be calcined under air for 5 hours at 350°C .
- iv. Calcined catalyst will be compressed using pellet press, milled, and separated using 40 (0.420 mm), 60 (0.250 mm), and 80 (0.177 mm) size meshes into 0.177 mm-0.250 mm, 0.250 mm-0.420 mm, and <0.177mm size particles.

c. $\text{Fe}_2\text{-Co}_6\text{-CeO}_2\text{-G}$ synthesis

- i. 0.0627 g of IPC and 0.01910 g of CPC, and 0.606 g guanidine will be physically mixed.
- ii. 1.4546 g CeO_2 will be grounded into CPC, IPC, and guanidine mixture.
- iii. Mixture will be calcined under N_2 for 5 hours at 350°C .
- iv. Calcined catalyst will be compressed using pellet press, milled, and separated using 40 (0.420 mm), 60 (0.250 mm), and 80 (0.177 mm) size meshes into 0.177 mm-0.250 mm, 0.250 mm-0.420 mm, and $<0.177\text{mm}$ size particles.

B. Catalyst performance testing

a. $\text{Fe}_2\text{-Co}_6\text{-CeO}_2$

- i. Approximately 0.1 g of $\text{Fe}_2\text{-Co}_6\text{-CeO}_2$ will be loaded into glass rod with quartz wool.
- ii. Glass rod will be placed in a Thermo Scientific Lindberg/Blue M furnace.
- iii. $\text{Fe}_2\text{-Co}_6\text{-CeO}_2$ will be reduced under 20 mL/min H_2 for 1 hour.
- iv. Reaction gas consisting of 24 mL/min H_2 , 8 mL/min CO_2 , and 8 mL/min He will be flowed through catalyst sample.
- v. Catalyst will be tested at 250°C , 275°C , and 350°C with 5 gas chromatography (GC) injections per temperature.

b. $\text{Fe}_2\text{-Co}_6\text{-CeO}_2\text{-G}$

- i. Approximately 0.1 g of $\text{Fe}_2\text{-Co}_6\text{-CeO}_2\text{-G}$ will be loaded into glass rod with quartz wool.
- ii. Glass rod will be placed in a Thermo Scientific Lindberg/Blue M furnace.

- iii. $\text{Fe}_2\text{-Co}_6\text{-CeO}_2\text{-G}$ will be reduced under 20 mL/min H_2 for 1 hour.
- iv. Reaction gas consisting of 24 mL/min H_2 , 8 mL/min CO_2 , and 8 mL/min He will be flowed through catalyst sample.
- v. Catalyst will be tested at 250°C, 275°C, and 350°C with 5 gas chromatography (GC) injections per temperature.

C. Catalytic activity testing

- a. Sample of $\text{Fe}_2\text{-Co}_6\text{-CeO}_2\text{-G}$ will be loaded into diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) testing chamber.
- b. $\text{Fe}_2\text{-Co}_6\text{-CeO}_2\text{-G}$ will be reduced under H_2 at 300°C.
- c. Background scan will be conducted during H_2 reduction.
- d. Reaction gas of 8 mL/min N_2 , 8 mL/min CO_2 , and 24 mL/min H_2 will be flowed through testing chamber.
- e. Temperature will be held at 250°C, 275°C, 300°C, 325°C, and 350°C for 30 minutes each.
- f. DRIFTS scans will be conducted at rate of one scan per minute.
- g. Fraction of product gasses will be sent to residual gas analyzer (RGA).

Risk and safety

- 1. **Human participants research;** not applicable
- 2. **Vertebrate animal research;** not applicable
- 3. **Potentially hazardous biological agents research;** not applicable
- 4. **Hazardous chemicals, activities, & devices**

A. 28 g Iron powder

Iron powder is a flammable solid. It is known to be toxic if inhaled or ingested. Inhalation can cause metal fume fever. Contact with iron powder may lead to skin irritation. Iron powder is known to decompose to iron oxide when exposed to heat or exposed to air. It is reactive if exposed to strong oxidizing agents, or strong acids or bases. The designated supervisor will supervise any instance where this chemical needs to be handled. Latex gloves and a disposable face mask will be worn while handling to avoid contact or ingestion. After handling, soap and water will be used to wash hands. Excess chemical will be disposed of in a designated waste disposal container.

B. 29 g Cobalt powder

Cobalt powder is a flammable solid. Inhalation of cobalt powder can cause metal fume fever. Inhalation or ingestion of cobalt powder is toxic. Exposure to cobalt powder is known to cause liver or kidney damage. Skin or eye contact with cobalt powder can cause irritation. Cobalt powder is stable if not exposed to intense heat or strong oxidizing agents or acids. The designated supervisor will supervise any instance where this chemical needs to be handled. Latex gloves and a disposable face mask will be worn while handling to avoid contact or ingestion. After handling, soap and water will be used to wash hands. Excess chemical will be disposed of in a designated waste disposal container.

C. 2.9092 g Cerium oxide

Cerium oxide is a nonflammable solid. Inhalation may cause respiratory tract inhalation. Contact with cerium oxide may cause eye or skin irritation. Cerium oxide is harmful if ingested. Cerium oxide is stable under most conditions. The designated supervisor will supervise any

may cause displacement of oxygen and lead to suffocation. Canisters of hydrogen will be secured by chain to prevent falling over. Regular checks of gas lines will be conducted to ensure no leakage occurs. Hydrogen canisters will be handled by the designated supervisor, qualified scientist, or other lab group members.

G. CO₂

CO₂ is a nonflammable, odorless, colorless gas. Pressurized gas canisters can explode if exposed to heat or blunt force. Leakage of gas may cause displacement of oxygen and lead to suffocation. Canisters of CO₂ will be secured by chain to prevent falling over. Regular checks of gas lines will be conducted to ensure no leakage occurs. CO₂ canisters will be handled by the designated supervisor, qualified scientist, or other lab group members.

G. Furnace

There is a possible risk of burn from furnaces. The designated supervisor will supervise in any instance where materials need to be removed or inserted into the furnace. Caution will be taken when handling objects obtained from the furnace. Before removing objects from furnace, hot gloves will be worn. Furnace will only be operated under a fume hood.

H. Gas chromatography

Leaks of hydrogen gas in gas chromatography could lead to ignition. Accumulation of gasses in gas chromatography could result in ignition. Operation of the gas chromatography machine will be only be performed under the supervision of the principal investigator. Gas purges will be regularly run to prevent gas accumulation within the gas chromatography machine. Regular checks of gas lines will be performed to ensure leakage does not occur.

Data analysis

Product yields were calculated by integrating the peak areas of chromatograms obtained through GC. Representative DRIFTS spectra were obtained by taking scan in the middle of each temperature interval. Peak areas for DRIFTS were integrated within 886.09 cm^{-1} and 818.86 cm^{-1} ; 3033.68 cm^{-1} and 2991.65 cm^{-1} ; 2921.2 cm^{-1} and 2765 cm^{-1} ; 886.09 cm^{-1} and 818.86 cm^{-1} .

Addendum

No additions were made.

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