

# Dual function materials for CO<sub>2</sub> capture and conversion using renewable H<sub>2</sub>

Melis S. Duyar<sup>1</sup>, Martha A. Arellano-Treviño<sup>2</sup>, Robert J. Farrauto<sup>1\*</sup>

<sup>1</sup>Columbia University, Earth and Environmental Engineering, 500 W 120<sup>th</sup> Street, 10027 New York, NY, USA

<sup>2</sup>Columbia University, Chemical Engineering, 500 W 120<sup>th</sup> Street, 10027 New York, NY, USA  
\*rf2182@columbia.edu

## Introduction

In order to prevent further accumulation of CO<sub>2</sub> in the atmosphere, it must be captured for storage or converted to useful products. Current materials and processes for CO<sub>2</sub> capture are energy intensive. We report novel dual function solid adsorbent/catalytic materials (DFM), both components of which capture CO<sub>2</sub> from an emission source and at the same temperature (320°C) in the same reactor convert it to synthetic natural gas, requiring no additional heat input. The DFM consists of Ru as methanation catalyst and nano dispersed CaO as a CO<sub>2</sub> adsorbent, both dispersed on a porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier. Upon the addition of stored renewable H<sub>2</sub> a spillover process drives CO<sub>2</sub> from the sorbent to the Ru sites where methanation occurs. This approach utilizes flue gas sensible heat and eliminates the current energy intensive and corrosive capture and storage processes without having to transport captured CO<sub>2</sub>. The CH<sub>4</sub> produced is recycled to the front end of the process where it is again combusted for power generation.

Our previous work has shown that CaO dispersed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) behaves radically different compared to bulk or unsupported CaO. This dispersion creates nano-sized islands of CaO, which are able to reversibly chemisorb CO<sub>2</sub> and therefore capture and release it at moderate temperatures (~300°C) compared to bulk CaO (~800°C)<sup>1,2</sup>. This is a critical advantage due to reversible adsorption and methanation at the same temperature.

## Materials and Methods

Dual function materials were prepared by incipient wetness impregnation of either Ru(NO)(NO<sub>3</sub>)<sub>2</sub> on 10 wt.% CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or of Ca(NO<sub>3</sub>)<sub>2</sub> on 10 wt.% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Detailed preparation procedures for CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>2</sup> and Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>3</sup> can be found in our previous work. All samples were dried in air at 120°C for 1 hour and calcined in air at 320°C for 2 hours. This pretreatment ensured the decomposition of Ru(NO)(NO<sub>3</sub>)<sub>2</sub> to Ru. The DFMs received in-situ pre-reduction in 4%H<sub>2</sub>/N<sub>2</sub> at 320°C for 2 hours at the beginning of each reactor test to ensure decomposition of Ca(NO<sub>3</sub>)<sub>2</sub> to CaO.

Cyclic testing in a packed bed reactor: 1.0344g powder 5%Ru,10%CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was packed inside a quartz tube housed in a furnace. Gas analysis was performed on-line via an Enerac, an IR based gas analyzer for combustion applications. The DFM was pre-reduced in-situ at 320°C for 2 hours using 5% H<sub>2</sub>/N<sub>2</sub> (46.3 mL/min). CO<sub>2</sub> capture was performed from a source of 8%CO<sub>2</sub>/21%H<sub>2</sub>O/Air (22.1 mL/min). One cycle consisted of CO<sub>2</sub> capture, He purge and methanation. After CO<sub>2</sub> capture for 20 minutes the reactor was purged with He until CO<sub>2</sub> and O<sub>2</sub> could no longer be detected at the exit. This was followed by methanation, with 5%H<sub>2</sub>/N<sub>2</sub> for 20 minutes. The cyclic experiment was performed with the same volume of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a background test during which methanation was not observed.

## Results and Discussion

CO<sub>2</sub> capture and subsequent methanation was demonstrated with Ru and CaO compositions that varied between 0-10 wt.% at a temperature of 320°C. 5%Ru 10%CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was chosen as the optimum composition and was further investigated under realistic power plant CO<sub>2</sub> capture conditions (in the presence of air and steam). Figure 1 displays stable methanation performance for the 20-cycle test where CO<sub>2</sub> capture was performed from 8%CO<sub>2</sub>/21%H<sub>2</sub>O/Air and subsequently methanated (both at 320°C). The average methanation capacity was 0.27 g-mol/kg DFM. The methane released had an average purity of 99.9% over all 20 cycles. The high purity of methane released creates the advantage of simplicity in overall process design. A high purity methane yield eliminates the need for downstream catalytic treatments to prepare the gas for injection to natural gas pipelines or recycle to the front end of the process.

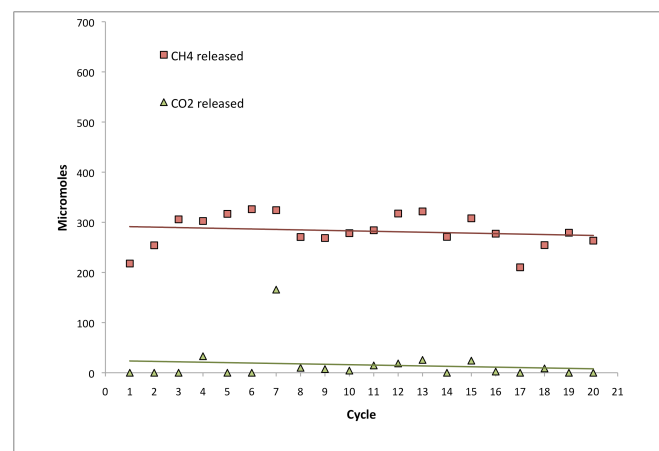


Figure 1: CH<sub>4</sub> and CO<sub>2</sub> released during methanation for 20 cycles. T=320°C.

## Significance

The use of synthetic fuels made from CO<sub>2</sub> as carriers for excess renewable electricity offers a solution to manage fluctuating output of renewable energy while mitigating CO<sub>2</sub> emissions and producing a useful fuel. Capturing CO<sub>2</sub> and releasing it as a fuel using a single reactor can make CCS more feasible by eliminating problems related to the energy intensity of sorbent regeneration, transportation and processing of captured CO<sub>2</sub> and injection of CO<sub>2</sub> underground for storage.

## References

1. P. Gruene, A. G. Belova, T. M. Yegulalp, R. J. Farrauto and M. J. Castaldi, *Industrial & Engineering Chemistry Research*, 2011, **50**, 4042-4049.
2. M. S. Duyar, R. J. Farrauto, M. J. Castaldi and T. M. Yegulalp, *Industrial & Engineering Chemistry Research*, 2014, **53**, 1064-1072.