

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

Environmental Engineering

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1.0. Introduction

1.1. Rationale

Environmental engineers all around the world have been working towards improving and innovating technologies for capturing CO₂ from the air (also known as Direct Air Capture or DAC) in an effort to combat the unprecedented increase in global atmospheric CO₂ levels. Dual Functional Materials, or DFM, is a novel technology for CO₂ capture proposed by our research group *Catalysis for a sustainable environment*. Thus far, DFM has been exclusively tested in regards to capturing CO₂ from large point sources of CO₂ emissions, which have applications in natural gas or coal-fired power plants, one of the largest contributors to anthropogenic CO₂ emissions. In this work, DFM is explored as a potential candidate for DAC technology. However, dissimilar to the gas tested in regards to fossil fuel power plants, CO₂ concentrations in air are extremely low at concentrations of 380-410 ppm. Therefore, the focus of this study was to optimize different testing conditions to maximize DFM's ability to adsorb CO₂ and convert it to CH₄ when tested under very low concentrations of CO₂.

1.2. Background

1.2.1. CO₂ Pollution: A Global Threat

Due to rising levels of atmospheric carbon dioxide, global warming has been identified as one of the key issues of this century [1]. Despite the increased implementation of renewable energy sources, CO₂ pollution remains at a record high [2]. According to the International Energy Agency's 2018 Global Energy and CO₂ Status Report, energy-related CO₂ emissions last year increased by 1.7% to an unprecedented 33.1 Gt of CO₂. This trend can be directly attributed to a global rise in energy consumption, which in 2018 was almost twice the average from 2010-2017 at an increase of 2.3%. Although energy efficiency saw an improvement in 2018, the energy intensity decrease of 1.3% was lower than seen in past years. 2018 marked the 3rd consecutive year of slowed improvement in energy efficiency [3].

According to the UN Environment's 2018 Emissions Gap Report, unless increased action on national levels to fulfill the Paris Agreement's NDCs is taken within the next 10 years, the goal set in 2015 of limiting global warming to 1.5 °C becomes impossible to achieve [4]. Furthermore, the IPCC's 2014 Synthesis Report on Climate Change states that rising global temperatures have had drastic effects on the environment, such as changing precipitation, melting snow and ice in polar regions, and rising sea levels [5]. If current CO₂ trends continue, then the effects on the ecosystem, environment, and humankind will become nearly impossible to reverse [6].

With the global population rising at an unprecedented rate, the IEA reported that international energy demand is set to increase by over 25% to 2040 [7]. Therefore, the use of combustible fossil fuels to meet humanity's energy needs is an assurance [8]. Traditional technologies for pre- and post-combustion CO₂ capture at points of large emissions of CO₂ have had success [9], but their applications are limited to reducing the rate of CO₂ emissions [10]. In order to advance the process of approaching negative carbon emissions, technologies that capture carbon dioxide directly from the air must be explored.

1.2.2. DFM in Direct Air Capture

In 2015, our research group *Catalysis for a sustainable environment* presented Dual Functional Materials (DFM) as a technology capable of bypassing the limitations of current Carbon Capture and Sequestration (CCS) technologies which rely on corrosive amines and energy-intensive CO₂ capture and purification processes [11]. Furthermore, CCS processes are predicted to have low rates for recycling energy and require long distances to transport captured CO₂ to sequestration sites, making CCS logistically and economically unappealing for large scale operations [12-13].

Dual Functional Materials have been proposed to operate in a fashion that overcomes the prior stated limitations through the use of an adsorbent and a metal catalyst supported on the same high-surface-area carrier. As the name suggests, DFM serves two functions. Firstly, the Na₂O solid adsorbent adsorbs CO₂ from a mixture of gas. H₂-- supplied through water electrolysis, powered by a renewable energy source such as excess solar or wind power-- is used to hydrogenate the adsorbed CO₂ into CH₄ in conjunction with the metal catalyst. The CH₄ can then be combusted, providing a large quantity of energy that can be harnessed for a variety of applications, notably recycling power in the applied location [14-17]. The recycling of products based off of adsorbed CO₂ is economically attractive as it offsets the unappealing costs of implementing DFM technology by reducing the costs spent on power.

Technologies to capture CO₂ directly from the air are a necessity due to humanity's assured reliance on the use of fossil fuels. DFM has demonstrated a strong ability to capture and convert CO₂ from gaseous mixtures with concentrations of 7-10% CO₂ [18]. This indicates that DFM holds considerable potential for capturing and converting CO₂ from gaseous mixtures with extremely low concentrations of CO₂, which is applicable to direct air capture (DAC), as air currently contains 407.4 ppm of CO₂. One of the main concerns was if the DFM could be fully saturated with CO₂ within a reasonable length of time to allow for optimal use of the material. Therefore, the purpose of my study was to explore and optimize different testing conditions, flow rate of gas and duration of the CO₂ adsorption time, to maximize DFM's ability to adsorb CO₂ and convert it to CH₄.

2.0. Methodology

**All figures presented were made by the author unless otherwise stated*

2.1. Materials Synthesis

DFM tested was composed of 0.5% Ru and 6.1% Na₂O supported on Al₂O₃ (0.5% Ru, 6.1% Na₂O/Al₂O₃). First, incipient wetness impregnation was used to prepare the Na₂O adsorbents using an aqueous precursor solution of Na₂CO₃ (Sigma Aldrich, USA) impregnated on γ -Al₂O₃ (SBA-150, BASF, USA) powder. Adsorbents then were dried at 140 °C for 2 h and calcined in air at 400 °C for 4 h. Following calcination and H₂ reduction, a loading of 6.1% “Na₂O”/Al₂O₃ of the adsorbent was achieved. Next, precursor salts of Ru-- (Alfa Aesar, USA)-- were impregnated onto the adsorbents supported on γ -Al₂O₃ to achieve the desired metal loading (by weight) of 0.5%Ru. DFM materials were then dried in air at 120 °C for 2 h and calcined in air at 250 °C for 2 h. Finally, the pre-reduction step was performed in situ at 320 °C with 10% H₂/N₂ overnight as a means of generating the active catalytic metal and converting any remaining carbonates and nitrates to their respective oxides [19].

2.2. Catalytic Tests

Table 1- A description of the 4 trials ran and their changing parameters in terms of the flow rate of air and adsorption time (10 ml/min for 15 minutes, 40 ml/min for 15 minutes, 10 ml/min for 30 minutes, 40 ml/min for 30 minutes) .

		Flow Rate of Air	
		10 ml/min	40 ml/min
Adsorption Time	15 min	10 ml/min 15 min Ads.	40 ml/min 15 min Ads.
	30 min	10 ml/min 30 min Ads.	40 ml/min 30 min Ads.

The testing of the DFM was performed using a ChemBET Pulsar TPR/TPD unit (Quantachrome) (Figure 1). Approximately 100 mg of powdered DFM was loaded into a U-tube made of inert quartz and then placed in the micro-reactor furnace. First, the sample was reduced overnight at 320 °C in 10% H₂/N₂. This ensured that all the RuO_x species were reduced to catalytically active Ru⁰. The sample was then exposed to a 1000 ppm CO₂/air (20% O₂/ 80% N₂) mixture at 320 °C and 1 atm. This step was denoted as the “adsorption” step. For this step, 4 different sets of conditions were tested. Firstly, the flow rate of the air was tested at 10 mL/min and 40 mL/min. Additionally, 2 different adsorption durations-- 15 minutes and 30 minutes-- were tested. Table 1 denotes the different parameters used for each trial.

Additionally, a “blank” control trial was run without any DFM loaded in the quartz tube. Following the adsorption step, He gas was flown through the reactor for 5 minutes in order to purge the system of any residual O_2 . This was necessary to prevent any unintentional mixture of O_2 and H_2 . Following this was a methanation step, which was composed of 10% H_2/N_2 running through the reactor at 30 mL/min for 20 minutes. These steps-- adsorption, purge, methanation-- were classified as one cycle. For each trial, 3 cycles were performed. In order to monitor the composition of the gas as it exited the reactor, an Enerac portable emissions analyzer, capable of continuously monitoring CO_2 and CH_4 concentrations, was used. However, the precision of the Enerac was limited to detecting concentrations of gases at 0.1%. Since the adsorption step used air at a concentration of 0.1% CO_2 , the Enerac was not able to detect changes in the concentrations of CO_2 . Therefore, the results were limited to quantifying the amount of CH_4 produced. The Enerac gathered data from the product gas every second [15]. OriginPro was used to analyze the data.

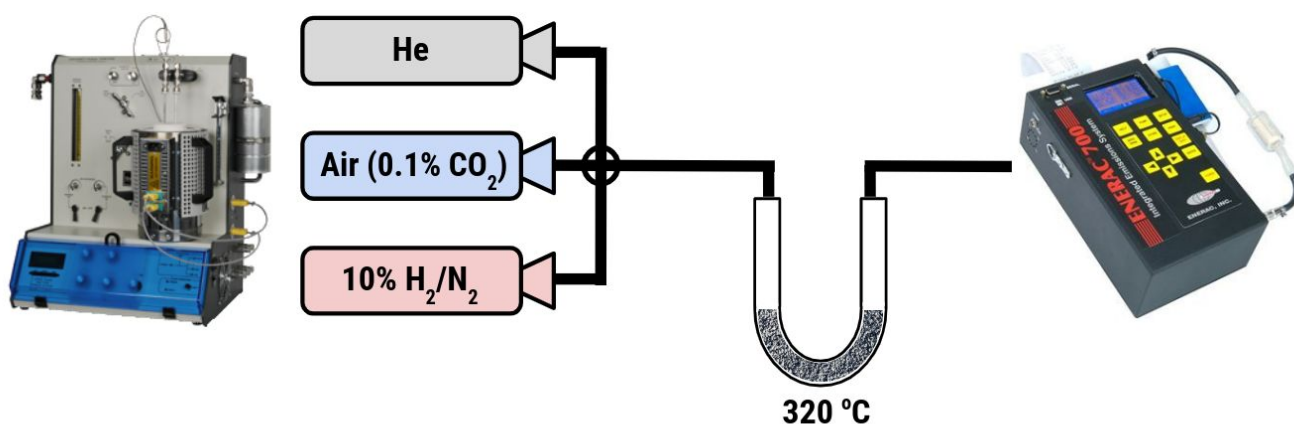


Figure 1- Visual display of the setup used for catalyst testing. Depicted on the left is the ChemBET Pulsar TPR/TPD unit (Quantachrome). Gases used in testing were Helium, Air (0.1% CO_2), and 10% H_2/N_2 at 320 °C. Depicted on the right is an Enerac 700, used for sample analysis of the gases.

3.0. Results and Discussion

3.1. Catalyst Testing

4 trials were run using DFM, each testing different combinations of parameters that pertained to the adsorption step in order to determine the favorable operating conditions for adsorption. The parameters tested were the flow rate of the air (10 mL/min & 40 mL/min) and the duration of the adsorption or adsorption time (15 min & 30 min). These trials can be denoted by the parameters of which they were testing [(10 mL/min, 15 min), (40 mL/min, 15 min), (10 mL/min, 30 min), (40 mL/min, 30 min)].

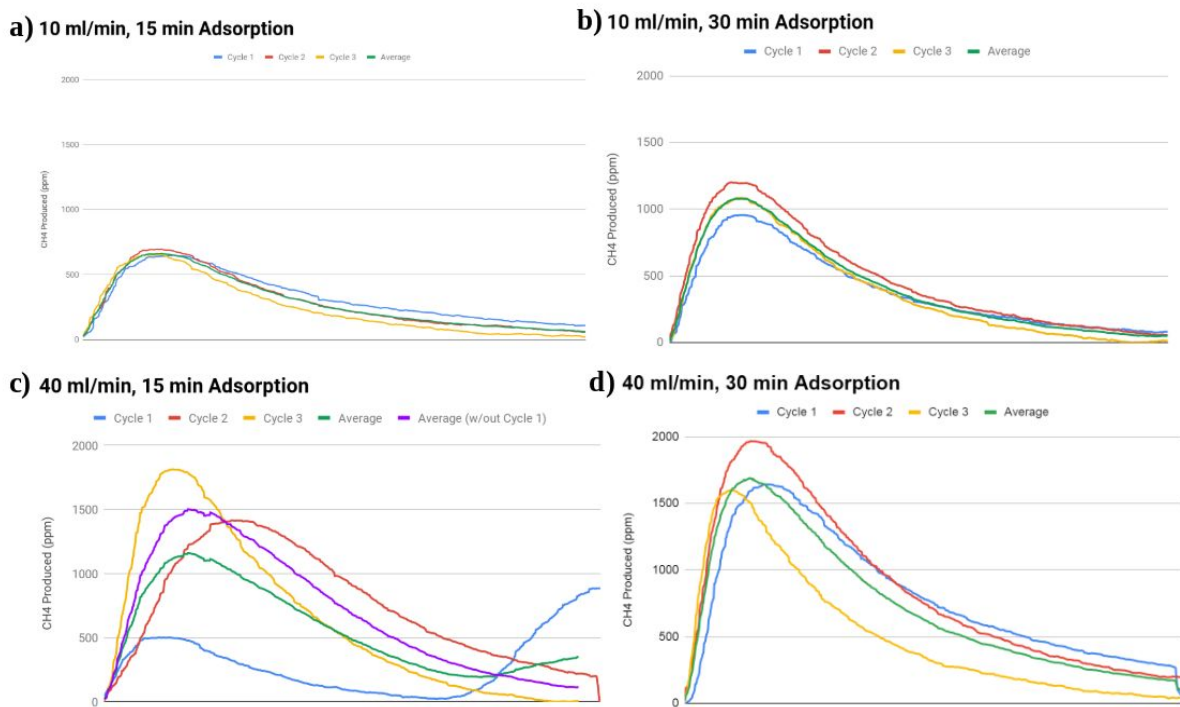


Figure 2- Methane production profiles in ppm per second, graphed by cycle (cycle 1=blue; cycle 2=red; cycle 3=yellow; average=green). Each cycle is graphed over a 20 minute time period. a) 10 mL/min, 15 min, b) 40 mL/min, 15 min, c) 10 mL/min, 30 min, d) 40 mL/min, 30 min

3.1.1. Flow Rate of Air

By comparing the methane profiles of figures 2a/2c and 2b/2d, the effects of changing the flow rate of air in adsorption can be seen. It should be noted that although these results display values for CH₄ production, differences between trials are a direct result of variance in parameters tested during adsorption, as all other parameters between trials remained constant. The faster flow rate of 40 mL/min had comparatively steeper slopes and greater areas under the curve than 10 mL/min, as shown in figures 2 and 3. This is further supported by the data displayed in table 2 and figure 6, which show that at a 15-minute adsorption time, a flow rate at 40 mL/min produced 49.51 μmol of CH₄ per gram of the catalyst, 1.4 times more than the 35.33 μmol of CH₄ produced at the 10 mL/min flow rate. Additionally, at a 30-minute adsorption time, a flow rate of 40 mL/min produced 122.41 μmol of CH₄ per gram of catalyst, 1.5 times more than the 81.77 μmol of CH₄ produced at the 10 mL/min flow rate. Overall, the results support the conclusion that a faster flow rate of air leads to greater levels of CO₂ saturation of the DFM. Additionally, it has been shown that higher gas velocities induce higher rates of particle contact in gas-solid setups [20]. This means that because the gas was flowing at a faster rate (40 mL/min), more CO₂ molecules attached to the DFM which led to more CH₄ being produced.

$\mu\text{mol CH}_4$ Produced/ g of Catalyst:				
Trial:	Cycle 1:	Cycle 2:	Cycle 3:	Average:
10 mL/min for 15 minutes:	44.26204535	35.70292994	26.01967505	35.32821678
40 mL/min for 15 minutes:	45.12435243	50.15721199	53.2468424	49.50946894
10 mL/min for 30 minutes:	48.79290946	109.6914371	86.83351231	81.77261962
40 mL/min for 30 minutes:	135.7757564	145.2301949	86.22763234	122.4111946

Table 2- Table displaying the μmol of CH_4 produced per gram of catalyst for each trial.

3.1.2. Adsorption Time

By comparing the methane profiles of figures 2a/2b and 2c/2d, the effects of changing the adsorption times can be seen. Comparatively, figures 2b and 2d, which represent the 30-minute adsorption, show higher peaks and steeper slopes than 2a and 2c, which represent the 15-minute adsorption. Furthermore, table 1 and figure 4 show that at a 10 mL flow rate a 30 min adsorption produced 2.3 times more μmol of CH_4 per gram of catalyst than a 15 min adsorption. Additionally, at a 40 mL flow rate, a 30 min adsorption produced 2.5 times more μmol of CH_4 per gram of catalyst than a 15 min adsorption. Evidently, it can be concluded that a longer adsorption time of 30 minutes is comparatively better than 15 minutes for the adsorption of CO_2 and the production of CH_4 .

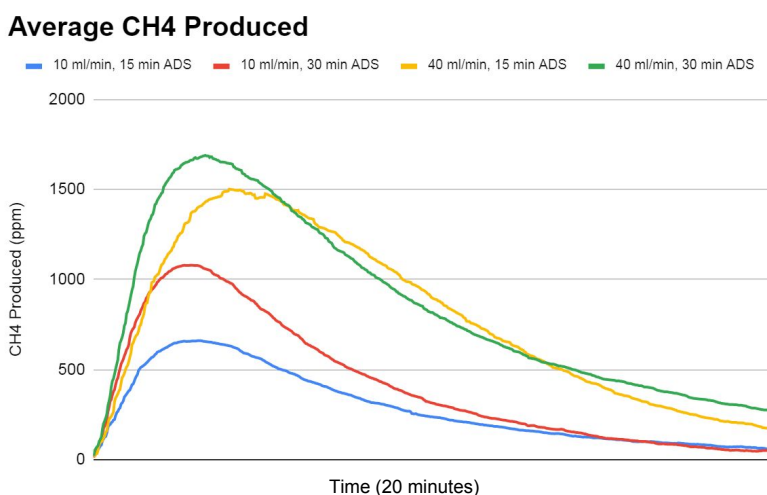


Figure 3- Graphical display over 20 minutes of the averages of the values of each trial for CH_4 produced in ppm, read by the Enerac 700 (Blue=10 mL/min for 15 min; Red=10 mL/min for 30 min; Yellow=40 mL/min for 15 min; Green=40 mL/min for 30 min)

Overall, relative to the four trials ran, an adsorption time of 30 minutes and a flow rate of 40 mL/min of air produced the most CH₄ per gram of catalyst. This suggests that longer adsorption times and faster flow rates of air yield greater levels of CO₂ adsorption, and therefore better DFM performance. All p-values calculated (shown in figure 4) were less than 0.05, indicating statistical significance.

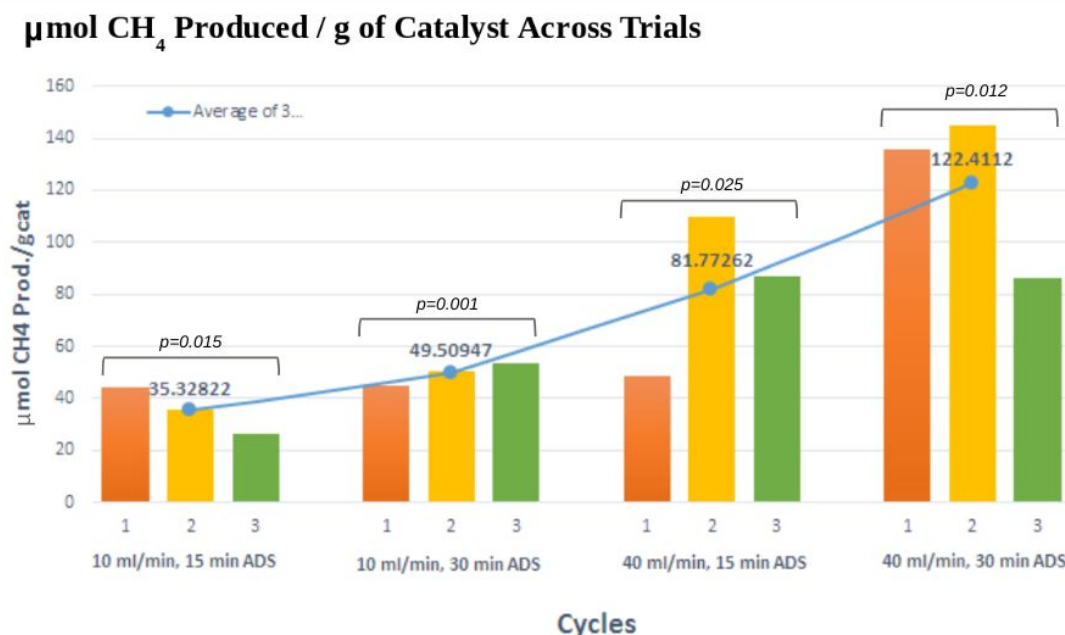


Figure 4- Graphical display of data in Table 2. Cycles are represented using 3 different colors within trials (1=Orange, 2=Yellow, 3=Green). Blue points represent average values of 3 cycles between trials. All calculated p-values < 0.05

3.2. Limitations

The limitations of this study were primarily based on two factors. The first was a lack of time. Due to the time constraints placed on this study-- it could only be performed over the 2-month summer break-- there was not enough time to run all the trials that were intended. If given more time, trials would be conducted at temperatures ranging from 250 °C to 320 °C. A second limitation was equipment-based. Due to the Enerac 700 only being able to detect changes in CO₂ concentration as low as 0.1% and the concentration of CO₂ in air being 0.1%, significant changes in CO₂ concentration could not be recorded. Additionally, since the DFM produced significantly different amounts of CH₄ between the 4 trials, it is very unlikely that the catalyst was ever fully saturated with CO₂. This is further supported by the fact that previous studies with DFM using flue gas (10-15% CO₂) have yielded about 200 μmol of CH₄ per gram of catalyst, compared to the 122.4 μmol of CH₄ produced using 0.1% CO₂ at 40 mL/min for 30 minutes. Furthermore, 1000 ppm is not totally representative of CO₂ concentrations in ambient air (~400 ppm).

Therefore, further tests with the correct concentration need to be run in order to create more accurate results and analysis.

4.0. Conclusion and Future Applications

Dual Functional Materials, or DFM, composed of 0.5% Ru, 6.1% Na₂O supported on Al₂O₃, was tested using air with extremely low concentrations of CO₂ (1000 ppm) for prospective application to Direct Air Capture. The objective of this study was to determine favorable air flow rates and adsorption times for DFM to operate under in order to maximize CO₂ adsorbed and CH₄ produced. After completion, it can be concluded that a flow rate of 40 mL/min of air and an adsorption time of 30 minutes are the most optimal pair of conditions out of the ones tested.

Further testing should be conducted of more operating conditions-- such as temperature-- in order to further optimize the adsorption of CO₂. Additionally, since it is unlikely that any of the combinations of conditions tested in this study yielded a fully saturated sample, future tests should ensure that the adsorption time is long enough for the sample to approach full saturation. Overall, the encouraging results of this study demonstrate that DFM is a promising candidate for applications in DAC.

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