Research Plan

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Optimizing the Adsorption Operating Conditions for Dual Functional Materials in Direct Capture of CO2

from Air

Environmental Engineering

A. **Rationale**

Since the Industrial Revolution, there has been a global increase in greenhouse gas emissions, due to the proportionately increased usage of fossil fuels. These emissions are likely to cause drastic and irreversible effects on the global environment. Evidently, it is imperative to take immediate action to limit and reverse GHG emissions[1]. Many efforts have been made to work towards this goal across the scientific community. Currently, one of the main technologies for preventing CO_2 emissions is carbon capture and sequestration (CCS)[3]. Although CCS has potential for CO_2 capture in high quantities, its applications are limited by the high energy the system requires to operate and its reliance on corrosive amines[4,5]. The research of this laboratory proposes a novel, alternate technology that prevents new CO_2 from entering the atmosphere and overcomes the previously-stated limitations of CCS. Dual Functional Materials (DFM) were introduced by my mentor's research group, *Catalysis for a Sustainable Environment,* in 2015 to capture CO_2 from power plant flue gas (capture step) and simultaneously convert it to synthetic natural gas (CH_4) to be recycled as energy for the power plant (methanation)[6]. Methanation is to be achieved through the hydrogenation of CO_2 in which H_2 is sourced from renewable energy sources[7,8]. Composed of a high surface area supported solid alkaline adsorbent in intimate contact with a metal catalyst, a key characteristic of DFMs is their ability to operate in an isothermal system. The temperature of 320 ℃ is optimal for the DFM due to its favorability in production of synthetic natural gas (methanation) and can be achieved using the sensible heat of the power plant flue gas[12-15]. Finally, CH_4 produced by the system is proposed to be recycled as energy for the plant inlet through harnessing heat released by the exothermic combustion of CH_4. This process closes the carbon cycle, eliminating the need for captured CO_2 storage and reducing the amount of external fuel supplies used to power the plant[16-17]. Current research is focused on maximizing the efficiency of DFM capabilities in terms of CO_2 capture and CH_4 production quantities. Previous studies have worked to finalize an optimal set of parametric conditions for DFM

operation including GSHV, temperature, and CO_2 adsorption duration, as well as identifying Ru and Na_2O as the superior candidates for DFM[18]. Research is required in order to optimize the quantities of alkaline adsorbent in ratio to metal catalyst present in the DFM. Another application of DFMs being explored is in air capture. Reversing the CO_2 pollution humans have caused is of the utmost importance in order to limit global temperature warming to 1.5 degrees Celsius, based off the goal set by the the Intergovernmental Panel on Climate Change Paris Agreement[1]. DFM offers a system for CO_2 Capture in air that is viable in multiple different climates, works isothermally, and with very little energy input. Therefore, optimizing the DFM to explore it's air capture potential will be the main focus of my research.

B. Research Objectives/Expected Outcomes

a. Research Objectives:

    i. To explore the potentials for DFM as a mechanism for CO_2 capture from air.

    ii. To explore how effective DFM is at capturing CO_2 from air at 300 °C, which is extremely diluted (400 ppm)

b. Expected Outcomes:

    i. Thus far, testing with DFM and flue gas, where the CO_2 concentration is relatively high, has been successful. However, since air is very dilute in terms of CO_2 concentration (400 ppm), the DFM is expected to be less efficient in terms of CO_2 adsorbent ability. In contrast, the lesser CO_2 concentration is expected to decrease the strength of the oxidation reaction of the metal catalyst, making it easier to reduce later on.

C. Research Methods

a. Procedure:

i. DFM Synthesis:

    1. Adsorbents will first be prepared using incipient wetness impregnation using aqueous precursor solutions of the various metal oxides. Adsorbents will then be dried at 140 °C for 2 hours, calcined in air at 400 °C for 4 hours, and then reduced. To synthesize the DFM, the metal catalyst precursor salts will be impregnated onto the adsorbents. DFM will then be dried in air at 120 °C for 2 hours and calcined in air at

500 °C for 2 hours. The alkaline adsorbent that will be used is Na_2O, with a precursor of Na_2CO_3 with a carrier support of y-Al_2O_3, used for its porous structure. The metal catalyst that will be used is Ruthenium, with a precursor of Ruthenium (III) nitrosyl nitrate.

ii. DFM Testing:

1. The DFMs will be tested using a fixed bed reactor. The samples will first be reduced for over 12 hours at 320 °C in 10% H2/N2 at a flow rate of 30 ml/min to ensure that all the all the precursor salts decomposed to their reduced and active form. Once the samples are reduced, 100 mg of powdered DFM will be placed into a fixed bed ChemBET Pulsar TPR/TPD unit, and tested for CO_2 capture. Each sample will be exposed to a 0.1% CO_2/N_2, to simulate the dilute air, at 320 ºC for 40 min, at a flow rate of 30 ml/min. Next, hydrogen will be introduced to gather data on methanation of the adsorbed CO_2. This step will be performed with 10% H_2/N_2 at a flow rate of 30 ml/min for 1 hour. Three cycles will be tested, and the results will be averaged. Gas compositions at the exit of the reactor will be monitored using an Enerac portable emissions analyzer, capable of continuously monitoring CO_2, CH_4 and CO concentrations.

2. Steps in one cycle of testing:
   a. CO2 adsorption in ideal (0.05% CO2/N2) or simulated real air conditions for 20 min at a total flow rate of 100 ml/min (GHSV: 4000 h−1)
   b. 4 min N2 purge at 150 ml/min (GHSV: 6000 h−1)
   c. Methanation for 1 h with 15%H2/N2 at 200 ml/min (GHSV: 8000 h−1).

iii. Hydrogenation Rates and CO_2 Capture Capacity Measurements

1. 100 mg of powder DFM materials will be placed in an alumina crucible and undergo a cycle of CO2 adsorption/hydrogenation in a Netzsch TGA-Libra instrument to measure hydrogenation rates and CO_2 capture capacity. All samples will receive in-situ pre-reduction at 320 °C in 13.26% H2/N2 (60 ml/min) for 6 h. Each sample will then undergo CO2 adsorption at 320 °C with 0.1% CO2/N2 (40 ml/min) for 30 min.

The weight increase measured is the amount of CO_2 adsorbed. This will be followed by a 10 min N_2 purge, and then a catalytic hydrogenation step using 13.26% H_2/N_2 (60 ml/min) for 6 h at 320 °C. The weight decrease (removal of adsorbed CO_2) after the addition of H_2 will give a relative measure of weight loss associated with CO_2 converted to CH_4 or simply desorbed. Confirmation of the products will be determined in fixed bed reactor tests using the Enerac analyzer. H_2 chemisorption tests will be performed using a ChemBET Pulsar TPR/TPD unit (Quantachrome) with fresh DFM powder samples.

b. **Risk and Safety**

  i. This study will involve the use of potentially dangerous chemicals such as hydrogen (H_2), methane (CH_4), and nitric acid (HNO_3). Hydrogen will be used in reactions with air, which could lead to potentially explosive mixtures. To ensure safety, hydrogen will be diluted with nitrogen (N_2). Methane is combustible with oxygen, making it a potential explosive as well. In the lab, all work with methane will be vented to remove air contaminants from the work site. Nitric acid has a pH of 3.01 and is highly corrosive. Therefore, nitric acid will be used in small amounts to reduce the chance of injury. Furthermore, proper use of laboratory PPE equipment, such as nitrile gloves, goggles, and a lab coat, can minimize the chance of chemical-related injuries.

c. **Data Analysis**

  i. Data will be analyzed in Excel and Origin. Origin will be used to calculate the total amount of CH_4 produced in each trial, by finding the area under the curve of each methane profile. Excel will be used to calculate umol of CH_4 produced per gram of catalyst, and p-values for each of the trials.

D. **References**

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Item #1. Human Participants Research:

1. No human participants were used.

Item #2. Vertebrate Animals Research:

1. No vertebrate animals were used.

Item #3. Potentially Hazardous Biological Agents

1. No potentially hazardous biological agents were used.

Item #4. Hazardous Chemicals, Activities & Devices:

1. The handling of all hazardous chemicals will be done under the supervision of qualified lab personnel. Potentially hazardous chemicals will include hydrogen (H_2), methane (CH_4), nitric acid (HNO3), sodium carbonate (Na_2CO_3), and Ruthenium (III) nitrosyl nitrate. Proper training will be undertaken in order to learn techniques for safe operation and handling of necessary chemicals and machinery. Proper equipment will be worn to minimize chemical exposure.

Hydrogen Gas (H_2/N_2) Compressed- ~10.0% H_2

- Product 295396, Sigma-Aldrich
  - Hydrogen gas is a highly flammable gas. Thus, various safety measures and precautions will be taken to prevent injuries. The gas will be kept in a metal cylinder that is tightly closed in a dry and well-ventilated place. The container will be kept away from heat/sparks/open flames/hot surfaces.

Methane (CH_4) Compressed- >99.99%

- Product 463035, Sigma-Aldrich
  - Methane gas is a highly flammable gas. Thus, various safety measures and precautions will be taken to prevent injuries. The gas will be kept in a metal cylinder that is tightly closed in a dry and well-ventilated place. The container will be kept away from heat/sparks/open flames/hot surfaces.

Nitric Acid (HNO_3) ~70%

- Product 438073, Sigma-Aldrich
  - Nitric acid is a corrosive liquid. Thus, various safety measures and precautions will be taken to prevent injuries. The liquid will be stored in a corrosive resistant container with a

resistant inner liner and kept in well-ventilated place. All use with nitric acid will be performed in a well-ventilated area while wearing the proper PPE.

Sodium Carbonate (Na₂CO₃)

- Product S2127, Sigma-Aldrich
    - Sodium Carbonate is a liquid that can cause irritation to the eyes or skin upon physical contact. Thus, various safety measures and precautions will be taken to prevent injuries. Skin will be washed thoroughly after handling. All use with sodium carbonate will be performed while wearing the proper PPE.

Ruthenium (III) Nitrosyl Nitrate

- Product 373567, Sigma-Aldrich
    - Ruthenium (III) Nitrosyl Nitrate is a corrosive liquid. Thus, various safety measures and precautions will be taken to prevent injuries. The liquid will be stored in a corrosive resistant container with a resistant inner liner and kept in well-ventilated place. All use with Ruthenium (III) Nitrosyl Nitrate will be performed in a well-ventilated area while wearing the proper PPE.

NO ADDENDUMS EXIST