

Article

The Role of Ruthenium in CO₂ Capture and Catalytic Conversion to Fuel by Dual Function Materials (DFM)

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Abstract: Development of sustainable energy technologies and reduction of carbon dioxide in the atmosphere are the two effective strategies in dealing with current environmental issues. Herein we report a Dual Function Material (DFM) consisting of supported sodium carbonate in intimate contact with dispersed Ru as a promising catalytic solution for combining both approaches. The Ru-Na₂CO₃ DFM deposited on Al₂O₃ captures CO₂ from a flue gas and catalytically converts it to synthetic natural gas (i.e., methane) using H₂ generated from renewable sources. The Ru in the DFM, in combination with H₂, catalytically hydrogenates both adsorbed CO₂ and the bulk Na₂CO₃, forming methane. The depleted sites adsorb CO₂ through a carbonate reformation process and in addition adsorb CO₂ on its surface. This material functions well in O₂- and H₂O-containing flue gas where the favorable Ru redox property allows RuO_x, formed during flue gas exposure, to be reduced during the hydrogenation cycle. As a combined CO₂ capture and utilization scheme, this technology overcomes many of the limitations of the conventional liquid amine-based CO₂ sorbent technology.

Keywords: supported Ru and sodium carbonate; dual function material; CO₂ capture in flue gas; conversion to synthetic natural gas; redox properties of Ru

1. Introduction

As predicted by the Intergovernmental Panel on Climate Change (IPCC), carbon dioxide in the atmosphere may reach 570 ppmv by the year of 2100, accompanied by a rise in the mean global temperature of 1.9 °C and mean sea level by 38 cm [1–3]. Excess carbon dioxide emission results primarily from anthropogenic activities by fossil fuel combustion for power generation, industrial manufacturing, and transportation [4]. Due to the CO₂ accumulation and the rising demand of energy, sustainable energy development [5,6], and CO₂ capture, storage and utilization (CCSU) [7] are two efficient methods to combat green-house gas emissions and associated climate change.

For a decade, various processes and materials have been proposed for CO₂ capture, with extensive reviews available [8,9]. The aqueous amine-based sorbent technology is still the most popular and developed approach toward capturing CO₂ from flue gas. However, the sorbent regeneration for separation of CO₂ and H₂O from the amine solution by distillation is highly energy intensive. The separated CO₂ must then be transported to a recovery site for processing, which adds to the expense. Furthermore, the O₂ containing flue gas deteriorates the amine, limiting its ability to be recycled [10].

Recently, several unique material combinations and processes for upgrading CO₂ have been reported. A super-dry reforming process involving chemical looping in which CO₂ is utilized for enhancing CO production at 750 °C has been reported. Nickel catalyzes the dry reforming of CH₄

leading to a redox reaction of iron oxides. CO₂ is adsorbed on CaO/Al₂O₃, providing a series of equilibrium shifts enhancing CO production for ultimate use in synthesis gas reactions [11]. Another interesting approach for enhanced CO production combines a reduced Fe, Cr, Cu reverse water gas shift (RWGS) catalyst with K₂CO₃ as a CO₂ adsorbent. Approximately 6% CO₂ in N₂ is adsorbed on K₂CO₃ at 550 °C. At the same temperature, injected H₂ reacts with adsorbed CO₂ generating CO and H₂O via the RWGS reaction. A weakness in the process is the deterioration of performance in O₂, limiting this to O₂-free CO₂ streams [12].

Ruthenium is a well-known noble metal catalyst often used commercially for homogeneous or heterogeneous catalytic reactions requiring a high degree of product selectivity, including aromatic ring saturation to cyclo-hexyl derivatives, saturation of allyl compounds, organic acid hydrogenation to alcohols, hydrogenation of sugars [13], steam reforming of hydrocarbons for H₂ production [14], selective homogeneous catalysis for the oxidation of primary alcohols to aldehydes [15], and homogenous chiral synthesis [16]. It is also used for ammonia synthesis [17], preferential oxidation of CO in H₂ [18], Fischer-Tropsch processes [19], electrochemical chlorine evolution [20], and methanation of CO and CO₂ [21–23]. In representative reactions, such as those mentioned above, all require either the metal, its oxide, or an organo-metal complex form of Ru as the catalyst. A unique feature of Ru/RuO_x is its redox chemistry of rapid and reversible transformation between its oxide and metallic states.

We are now reporting a work-in-progress combining a series of adsorption and catalytic reactions for converting adsorbed CO₂ emitted from power plant oxygen-containing flue gas where the redox property of Ru/RuO_x is critical for successful use. The material used for this process is composed of a nano-dispersed [24] alkaline component in intimate contact with Ru on a high surface area carrier (Al₂O₃), referred to as a Dual Function Material (DFM). It adsorbs CO₂ on its alkaline component and catalytically converts it to synthetic natural gas (i.e., CH₄) in the subsequent step over the Ru catalyst approaching a closed loop for carbon utilization. The sequential steps will be discussed below.

Alkaline carbonates have been reported to be efficient for CO₂ adsorbents [25]. What is the most relevant to our new materials is the ability to adsorb CO₂ and then hydrogenate catalytically to methane. The catalytic hydrogenation of a series of carbonates was first reported by Tsuneto et al. in 1992 [26] and Yoshida et al. in 1999 [27]. A variety of transition metal catalysts (but not Ru) were physically mixed with the carbonates and hydrogenation was conducted. The carbonate was completely hydrogenated but there was no attempt to reform the carbonate by CO₂ capture.

We have demonstrated that a DFM, containing 5% Ru, 10% Na₂CO₃/Al₂O₃, captures CO₂ both on the carbonate surface and depleted bulk carbonate sites, which are subsequently hydrogenated to CH₄. In a typical implementation of this material, the methane produced is dried and compressed and recycled to the inlet of the power plant or integrated into the natural gas grid, ideally closing the carbon cycle. Thus, this material provides an additional source of sites for CO₂ capture by carbonate reformation, yielding an increase in subsequent methane production. For this scheme to be used, H₂ used for methanation needs to be generated from water electrolysis, the energy of which is provided by excess solar or wind energy [22]. Installations for water electrolysis powered by solar energy for H₂ vehicle fueling stations has been announced between Guangdong Synergy Hydrogen Power Technology (Guangdong, China) and Proton On Site (Wallingford, CT, USA). Installations in Foshan and Yunfu, cities in China, will be initial locations [28]. Thus it is expected that renewable H₂ will be available in selected locations.

The two-step sequential reactions involve first the selective adsorption of CO₂ from O₂-containing flue gas on the DFM. During this step, the Ru in the DFM is oxidized to RuO_x. Upon CO₂ saturation, the flue gas is diverted to an identical parallel reactor where CO₂ capture continues. Renewable H₂ is added to the reactor containing the saturated DFM where it rapidly reduces the RuO_x to its metallic and active state, and methanation proceeds via CO₂ spill over to the Ru sites. All steps are conducted at the same temperature (~320 °C) [29]. Therefore, the reversibility of the redox chemistry of Ru/RuO_x

makes it unique for this process relative to commonly used Ni, which when oxidized will not reduce under the conditions of this process [30–32].

This paper reports cyclic aging studies from a simulated flue gas demonstrating stable repeatable cycles of CO₂ adsorption and methanation. The importance of H₂ exposure intensity will also be discussed. The price of Ru should not be confused the more expensive among precious metal catalysts. Its price per gram as of 21 December 2016, was Ru \$1.25, Rh \$24.53, Pt \$28.40, and Pd \$20.60 with all recycled for continued use.

2. Results and Discussion

2.1. Na₂CO₃ Loading Study

Various carbonate-containing materials were evaluated on a thermal gravimetric analysis (TGA) for reversible CO₂ adsorption. The CO₂ adsorbed and methanation in mmol per gram on Al₂O₃ supported K₂CO₃, Na₂CO₃, and MgO powder adsorbents with weight loadings from 5% to 20% were previously reported [30]. In this study K₂CO₃ and Na₂CO₃ showed the largest CO₂ adsorption relative to Al₂O₃ supported CaO and MgO. 10% Na₂CO₃ on Al₂O₃ achieved the highest adsorption capacity (0.11 mmol/g), and was therefore selected for additional adsorption studies. Figure 1 shows TGA results for CO₂ adsorption and reversible desorption for dispersed Na₂CO₃ on Al₂O₃ at different loadings.

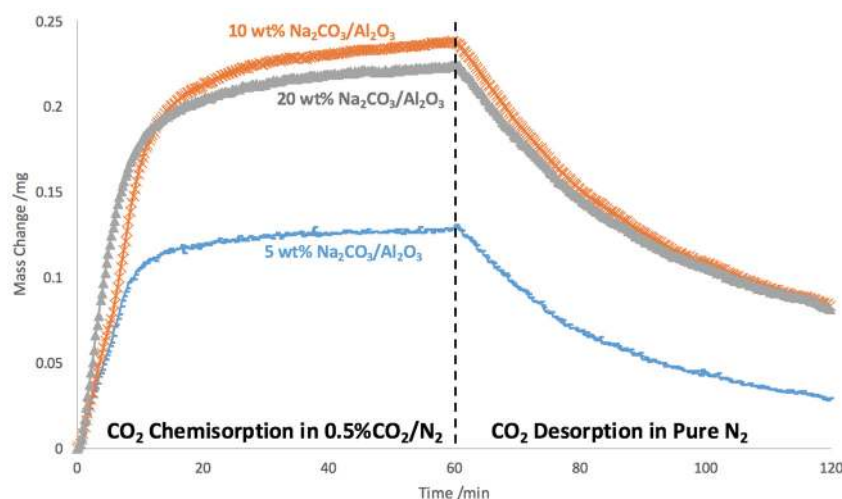


Figure 1. Thermal Gravimetric Analysis (TGA) adsorption studies conducted at 320 °C for 50 mg of powder. Before the adsorption the samples were degassed in 2% H₂/N₂ for 2 h, then exposed to 0.5% CO₂ in N₂ and subsequently pure N₂.

Figure 1 indicates 10 wt % Na₂CO₃/Al₂O₃ obtained the highest capacity of CO₂ adsorption (0.11 mmol/g) among other Na₂CO₃ loadings. The pure N₂ purge verifies that Na₂CO₃ dispersed on γ -Al₂O₃ powder has the ability of desorb the CO₂ reversibly in situ, consistent with dispersed CaO/Al₂O₃ substantiating that the binding interaction between CO₂ and adsorbents is weak [33]. This property insures the desorption and spill-over of CO₂ to Ru catalytic sites for methanation.

Based on the methanation capacities, DFM composed of 5% Ru, 10% Na₂CO₃/Al₂O₃ generated the most methane (1.05 mol CH₄/kg of DFM) compared to other adsorbents at the same loading [30]. Herein, further studies were conducted on Al₂O₃ supported Ru-Na₂CO₃ DFM.

2.2. Carbonate Hydrogenation Study

A H₂ activation (reduction) step was conducted using unsupported Ru-Na₂CO₃ to understand the decomposition profile of Ru nitrosyl nitrate used in the powder preparation procedure. However,

a greater weight loss than expected was observed indicating hydrogenation of the carbonate in the sample was also occurring. Results all conducted at 320 °C using the TGA is shown in Figure 2 in which the final step shows CO₂ adsorption.

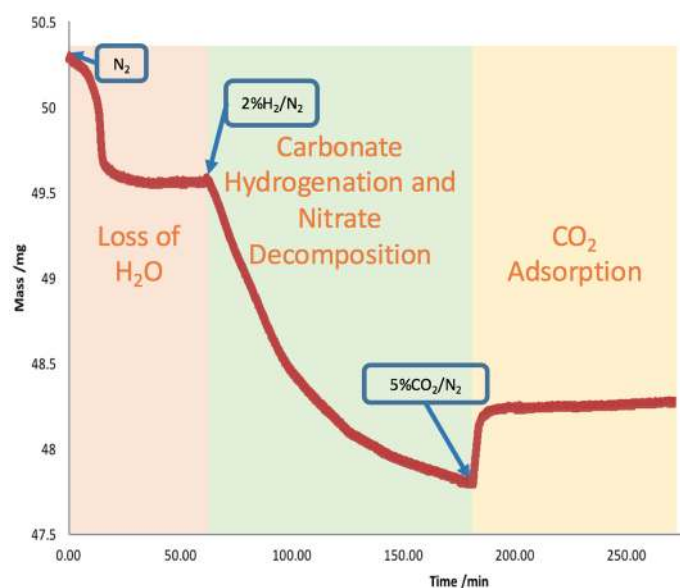


Figure 2. TGA result of Ru salts and carbonate hydrogenation study operated at 320 °C for 50 mg of 1.44% Ru/Na₂CO₃ powder sample.

During the sample preparation, the 50 mg of 1.44% Ru/Na₂CO₃ was dried at 120 °C for 2 h and calcined at 250 °C for 2 h in air. When the precursor Ru(NO)(NO₃)₃ is heated, it has been reported that a mixture of oxides such as RuO, RuO₂, RuO₃, and RuO₄ [33,34] form depending on the temperature.

After a one-hour N₂ purge at 320 °C, the sample achieved stable weight as water and/or other volatile components evaporated. At this point, 2% H₂/N₂ was introduced. During the two-hour H₂ exposure, Ru is expected to reduce, nitrate decompose, and some carbonate hydrogenate. The stable weight decreased by 1.763 mg. Assuming the Ru(NO)(NO₃)₃ remained in its original form as it is in the precursor, the expected weight loss would be 1.332 mg or 65.37% of the total mass loss. Therefore, the residual mass loss (an additional 34.63%) can be explained by carbonate hydrogenation catalyzed by the newly formed Ru metal. It is clear from Figure 2 that a continuing weight loss likely occurs due to the slow hydrogenation of the carbonate. After about 120 min of pretreatment, the sample showed an ability to re-adsorb CO₂ in depleted sites, replacing some of that which was hydrogenated.

2.3. Hydrogen Exposure Time Study

50 mg of 5% Ru, 10% Na₂CO₃/Al₂O₃ powder sample was subjected to a one-hour pretreatment in 2% H₂/N₂ at 320 °C. In Figure 3, a rapid adsorption of CO₂ up to 1.2 mg from a feed gas of 5% CO₂ in N₂ was observed. Upon the addition of 2% H₂/N₂ three distinct slopes of weight loss vs time are observed. The largest slope, between 30 and 35 min, was 0.086 mg/min. The second between roughly 35 and 70 min was 0.00952 mg/min and the third about 0.00195 mg/min from 70 to 660 min. The first loss, associated with the largest slope, occurs from 1.2 mg to 0.66 mg is likely due to methanation of the CO₂ adsorbed on the Ru metal. This weight loss is approximately 50% of the Ru atoms present assuming 1 CO₂ adsorbed per Ru site. It is also possible 1 CO₂ adsorbs on two Ru sites for dissociative adsorption to CO and atomic O [23]. The second slope has a weight loss of about 0.45 mg which is twice that observed for CO₂ adsorbed on 10% Na₂CO₃/Al₂O₃ (see Figure 1) suggesting that additional sites for CO₂ adsorption have become available due to the depleted sites generated by the hydrogenation of the bulk carbonate itself upon the addition of H₂. The second slope is speculated to be the hydrogenation weakly adsorbed CO₂ on the carbonate surface most of which

has spilled over to the Ru sites where the heat liberated (not shown) is indicative of methanation. The weight loss associated with the lowest slope is less than 0.2 mg as is believed to be hydrogenation of the bulk carbonate. This is speculative, since Figure 1 was generated with a feed gas of only 0.5% CO₂/N₂ while Figure 3 was conducted with 5% CO₂/N₂. However, CO₂ chemisorption reaches a plateau where it becomes independent of partial pressure.

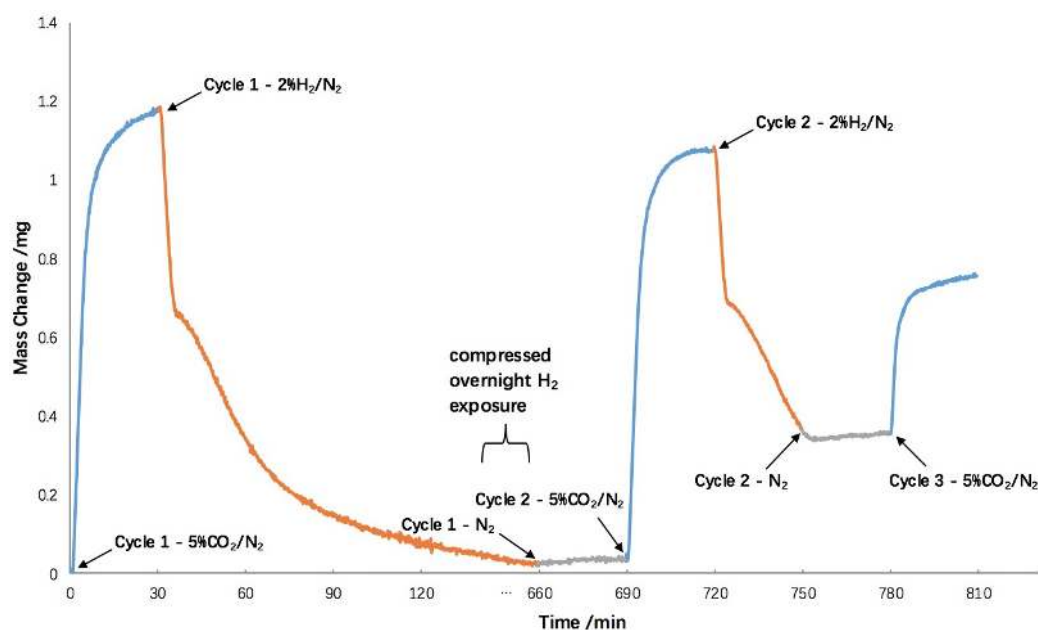


Figure 3. TGA result of the 3-cycle test for 50 mg of 5% Ru, 10% Na₂CO₃/Al₂O₃ at 320 °C. The plot excluded the over-night activation step at 320 °C in 2% H₂/N₂. The long tail of low weight loss in the first cycle was compressed indicating an overnight (10.5 h) hydrogen exposure at 320 °C.

For the 2nd cycle, the mass gain for CO₂ adsorption was similar to the first cycle. However, with only 30 min of hydrogen exposure, the weight loss was significantly less than after the longer time exposure in cycle 1. In the third cycle it is likely only the Ru metal and the surface of Na₂CO₃ adsorb CO₂ since insufficient hydrogenation of the bulk carbonate had occurred with only a 30-min exposure. It is clear that bulk carbonate hydrogenation is dependent on exposure time and hydrogen partial pressure. This will be demonstrated in the following studies.

2.4. 10-Cycle Test in CO₂ Feed

Although the primary commercial target of our research is focused on power plant exhaust gases containing O₂ and steam, there are applications where they are not present, such as fermentation, land fill, and cement manufacturing effluents. Therefore, an aging test consisting of 10 cycles using 7.5% CO₂/N₂ for the adsorption was conducted in our scaled up reactor with DFM pellets. This is more consistent with industrial processes since fine powdered materials create operational, technical and health problems for workers. For example, in a fixed bed reactor, powders have high pressure drop [35] and expose operators to possible risk of chronic human health issues such as respiratory problems and lung cancer [36]. In order to avoid such issues and facilitate commercialization, a process was conducted with 10 grams of freshly prepared pelleted DFM (5 mm × 5 mm tablets of γ-Al₂O₃) and cycle tested in a larger scale fixed bed reactor.

The results for CO₂ adsorption and methanation under O₂-free conditions are shown in Figure 4. Given the slow kinetics for bulk carbonate hydrogenation experienced in Figure 3, the H₂ was increased to 5% H₂/N₂. The Ru-Na₂CO₃ DFM achieved stable adsorption and methanation performance for 10 successive cycles and is expected to maintain this advantage over many more cycles. However,

the average conversion efficiency of the adsorbed CO₂ converted to methane was only 60.5%. A large amount of desorbed CO₂ was observed at the reactor outlet. The 39.5% unreacted CO₂ released is likely due to its premature desorption caused by the large exotherm of methanation. We intend to address this by performing parametric studies for feed gas components (i.e., H₂ partial pressure) and process variations. It is also logical to locate a small Ru catalyst downstream to complete methanation of the unconverted CO₂. Conditions of our experiments were controlled to avoid CO formation. CO is only produced at higher temperatures and space velocities over Ru as shown in reference [23].

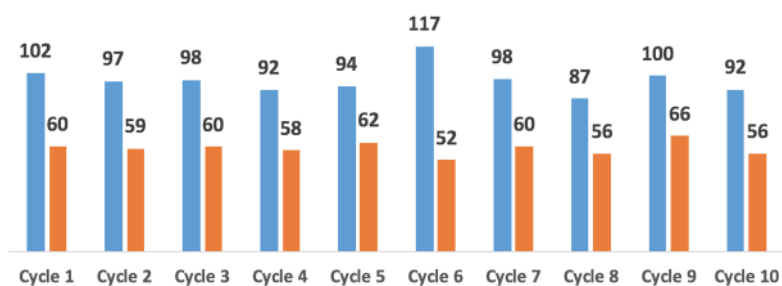


Figure 4. CO₂ adsorption and methanation cycles (10) using 10 grams of the Ru-Na₂CO₃ DFM (5% Ru, 10% Na₂CO₃/Al₂O₃) pellets in a fixed packed bed reactor with 7.5% CO₂/N₂ at 320 °C. A 150-min of 5% H₂/N₂ exposure was used during pretreatment followed by 10 identical CO₂ adsorption-methanation cycles. 5% H₂/N₂ for 30 min was used for the methanation cycles. The volumes of CO₂ adsorbed and CH₄ produced are shown in the figure.

2.5. 12-Cycle Test in Simulated Flue Gas

Performance of the pelleted Ru-Na₂CO₃ DFM in simulated O₂-and-steam-containing flue gas is another key factor for its commercialization and application. A 12-cycle test was conducted in the fixed bed reactor with the performance shown in Figure 5. The results of BET specific surface area of the fresh and after-12-cycle Ru-Na₂CO₃ pelleted DFM sample is shown in Table 1, in which the small change is consistent with the stable performance of the sample. Table 1 reports the BET and Ru crystallite sizes for fresh and cyclic aged DFM. Some sintering is observed. However, given the low temperatures of the process, this is not expected to be a major source of deactivation. Extended cyclic aging will be necessary to more definitively determine the major sources of deactivation. These studies will be soon initiated. Crystallite sizes (d) were calculated from the equation $d = (103/\%D)$ where %D = % dispersion and 103 is the constant related to the number of Ru atoms present in the samples determined from room temperature H₂ chemisorption [37].

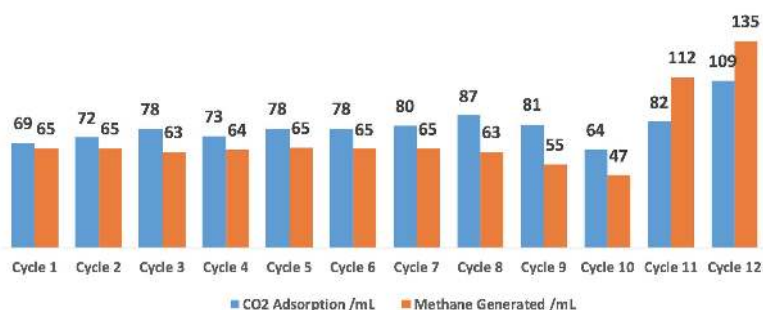


Figure 5. CO₂ adsorption and methanation using 10 grams of the Ru-Na₂CO₃ DFM (5% Ru, 10% Na₂CO₃/Al₂O₃) pellet for the 12-cycle test conducted in the fixed bed reactor in simulated flue gas at 320 °C. Pretreatment of the DFM was conducted with 5% H₂/N₂ for 150 min before the first cycle. For cycles 2–10, hydrogen exposure was 30 min. Before cycle 11 another 150-min 5% H₂/N₂ exposure was added, and for cycle 12, 48 h H₂ exposure. The volumes shown in the figure are for CO₂ adsorbed and CH₄ produced.

Table 1. Brunauer-Emmett-Teller (BET) specific surface area of the fresh and flue gas cyclic aged Ru-Na₂CO₃ DFM pellets. Ru crystallite sized for fresh and cyclic aged samples based on H₂ chemisorption assuming H/Ru = 1/1.

| Sample | BET Specific Surface Area (m ² /g) | Ru Crystallite Sizes (nm) |
|--|---|---------------------------|
| Fresh Ru-Na ₂ CO ₃ DFM pellet | 103 | 3.98 |
| Flue gas cyclic aged Ru-Na ₂ CO ₃ DFM pellet | 89 | 5.15 |

The CO₂ adsorption capacity was reduced compared to the O₂ free process of Figure 4, because Ru was inactivated—for CO₂ adsorption—to RuO_x by O₂ in the simulated flue gas. Both adsorption and methanation capacity remained relatively stable until the 9th cycle, when reduction in both CO₂ adsorption and CH₄ produced was noted. Since both CO₂ adsorption and methanation are linked to Ru activity, it was reasonable to assume that the RuO_x was not sufficiently reduced, causing a loss in both performances.

Before the 11th cycle, the material was given an extra 150-min of hydrogen exposure, resulting in a recovery of both CO₂ adsorption and methanation. When the extra hydrogen exposure was extended to 48 h before the 12th cycle, both capacities reached even higher levels. This apparent deactivation was not observed in the O₂ free cycle tests of Figure 4. This again demonstrated the importance of H₂ partial pressure in maintaining Ru reduced while enhancing the rate of bulk carbonate hydrogenation.

The average conversion of adsorbed CO₂ converted to methane during the 12-cycle test was 89.6%, which is a great improvement compare to the 10-cycle test in the dry CO₂ feed (60.5%). Though the overall CO₂ adsorption of the 12-cycle test in the simulated flue gas was lower than in the 10-cycle test, the conversion efficiency of 12-cycle test is preferred. Water generated at the surface during methanation may oxidize the surface of Ru. Therefore, a minimum H₂ partial pressure is required to maintained Ru in the reduced and active state. We have found that H₂ partial pressure is a critical parameter necessary for reducing the RuO_x formed during CO₂ adsorption (Figure 5) and methanation (Figure 6). This will be confirmed in the future.

2.6. Effect of H₂ Partial Pressure on CO₂ Hydrogenation and RuO_x Reduction

As observed for Figure 5, the loss in performance was reversed by increasing the exposure time of the DFM to H₂. It is reasonable to assume that increasing the partial pressure of H₂ would have the same effect by maintaining the Ru in the metallic and active state while increasing the extent of carbonate hydrogenation. This was demonstrated in Figure 6 where 10% H₂/N₂ dramatically increased the amount of methane produced (131 mL) compared to 5% H₂/N₂ (58.66 mL). This also points to the importance of the redox chemistry of Ru/RuO_x. It is logical to assume that during the 12-cycle simulated flue gas test (Figure 5), Ru was oxidized and there was insufficient H₂ to re-reduce it.

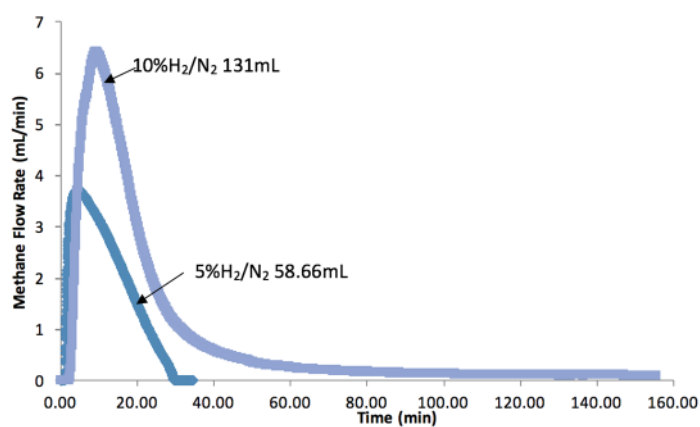


Figure 6. Methane production comparison of 5% H₂/N₂ and 10% H₂/N₂. The test was operated using 10 grams of 5% Ru, 10% Na₂CO₃/Al₂O₃ pellets in the large fixed bed reactor. The operational conditions were at 320 °C, 300 mL/min of 7.5% CO₂/N₂ for CO₂ adsorption. The volume of methane produced are shown.

The rate and extent of RuO_x reduction is critical for the flue gas operation. In TGA experiments the rate and extent of RuO_x reduction was to understand the minimum H₂ content needed for rapid reduction of the oxides of Ru. Results are shown in Figure 7. It is clear the reduction rate (slope) increases with H₂ content (0.069 mg/min at 1.30% H₂ to 0.370 mg/min at 2.86% H₂). The most dramatic increase occurs for H₂ > 1.3%. Equally as significant is the decrease in time for initiation of reduction as the H₂ content increases. This points to the reducibility of RuO_x to Ru, making it more suitable for the DFM flue gas process relative to NiO_x to Ni metal [32] that requires temperatures in excess of 500 °C for reduction.

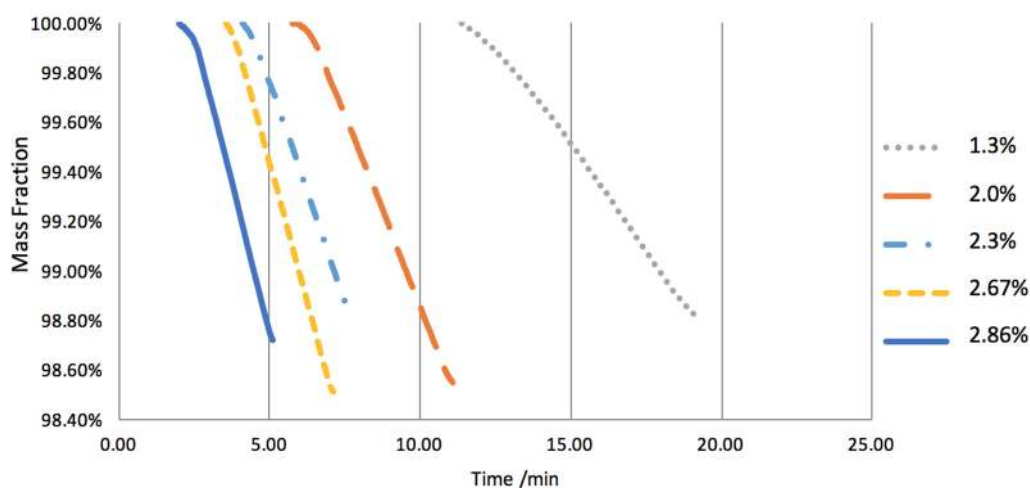


Figure 7. TGA results of RuO_x reduction on 50 mg 5% Ru/Al₂O₃ powder samples H₂ partial pressures from 1.3% to 2.86% at 300 °C. Only reduction sections are shown in the figure.

2.7. Speculated Functional Pathway of the Ru-Na₂CO₃ DFM

The speculated pathways for each step and component in DFM are summarized in Table 2. The RuO_x, as prepared, must be activated to its active metallic state for methanation. For feeds containing O₂, it will be oxidized and lose its ability to adsorb CO₂. However, during methanation it will be reduced and re-activated for methane production. For O₂-free feed gas, Ru is both active for CO₂ adsorption and methanation.

Table 2. Speculated function pathway of Ru and Na₂CO₃ in the Ru-Na₂CO₃ DFM.

| Section | Ru Pathway | Na ₂ CO ₃ Pathway |
|--|--|--|
| Pretreatment | $\text{RuO}_x + x\text{H}_2 \rightarrow \text{Ru} + x\text{H}_2\text{O}$ | $\text{Na}_2\text{CO}_3 + 4\text{H}_2 \xrightarrow{\text{Ru}} 2\text{NaOH} + \text{CH}_4 + \text{H}_2\text{O}$ |
| O ₂ -free CO ₂ feed ¹ | $\text{Ru} + \text{CO}_2 \rightarrow \text{Ru} \cdots \text{CO}_2$ | $4\text{NaOH} + 4\text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3_{\text{bulk}} + \text{Na}_2\text{CO}_3_{\text{surface}} \cdots \text{CO}_2 + 2\text{H}_2\text{O}$ |
| O ₂ -containing CO ₂ feed | $\text{Ru} + \frac{x}{2}\text{O}_2 \rightarrow \text{RuO}_x$ | $4\text{NaOH} + 4\text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3_{\text{bulk}} + \text{Na}_2\text{CO}_3_{\text{surface}} \cdots \text{CO}_2 + 2\text{H}_2\text{O}$ |
| Methanation & hydrogenation | $\text{RuO}_x + x\text{H}_2 \rightarrow \text{Ru} + x\text{H}_2\text{O}$ | $\text{Na}_2\text{CO}_3_{\text{surface}} \cdots \text{CO}_2 + 8\text{H}_2 \xrightarrow{\text{Ru}} 2\text{CH}_4 + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3_{\text{surface}}$ $\text{Na}_2\text{CO}_3_{\text{bulk}} + 4\text{H}_2 \xrightarrow{\text{Ru}} 2\text{NaOH} + \text{CH}_4 + \text{H}_2\text{O}$ |

¹ Na₂CO₃_{bulk} and Na₂CO₃_{surface} are the same component but bulk and surface are distinguished.

For Ru-Na₂CO₃ DFM, bulk carbonate hydrogenation occurs during pretreatment, producing NaOH and CH₄ with CO₂ spill-over to Ru sites. Upon exposure to CO₂, it is reformed to a bulk carbonate species where CO₂ adsorbs on the surface Na₂CO₃ ··· CO₂ and reforms bulk carbonate. The slowest step is the hydrogenation of the reformed bulk carbonate. Table 2 is still speculative and is the focus of on-going kinetic and characterization studies.

3. Experimental

3.1. Material Synthesis

The powder materials tested were prepared via incipient wetness method on a high surface area γ - Al_2O_3 (SBA-150, BASF, Iselin, NJ, USA) support using ruthenium(III) nitrosyl nitrate ($\text{Ru}(\text{NO})(\text{NO}_3)_3$, Ru 31.3% min, Alfa Aesar, Tewksbury, MA, USA) and Na_2CO_3 (Sigma-Aldrich, St. Louis, MO, USA) as the precursors for Ru and Na_2CO_3 , respectively. Repeated impregnations were conducted to reach the designed loadings if necessary. The Al_2O_3 supported alkaline materials (Na_2CO_3) were dried at 120°C for 2 h and then calcined at 400°C for 4 h in air. For Ru deposition, the material was dried at 120°C for 2 h followed by calcination at 250°C for 2 h in air after metal catalyst (Ru) impregnations.

The pellet materials (5 mm \times 5 mm tablets) used for the cyclic tests were prepared via a precipitation method with the target composition of 5% Ru, 10% $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ (TH100, SASOL, Hamburg, Germany). The principle procedure of the precipitation method was derived from the work done by Zheng et al. [31], but the impregnation order, selected precursors, and calcination programs were modified (see Figure 8 for the preparation process flow). Ruthenium(III) chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, 99.9% PGM basis, Ru 38% min, Alfa Aesar, Tewksbury, MA, USA) and sodium carbonate (Sigma-Aldrich) were the chosen precursors for Ru and Na_2CO_3 , respectively. Using RuCl_3 as the Ru precursor for pellet sample instead of $\text{Ru}(\text{NO})(\text{NO}_3)_3$ achieved more uniform penetration within the pellets, consequently improved dispersion of Ru, and avoided residual of precursor in the sample. The highest calcination temperature was 250°C to avoid generation of high temperature volatile ruthenium oxides ($>300^\circ\text{C}$ in air). The water wash was introduced, after precipitation of water-insoluble $\text{Ru}(\text{OH})_x$ to remove unwanted chlorides. The carbonate salts were then impregnated and processed as shown in Figure 8.

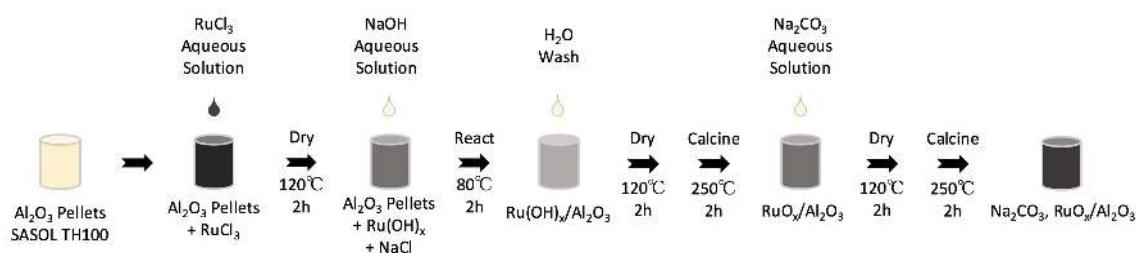


Figure 8. Ru- Na_2CO_3 DFM pellet preparation process flow using the precipitation method. A slight excess of NaOH was used with a ratio of Ru:OH = 1:4.5 to precipitate $\text{Ru}(\text{OH})_x$. A water wash and filtration (40 times of water immersion and separation) was used to remove any NaCl. Drying and calcination steps were conducted in air.

3.2. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis were conducted using either a TG 209 F1 Libra NETZSCH or SAT 449 F3 Jupiter NETZSCH unit for the Na_2CO_3 loading, carbonate hydrogenation, and hydrogen exposure time study. For each test, 50 mg of the prepared powder sample was placed in an alumina crucible and located in the instrument. The temperatures for carbonate hydrogenation and nitrate decomposition, CO_2 adsorption/desorption, and CO_2 methanation, were all conducted at 320°C , while the feed gases and corresponding time periods were varied. Table 3 shows the programs in detail for each test. The total flow rates were always 40 mL/min for each feed gas. Before each test, the sample was heated to 320°C in pure nitrogen until a stable final weight was observed. Hydrogen was introduced in pre-treatments to decompose the ruthenium nitrate to active metallic ruthenium while decomposing the remaining nitrate compounds until stable mass was observed. Pure nitrogen was used only to de gas each sample.

Table 3. Programs of TGA tests at 320 °C related to the results discussed in this paper.

| Test | Pre-Treatment | Step 1 | Step 2 | Step 3 |
|---|---|--|--|----------------------------|
| Na ₂ CO ₃ Loading Study | 2% H ₂ /N ₂ , 2 h | 0.5% CO ₂ /N ₂ , 1 h | Pure N ₂ , 1 h | - |
| Carbonate Hydrogenation Study | Pure N ₂ , 1 h | 2% H ₂ /N ₂ , 2 h | 5% CO ₂ , 2 h | - |
| Hydrogen Exposure Time Study ¹ | 2% H ₂ /N ₂ , 1 h | 5% CO ₂ /N ₂ , 30 m | 2% H ₂ /N ₂ , 10.5 h | Pure N ₂ , 30 m |

¹ The step 2 shows in the table was for the first cycle of the test only. For the 2nd and the 3rd cycle, step 2 lasted only for 30 min, while the other steps were the same as it was in cycle 1.

3.3. Scaled-Up Fixed Bed Reactor

Cyclic tests of CO₂ adsorption and catalytic conversion to methane in a fixed bed reactor are shown in Figure 9. The reactor consisted of gas feed system, furnace, fixed bed reactor, and product analyzer. The gas feed system includes cylinders of compressed designed gases (TechAir, White Plains, NY, USA), rotameters (Key Instruments, Hatfield, PA, USA) calibrated with a precise bubble meter for flow rate control, and a syringe pump (Cole-Parmer, Vernon Hills, IL, USA) along with heating tape (maintains temperature at 125 °C) for steam introduction. The fixed bed reactor is housed in a microthermal furnace (MTSC12.5R-0.75x18-1Z-IOT, Mellen, Concord, NH, USA) and is composed of a standard quartz tube (O.D. = 25 mm, I.D. = 20 mm, length = 570 mm), a thermocouple (K-type, Omega, Norwalk, CT, USA) was placed at gas inlet. An uncoated ceramic monolith was used to secure the pellets and glass beads (DI of 6 mm, Fisher Scientific, Hampton, NH, USA), the latter used to fill the downstream dead volume. Water (steam) in the gas outlet, from the feed gas and water produced from methanation, was condensed by an ice cold trap before flowing into the analytical unit. The exhaust gas analyzer was an Enerac Model 700 equipped with electrochemical sensors for CO, CO₂, and hydrocarbons, and nondispersive-infrared sensor for O₂. It operates with a frequency of 1 Hz, allowing gas measurements every one second. No pressure drop was observed during the reactor tests from the inlet to the outlet.

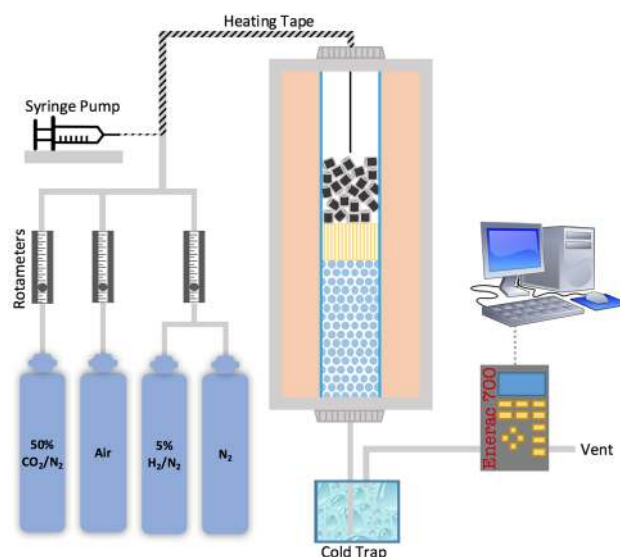


Figure 9. Diagram of scaled-up fixed bed reactor. The N₂ cylinder was used either exclusively or simultaneously with the 50% CO₂/N₂ cylinder to dilute the CO₂ concentration to 7.5% for feeding. The computer connected to the Enerac unit equipped with infrared/electrochemical sensors recorded data every second. Total flow rate of each gas feeding was 300 mL/min.

The two cyclic tests each contained 10 grams of 5% Ru, 10% Na₂CO₃/Al₂O₃ pellets at 320 °C and 300 mL/min (GHSV = 1432 h⁻¹) for total flow rates. The process flow for each cycle in these two tests is shown in Figure 10. The pre-reduction step for both was designed to reduce the RuO_x to Ru metal during preparation. For the 10-cycle test, only 7.5% CO₂ in N₂ was used for the CO₂ adsorption step.

No N₂ purge between adsorption and methanation was needed since no O₂ was present in this series of tests.

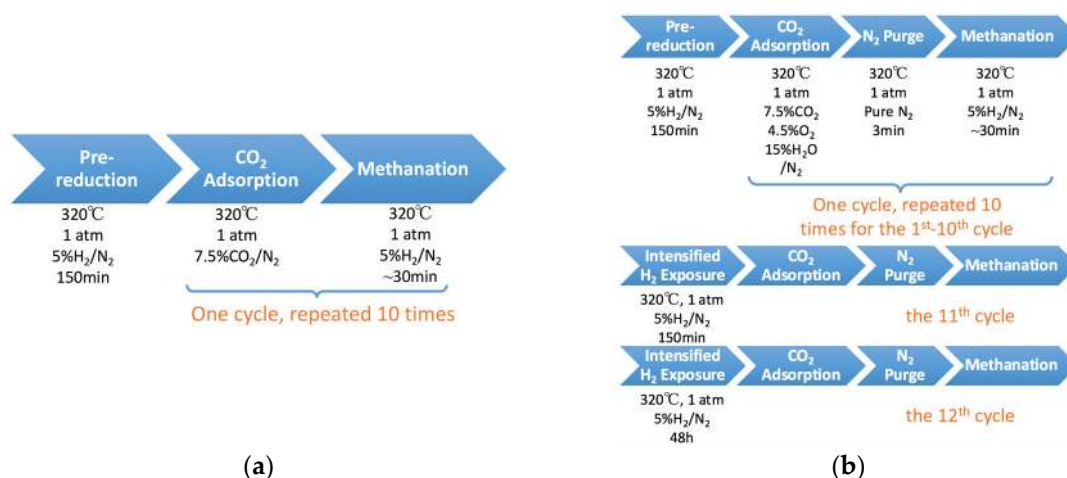


Figure 10. Process flow for the two different cyclic tests operated on the scaled-up fixed bed reactor. (a) O₂- and steam-free CO₂ adsorption and hydrogenation for the 10-cycle test. Pre-reduction was utilized only once before the first cycle. The subsequent ten cycles were conducted repeatedly under identical experimental conditions; (b) Simulated flue gas 12-cycle test with the pretreatment used only before the first cycle followed by 10 identical cycles. A N₂ purge was needed between each cycle to avoid H₂-O₂ contact. Before the 11th and the 12th cycle, a prolonged H₂ exposure was utilized while subsequent steps remained the same as the first ten cycles.

The 12-cycle test was performed in simulated natural gas fired power plant flue gas, containing 7.5% CO₂, 4.5% O₂, 15% H₂O and balance N₂. A 3-min N₂ purge between CO₂ adsorption and methanation and the reverse was added to avoid contact of H₂ and O₂. The first ten cycles were operated continuously and identically, while the last two cycles required a prolonged H₂ purge before CO₂ feed was introduced. The 11th cycle underwent a 150 min 5% H₂/N₂ exposure and the 12th for 48 h. The prolonged H₂ exposure was needed to regenerate the re-oxidized ruthenium.

4. Conclusions

The bulk carbonate present in Ru-Na₂CO₃ DFM can adsorb and convert CO₂ to CH₄. Additionally, the bulk carbonate can also be catalytically hydrogenated to CH₄ providing “depleted” sites for additional CO₂ adsorption from flue gases. Ru plays a key role as a methanation catalyst for O₂-containing flue gas due to its ease of reduction once oxidized. Once in its reduced state it provides an additional site for CO₂ capture as well as effective methanation. This technology overcomes some of the limitations of aqueous amine CO₂ scrubbing by having the dual capability of both capturing CO₂ in O₂-flue gas and subsequently methanating the CO₂ at one temperature using renewable H₂. The methane produced is dried, compressed, and recycled to the front of the plant ideally closing the carbon balance, with conversion of 89.6% of the captured CO₂ in simulated flue gas.

The Ru-Na₂CO₃ DFM demonstrated stable performance for at least 10 cycles of CO₂ adsorption and methanation in an O₂-free CO₂ feed gas. In simulated flue gas, due to the presence of oxygen, part of active metallic Ru is oxidized and loses its activity for CO₂ adsorption and methanation. Stable performance was observed in the flue gas up to the point where Ru becomes less effective due to oxidation. This apparent deactivation can be reversed by prolonged exposure to H₂ or preferably by a high H₂ content. The reversibility is due to the ease of reduction of RuO_x to Ru.

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Conflicts of Interest: The authors declare no conflict of interest.

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