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In-situ DRIFTS study of two-step CO₂ capture and catalytic methanation over Ru, “Na₂O”/Al₂O₃ Dual Functional Material[☆]

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ABSTRACT

Dual Function Materials (DFM) are composed of an alkali or alkaline earth CO₂ adsorbent phase and a supported catalyst. It selectively captures CO₂ which is then methanated using renewable H₂. Both the capture and methanation steps are conducted at about 320 °C so no temperature swings are required allowing for continuous operation using two parallel reactors operating in tandem. This process approaches carbon neutral power generation by recycling the CH₄ produced for re-combustion. This two-step process was studied by *in-situ* DRIFTS at 320 °C over 5%Ru-6.1%“Na₂O”/Al₂O₃ DFM and compared with the 5%Ru/Al₂O₃ traditional methanation catalyst. In the DFM the Na₂CO₃/Al₂O₃ pre-cursor is reduced to “Na₂O” catalyzed by Ru metal. For both Ru/Al₂O₃ and DFM CO₂ adsorbs on Ru active sites and Al₂O₃ OH groups during the capture step. For DFM large amounts of CO₂ adsorb on the Al-O⁻-Na⁺ species forming bidentate carbonates. During the H₂ reduction step (*i.e.*, methanation step), adsorbed bicarbonates and bidentate carbonates spill over onto the Ru-support interface, where methanation takes place through sequential hydrogenation with formates as reaction intermediaries. Although CO₂ was mainly adsorbed on the alkaline support methanation occurs over Ru, supporting the hypothesis that the reaction occurs at the Ru-support interface. Therefore, the multiple adsorption sites over the DFM explain the high CO₂ adsorption capacity by the formation of bidentate carbonates that spill over onto the Ru-support interface, during the two-step methanation process.

1. Introduction

World energy consumption has been increasing for the last decades; in 2015 energy consumption was about 1.17×10^{23} kWh and it is expected to be 2.15×10^{23} kWh by 2040 [1]. World energy demand is satisfied, mainly, from combustion of fossil fuels like coal, petroleum and natural gas. Among those, natural gas provides 24% in world energy production and has the fastest growing trend of about 1.4% per year [1]. Despite the least source of CO₂ emissions ($\cong 181$ kg CO₂/Wh), natural gas has a significant impact on greenhouse gas emissions, representing the 22% of CO₂ world emissions [2].

Fossil fuel will be continued to be used in the near future and thus CO₂ must be abated. To mitigate CO₂ emissions, different renewable energy sources have been studied and implemented around the world, primarily wind and solar energy [3]. However, these energy sources fluctuate and must be balanced for electric grid stability [3,4].

Consequently, large energy storage capacity is required; for which Power to Gas alternatives has been considered [3,5,6], especially Power to Methane (methanation or synthetic natural gas). Using renewable H₂ is the only source that makes methanation possible. Methanation processes have an advantage over the standard liquid amine capture, separation, transportation and sequestration because the process is performed at the site of CO₂ generation with no transportation of CO₂ to another site. Also, it utilizes the temperature of the flue gas, so no energy needs to be added [6,7]. As an example of its viability, Audi and Etogas inaugurated in 2013 the first methanation plant (Audi e-gas plant) in Wertle, Germany with a 6300 kW power input capacity, using renewable H₂ generated from water electrolysis fed by wind power, showing the potential and viability of implementing this technology for CO₂ capture and utilization.

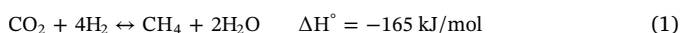
Dual Function Materials (DFM) are novel materials for CO₂ capture from a flue gas followed by a methanation processes. The material is

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composed of an alkali or alkaline earth CO₂ adsorbent phase and a catalyst supported on a high surface area carrier. DFM allows, at the same time, both residual renewable energy storage and CO₂ industrial emissions capture and utilization, by a two-step process. First, H₂ production from water electrolysis, using residual renewable energy and, second, its subsequent conversion to CH₄ by the methanation reaction (Eq. (1)) with CO₂ captured from industrial emission sources. Although H₂ could be used directly for energy storage, an infrastructure for CH₄ already exists and is well established [8] and the CO₂ emissions will continue to be a problem whenever fossil fuel is used for power generation. Recycling carbon *via* capture and methanation approaches carbon neutral power generation. This paper is designed to contrast the methanation process using Ru/Al₂O₃ with the newly developed DFM which includes an Al₂O₃ supported alkaline adsorbent as the primary site for CO₂ capture [7,9,10] in concert with Ru.



While water electrolysis is a well-known process, methanation mechanisms related to active and stable catalysts, reactor design, process conditions and reaction mechanisms are still under investigation [5,8,11]. More detailed understanding can be used to develop rigorous kinetic models that could be employed into accurate methanation reactor design and methanation process simulation [11].

In-situ Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTS) is widely used to characterize adsorption, desorption and intermediate formation over a catalyst surface to obtain qualitative information about the reaction mechanism. DRIFTS studies for Ni [12–16], Rh [17–20], Co [13,21] and Ru [22–29] methanation catalysts have been performed. Among these, Ru catalysts are the most studied due to its higher activity, selectivity and low deactivation rate. However, there is no agreement on CO₂ methanation mechanism over Ru catalysts and many authors have proposed different methanation mechanisms (Table 1). Dreyer et al. [23] proposed CO₂ dissociation as the initial step of methanation, then suggested that, either CO dissociates into C* and O* followed by hydrogenation to CH_x or it dissociates with the assistance of H* to form hydroxylmethylene (HCOH*) followed by O abstraction to form CH_x. Also, Eckle et al. [26] suggested CO₂ dissociation into CO and O, followed by the direct hydrogenation of CO to CH₄. Contrary, Garbariano et al. [27] and Marwood et al. [24] proposed a reaction mechanism that involves bicarbonates and formates as intermediates in the reaction (Table 1). According to Marwood et al. [24], first CO₂ adsorbs as bicarbonates on the support, then bicarbonate species react with H to form formate intermediates that rapidly spill over to the metal-support interface in order to methanation to occur.

The combination of CO₂ capture and subsequent methanation using Dual Functional Materials (DFM), has been developed to improve CO₂ capture and catalytic conversion to CH₄. Materials, including adsorbent phases of CaO [7,9,30,31], pre-reduced K₂CO₃ [9,31], pre-reduced Na₂CO₃ [9,10], MgO [9,31], Li₂CO₃, NaNO₃, KNO₃, CsNO₃ [32] and K-promoted hydrotalcite [6] with an active phase of Ru [9,32] and Ni [6,31] supported on Al₂O₃ [9] and TiO₂ [32], have been developed. Duyar et al. [9] and Petala and Panagiotopoulou [32] reported activity enhancements of Ru when combined with CaO [9], pre-reduced Na₂CO₃ [10] and NaNO₃ [32]. Among these, sodium salts showed

Table 1
Proposed CO₂ methanation reaction mechanisms.

Reaction mechanism	Reference
CO ₂ → CO* – Ru + O* – Ru CO* – Ru → C* + O* C* + H* → CH _x * or C* + H* → HCOH* → CH _x * + O*	[23]
CO ₂ + (OH) _s → (HCO ₃) _s + 2 H _M → (HCOO) ₁ → CO _M → CH ₄ + H ₂ O	[24]
CO ₂ → CO* – Ru + O* – Ru CO* – Ru + H* → CH ₄ * + H ₂ O	[26]
CO ₂ → HCO ₃ [–] → HCOO → CH ₄	[27]

higher CO₂ uptake. Wang et al. [10] studied CO₂ adsorption capacity for different reduced Na₂CO₃ loadings on Al₂O₃ by TGA at 320 °C and reported the highest CO₂ adsorption capacity – about 0.11 mmol/g – and achieved 89.6% CO₂ conversion to CH₄ over the DFM. It has been reported that when Na₂CO₃ is deposited on Al₂O₃ it undergoes decomposition at T < 200 °C due to the Al-O[–]-Na⁺ reaction [33]. In our study, all RuOx,Na₂CO₃/Al₂O₃ were pre-reduced at 320 °C in 20% H₂/N₂ to produce 5%Ru-6.1%“Na₂O”/Al₂O₃ DFM. The pre-reduction of Na₂CO₃/Al₂O₃, in the presence of Ru metal, leads to the formation of the DFM surface which is speculated to be a mixture of surface aluminates and Na oxide species. The absence of a definitive Na ion structure leads us to designate “Na₂O” as the adsorbent.

Keturakis et al. [34] studied CO₂ adsorption and desorption over Na₂O/Al₂O₃ sorbent by *in-situ* DRIFTS. Their results reported the Na₂O decomposition to an ionic form when supported on Al₂O₃, allowing CO₂ adsorption over different Al₂O₃ and Na₂O sites; on Al₂O₃, CO₂ adsorption occurs by the interaction of CO₂ with OH groups. For Na₂O, CO₂ adsorption results in the formation of bidentate carbonates, with bands at about 1300 and 1600 cm^{–1} and polydentate carbonates, evidenced by the appearance of bands between 1400 and 1580 cm^{–1} [34]. In previous work, we studied DFM catalytic activity, stability, CO₂ adsorption capacity and methanation capacity [7,9,10,35,36]. However, there is little information of adsorption, desorption and intermediate species in the capture and methanation reactions over DFM and *in-situ* DRIFTS studies over 5%Ru-6.1%“Na₂O”/Al₂O₃ DFM have not been performed.

This paper reports an *in-situ* DRIFTS study of CO₂ adsorption and methanation at 320 °C over the pre-reduced 5%Ru-6.1%“Na₂O”/Al₂O₃ DFM. Results were compared to the traditional 5%Ru/Al₂O₃ catalyst. Formation of reaction intermediate species was evaluated, and possible reaction pathways discussed.

2. Experimental

2.1. Materials preparation

All powder materials were prepared *via* incipient wetness impregnation on high surface area γ-Al₂O₃ (SBA-150, BASF, Iselin, NJ, USA) support using ruthenium(III) nitrosyl nitrate (Ru(NO)(NO₃)₃ (Ru 31.3% min, Alfa Aesar, Tewksbury, MA, USA) and for DFM an aqueous 20 wt% solution of Na₂CO₃ (Sigma-Aldrich, St. Louis, MO, USA). The ruthenium nitrate salt on Al₂O₃ was dried at 120 °C for 2 h and calcined in air at 250 °C for 2 h. All Na₂CO₃/Al₂O₃ materials were dried at 120 °C for 2 h and calcined at 400 °C in air as precursors to Na⁺AlO[–] species sorbent material. For DFM synthesis, Ru was deposited onto the sorbent materials, dried at 120 °C for 2 h and calcined at 250 °C for 2 h in air. Higher temperatures must be avoided to prevent RuO₂ volatilization. Prior to CO₂ adsorption and methanation DRIFTS tests, materials were heated at a rate of 10 °C min^{–1} (Harrick ATC/low voltage temperature control unit) to 320 °C under N₂ and pre-reduced in 20% H₂ to give 5% Ru-6.1%“Na₂O”/Al₂O₃ (from the 10%Na₂CO₃/Al₂O₃ precursor). It should be noted that we use the nomenclature of “Na₂O”/Al₂O₃, since during calcination and pre-reduction some surface aluminate species and residual Na are formed. Thus, the “Na₂O” adsorbent includes both, aluminates and residual Na in the DFM surface. The “Na₂O” molar content in the material was calculated stoichiometrically from the 10% Na₂CO₃ decomposition during calcination and pre-reduction after its impregnation.

2.2. *In-situ* DRIFTS measurements

CO₂ adsorption, desorption and methanation intermediates were evaluated by *in-situ* DRIFTS test in a Nicolet iS10 spectrum unit (Thermo Scientific, Waltham, MA, USA) equipped with a diffuse reflection attachment reaction cell DRK-3 Praying Mantis (Harrick, USA) in the range of 4000–1200 cm^{–1} with an average of 64 scans per

Table 2
Summary of experimentally detected bands.

Species	Structure	$\nu(\text{OCO})$ cm^{-1}	$\nu(\text{OH})$ cm^{-1}	$\nu(\text{CO-Ru})$ cm^{-1}	$\nu(\text{O-Ru})$ cm^{-1}	$\nu(\text{C-H})$ cm^{-1}
CO_2		3700	-	-	-	-
		3600	-	-	-	-
		2345	-	-	-	-
Bicarbonates		1650	3740	-	-	-
		1440	3640	-	-	-
Formates		1520	-	-	-	-
		1320	-	-	-	-
		2035	-	-	-	-
Bidentate carbonates		1600	-	-	-	-
		1370	-	-	-	-
Bridged carbonates		1620	-	-	-	-
Linear CO adsorption		-	-	2020	-	-
Linear O adsorption		-	-	-	1940	-
CH_4		-	-	-	-	3020

spectrum and a resolution of 4 cm^{-1} . About 35 mg of each powder sample was loaded into the high temperature Harrick reaction cell equipped with ZnSe windows. Each spectrum was obtained every 5 min by subtracting the background collected for the corresponded material at 320°C under N_2 atmosphere. A total flow of carrier and reactive gases was fixed in 120 ml min^{-1} in all tests.

With the aim of identifying the different CO_2 adsorption sites and reaction intermediates experiments over $5\% \text{Ru}/\text{Al}_2\text{O}_3$ catalyst, the sorbent phase ($6.1\% \text{Na}_2\text{O}/\text{Al}_2\text{O}_3$), and the DFM ($5\% \text{Ru}-6.1\% \text{Na}_2\text{O}/\text{Al}_2\text{O}_3$) were carried out at 320°C . After pre-reduction, a $15\% \text{CO}_2/\text{N}_2$ stream was fed into the reaction cell and held for 1 h (CO_2 capture step), followed by a reduction step with $20\% \text{H}_2/\text{N}_2$ for 1 h (methanation step); following the methodology reported by Duyar et al. [9]. All raw and processed Excel data can be downloaded from [dataset] [37].

3. Results and discussion

Two-step capture and methanation process was studied by DRIFTS over several materials by feeding a stream of $15\% \text{CO}_2/\text{N}_2$ for 1 h (i.e., CO_2 capture step) and followed by the reduction step with $20\% \text{H}_2/\text{N}_2$ for 1 h (i.e., methanation step). Table 2 presents a summary of the most experimentally observed bands during those tests. Additionally, a band at 2345 cm^{-1} corresponding to CO_2 molecular gas phase was observed [34,38,39]. Results are presented and analyzed for different materials in the following sections. Additionally, published raw and processed data are available in [dataset] [37].

3.1. DRIFTS studies of the two-step methanation process over $5\% \text{Ru}/\text{Al}_2\text{O}_3$ catalyst

CO_2 adsorption over $5\% \text{Ru}/\text{Al}_2\text{O}_3$ (Fig. 1a) shows bands at 3740, 3600, 1650 and 1440 cm^{-1} . Bands in the range between 3740 and 3600 cm^{-1} have been assigned to different sources. Eckle et al. [26] and Abdel-Mageed et al. [22] assigned bands at 3740 and 3640 cm^{-1} to OH vibration modes from bicarbonates. And Mageed et al. [22] and Garbarino et al. [27] assigned peaks at 3600 and 3700 cm^{-1} to CO_2 overtones. Contrary, Baltrusaitis et al. [40] and Dreyer et al. [23]

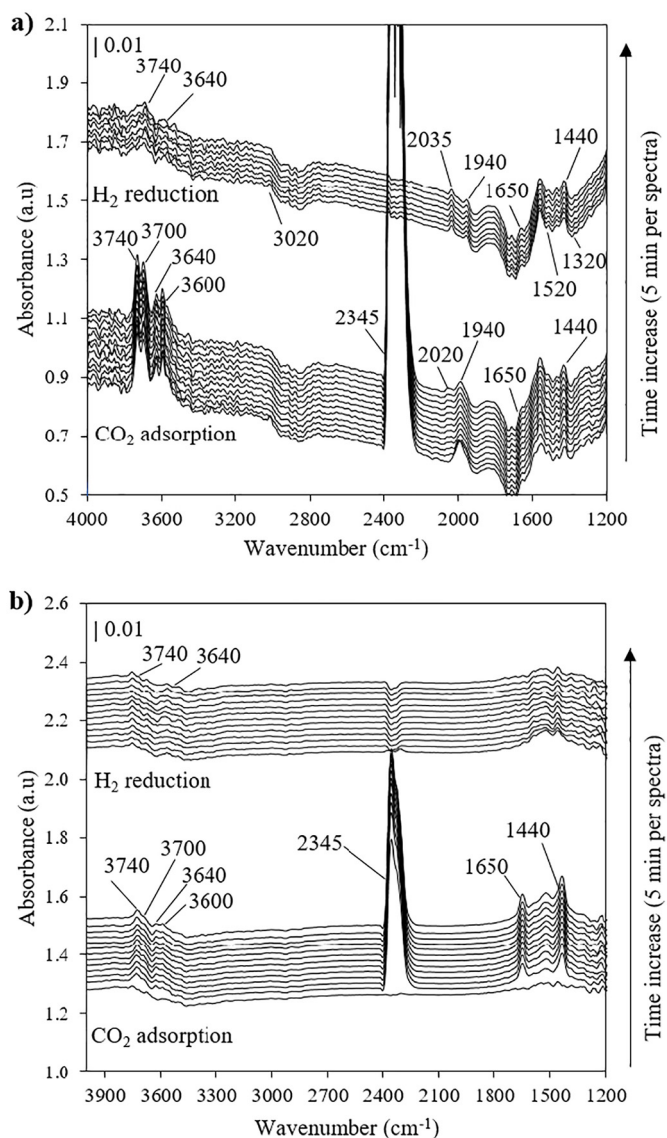


Fig. 1. In-situ DRIFTS of CO_2 adsorption and H_2 reduction over reduced (a) $5\% \text{Ru}/\text{Al}_2\text{O}_3$ and (b) Al_2O_3 at 320°C .

assigned bands at 3700 and 3600 cm^{-1} only to OH in adsorbed bicarbonates species. We believe that the presence of multiple peaks in this region can be attributed to both CO_2 overtones (3700 and 3600 cm^{-1}) and bicarbonates OH (3740 and 3640 cm^{-1}). On the other hand, bands at 1650 and 1440 cm^{-1} can be assigned to the O-C-O stretch of bicarbonates (Table 2) [38,41,42]. All these bands are also observed during CO_2 adsorption over $\gamma\text{-Al}_2\text{O}_3$ (Fig. 1b), indicating that $\gamma\text{-Al}_2\text{O}_3$ is active for CO_2 adsorption as bicarbonates. These bicarbonates could be formed by the reaction between Al_2O_3 hydroxyl groups and CO_2 , as reported by Baltrusaitis et al. [40] and Szanyi et al. [43] from their CO_2 adsorption studies over $\gamma\text{-Al}_2\text{O}_3$. Baltrusaitis et al. [40] also reported this by quantum chemical calculations of CO_2 adsorption on $\gamma\text{-Al}_2\text{O}_3$. On the other hand, bands at 2020 and 1940 cm^{-1} in Fig. 1a, assigned to different vibrational modes of CO-Ru bonds (Table 2) [28], including the linear adsorption of CO on Ru^0 [25,44,45] and the linearly CO adsorbed on Ru co-adsorbed with an adjacent O-Ru bond [45], appear during CO_2 adsorption. The appearance of these bands indicates CO_2 adsorption over Ru active sites. Therefore, CO_2 is interacting with both, Ru active sites [43,46] and Al_2O_3 OH groups [40,43] over $5\% \text{Ru}/\text{Al}_2\text{O}_3$ catalyst.

During H_2 reduction (methanation step) over $5\% \text{Ru}/\text{Al}_2\text{O}_3$ (Fig. 1a),

O–H stretching of bicarbonate species (bands at 3640 and 3740 cm^{-1}) decrease, but O–C–O stretch signals (1650 and 1440 cm^{-1}) are still present, indicating that bicarbonates are partially desorbed from Al_2O_3 . Bicarbonate desorption could be related to the appearance of bands at 3020, 1520, 1320 and 2035 cm^{-1} at the beginning of the methanation step. A slight band at 3020 cm^{-1} assigned to CH_4 C–H stretch vibrations [27,29,47] appears simultaneously with peaks at 1520 and 1320 cm^{-1} which are assigned to formate species (HCOO) [24,27]. CH_4 and formates were also reported by Wang et al. [29] in their DRIFTS-MS studies of the two-step methanation over 5%Ru/ Al_2O_3 , with a He purge between CO_2 capture and H_2 reduction. Also, Garbairano et al. [27] and Marwood et al. [24] reported CH_4 and formates when they co-fed a mixture of CO_2 , H_2 and N_2 during their *in-situ* DRIFTS studies over Ru/ Al_2O_3 and Ru/ TiO_2 , respectively. This implies that formate species are the reaction intermediates, where CO_2 is sequentially hydrogenated to CH_4 .

Moreover, the band at 2020 cm^{-1} formed during the CO_2 adsorption step and assigned to CO–Ru interactions, moves towards a smaller 2035 cm^{-1} band during H_2 reduction (Fig. 1a), showing a change in CO adsorption on Ru. We propose that this movement is related to the formate Ru–CO bond, that is formed when bicarbonates spill over onto the support-metal interface; where formate intermediaries form and convert to CH_4 . The spillover of adsorbed bicarbonate species to Ru is necessary (Fig. 1b). Neither formates (band at 1320 cm^{-1}) nor CH_4 (band at 3020 cm^{-1}) are formed over the support in the absence of Ru. This was also proposed by Marwood et al. [24] from their *in-situ* DRIFTS studies of the co-fed CO_2 methanation over Ru/ TiO_2 . However, Marwood et al. [24] proposed that bicarbonates react with H_2 in a co-fed process to form adsorbed formates on the support; those formate species then move to Ru active sites in order for methanation to occur. Otherwise, our results suggest that the methanation step occurs over 5%Ru/ Al_2O_3 catalyst when CO_2 is adsorbed as bicarbonates on Al_2O_3 OH groups. Then, with H_2 present, bicarbonates spill over onto the Ru–support interface to react with H_2 , forming formates and then CH_4 . In the absence of Ru, formates were not observed.

Therefore, based on our *in-situ* DRIFTS studies, two-step methanation mechanism over 5%Ru/ Al_2O_3 is schematically represented in Fig. 2 (right side). During the CO_2 adsorption step, Al_2O_3 OH groups and Ru active sites adsorb CO_2 . In steps (1a) and (2a), CO_2 is adsorbed over Al_2O_3 OH groups which results in the formation of adsorbed bicarbonate intermediates (bands at 3740, 3640 1650 and 1440 cm^{-1}). In step (3a) the proposed bicarbonates spill over; where C and O atoms from

bicarbonates adsorb onto Ru active sites. During H_2 reduction (methanation step or step (4) in Fig. 2), H_2 is dissociated into hydrides over Ru to form Ru–H species [16,21–23]. These hydrides are easily added into the bicarbonate structure; therefore, in step (5), formate species (bands at 2035, 1520 and 1320 cm^{-1}) are formed. In the same step, C–OH bond is cleaved by the introduction of a hydride from Ru–H to form H_2O . Finally, in steps (6) to (9), hydrides are sequentially added to the formates until the CH_4 molecule is completely formed and the Ru active sites are regenerated along with Al_2O_3 hydroxyl groups for a further adsorption-methanation cycle. At this point, methanation follows the hydrogenation pathway from formates that are formed over Ru. These formates are produced when CO_2 is adsorbed over Al_2O_3 as bicarbonates and spill over onto Ru to react with dissociated hydrides during the methanation step.

3.2. DRIFTS studies of the two-step methanation process over 5%Ru-6.1%“ Na_2O ”/ Al_2O_3 DFMs

CO_2 adsorption and further methanation was studied over 5%Ru-6.1%“ Na_2O ”/ Al_2O_3 DFM, which has been reported as a promising methanation material with an enhanced CO_2 adsorption capacity of 0.48 mmol/g DFM [10] compared to the 5%Ru/ Al_2O_3 adsorption capacity of 0.32 mmol/g catalyst [48]. Results are shown in Fig. 3a. During CO_2 adsorption, large bands at 1600 and 1370 cm^{-1} appear and are related to bidentate carbonate vibrational modes adsorbed on $\text{Al}-\text{O}^--\text{Na}^+$ species of the sorbent surface (Table 2). The $\text{Al}-\text{O}^--\text{Na}^+$ species were proposed by Keturakis et al. [34] due to the interaction of the Na^+ ions from the “ Na_2O ” and the Al_2O_3 support. Na^+ ions create an electronic discoordination observed by FTIR, which results in the formation of some surface aluminates with residual Na species. Nguyen et al. [33] performed X-ray Diffraction (XRD) characterizations of Na_2CO_3 supported on Al_2O_3 , where they did not observe the characteristic peaks of sodium crystalline phases, which could indicate that sodium is present either as an amorphous phase interacting with alumina support or as “ Na_2O ” nano-dispersed crystallites. This was also reported by Wang et al. [36] for DFM XRD characterizations, where the lack of sharp peaks indicates the absence of any sodium crystalline phase. For this, we feel this “ Na_2O ” designation is acceptable. In the $\text{Al}-\text{O}^--\text{Na}^+$ species, the O^- is very reactive for CO_2 adsorption, due to its high basic nucleophilic character. Consequently, CO_2 adsorption is likely occurring by a nucleophilic attack from the O^- to the C in CO_2 . Moreover, bands at 3640 and 3740 cm^{-1} indicate CO_2 adsorption over

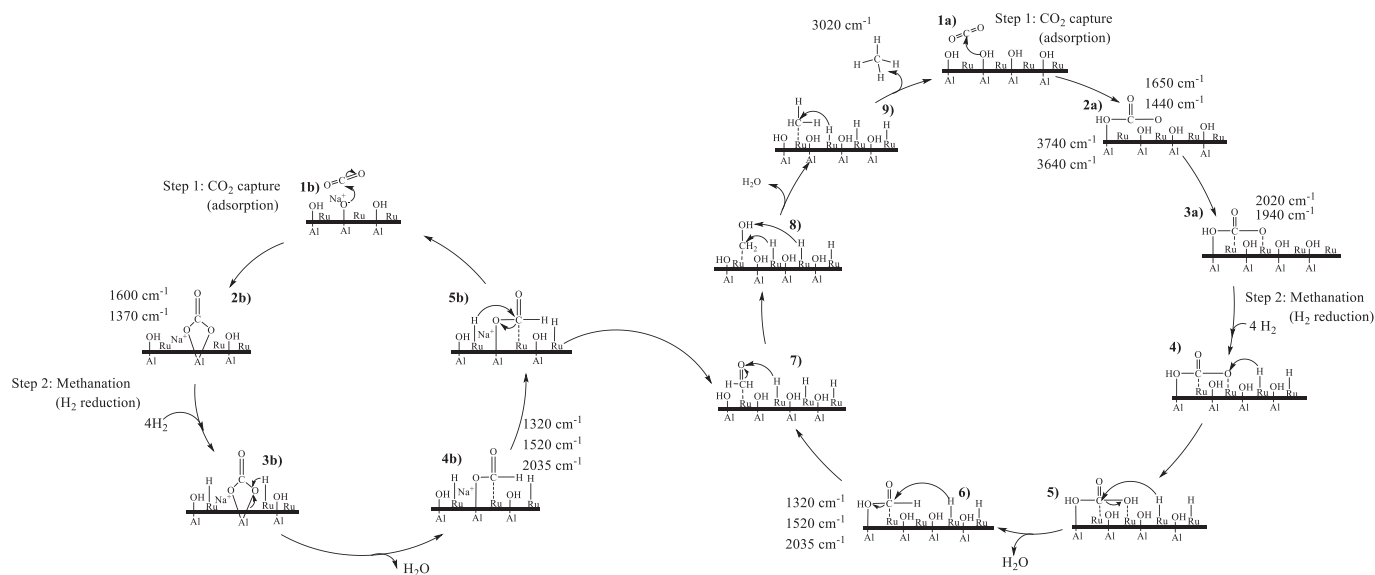


Fig. 2. Proposed CO_2 methanation mechanism over 5%Ru/ Al_2O_3 (right side) and extended (left and right sides) for over 5%Ru-6.1%“ Na_2O ”/ Al_2O_3 DFM.

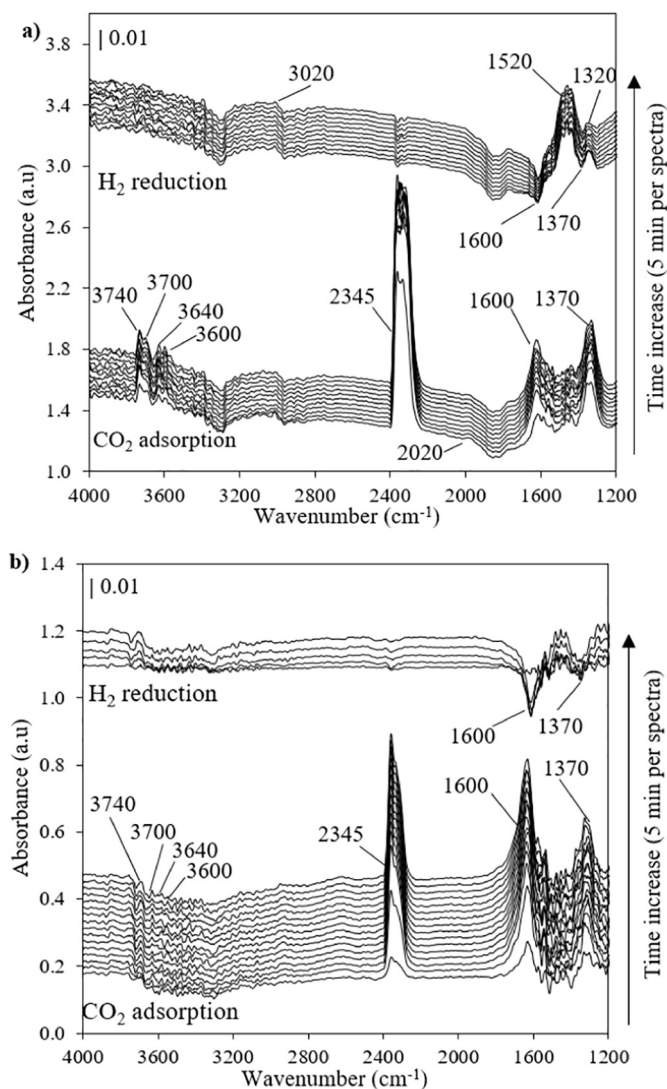


Fig. 3. *In-situ* DRIFTS of CO₂ adsorption and H₂ reduction over reduced (a) 5% Ru-6.1%“Na₂O”/Al₂O₃ and (b) 6.1%“Na₂O”/Al₂O₃ at 320 °C.

Al₂O₃ as bicarbonates (Fig. 3a), but O-C-O bicarbonates bands at 1650 and 1440 cm⁻¹ are covered by larger bidentate carbonate peaks at 1600 and 1370 cm⁻¹. Also, a weak signal between 1990 and 2000 cm⁻¹ [25,44,45], assigned to Ru-CO vibrational modes was observed. Therefore, CO₂ is largely adsorbed as bidentate carbonates (Table 2) rather than as bicarbonates on Al₂O₃ hydroxyl groups or over Ru active sites. Consequently, *in-situ* DRIFTS results showed that DFM has multiple CO₂ adsorption sites, *i.e.*, Al-O⁻-Na⁺ species, Al₂O₃ OH groups and Ru active sites.

During H₂ reduction (methanation step) on 5%Ru-6.1%“Na₂O”/Al₂O₃ DFM (Fig. 3a), bidentate carbonate bands (1600 and 1370 cm⁻¹) disappear simultaneously with the appearance of the characteristic peak of CH₄ at 3020 cm⁻¹ [25,26,28] and the intense formation of formate characteristic peaks at 1520 and 1320 cm⁻¹ [22–29]. Otherwise, over the sorbent phase (Fig. 3b) neither formate nor CH₄ signals appear, which indicates again that Ru is required for H₂ dissociation and formate species formation. Thus, over DFM, and similar to Ru/Al₂O₃, adsorbed bidentate carbonates species easily spill over onto Ru active sites to form CH₄, with formate species as reaction intermediates. Accordingly, on DFM the presence of multiple CO₂ adsorption sites is related with the previously DFM enhanced CO₂ adsorption (50% more than 5% Ru/Al₂O₃ catalyst [9,40]). This enhanced adsorption capacity produced a methanation activity of 1.05 CH₄ g mol/kg DFM [7].

Therefore, these tests revealed that, over 5%Ru-6.1%“Na₂O”/Al₂O₃ DFM, the “Na₂O” presence drives a large CO₂ adsorption as bidentate carbonates due to nucleophilic interaction between CO₂ with AlO⁻-Na⁺ species in the support. Fig. 2 shows the multiple CO₂ adsorption sites of 5%Ru-6.1%“Na₂O”/Al₂O₃ DFM, where not only Al₂O₃ is capable of adsorbing CO₂ (right side), but also the “Na₂O” sorbent (left side) adsorbs CO₂ in larger amounts. Therefore, DFM is capable of adsorbing CO₂ on AlO⁻-Na⁺ sites, Al₂O₃ OH groups and on Ru active sites. In the methanation step, it is proposed that bidentate carbonates spill over to the Ru-support interface, where they are methanated with formate species as intermediates through a sequential hydrogenation. This process is explained as follows.

In steps (1a) and (2a), CO₂ is adsorbed over Al₂O₃ OH groups, but alongside, in step (1b) the nucleophilic attack from the AlO⁻-Na⁺ surface species to CO₂ takes place, forming bidentate carbonates (bands at 1600 and 1370 cm⁻¹) in step (2b). In the presence of H₂ (step (3b) to (5b) in Fig. 2), bidentate carbonates spill over onto Ru. In step (3b) the newly Al–O bond, which is formed during CO₂ adsorption as bidentate carbonate, is cleaved and hydrides are added to O forming H₂O. Then, in step (4b) C bidentate carbonates adsorb on Ru active sites, which produces formate intermediates adsorbed on the support-metal interface. Then, C–O bond is cleaved and a hydride is added to adsorbed C. At this point, methanation follows the hydrogenation cycle in step 7 and AlO⁻-Na⁺ species are regenerated and became active to adsorb more CO₂ in cycle of absorption-methanation. Therefore, we observe that the larger CO₂ adsorption capacity is the main feature that makes DFM more active during the two-step methanation, but once CO₂ is adsorbed, either as bicarbonates or bidentate carbonates, it spills over onto the Ru-support interface to produce CH₄ through the formate intermediates pathway.

4. Conclusions

The novel two-step CO₂ capture and methanation process was studied over a 5%Ru/Al₂O₃ catalyst and 5%Ru-6.1%“Na₂O”/Al₂O₃ DFM by *in-situ* DRIFTS. Differences between both materials were observed in the amount and nature of CO₂ adsorbed species. Over 5%Ru/Al₂O₃, CO₂ is adsorbed over Al₂O₃ OH groups (bands at 3740, 3640, 1650 and 1440 cm⁻¹) and over Ru sites (bands at 2020 and 1940 cm⁻¹) during CO₂ capture. Instead, over DFMs, the Al-O⁻-Na⁺ species allows CO₂ adsorption by the formation of bidentate carbonates over the sorbent surface, evidenced by the bands at 1600 and 1370 cm⁻¹. This type of adsorption over the sorbent is possible due to “Na₂O” interaction with Al₂O₃ hydroxyl groups in the support which leads to Al-O⁻-Na⁺ species formation over the DFM surface. Therefore, DFM exhibits CO₂ adsorption on Ru active sites, Al₂O₃ OH groups and bidentate carbonates. During H₂ reduction step (*i.e.*, methanation step), all the CO₂ adsorbed behaves similarly, in that they spill over onto catalytic Ru sites, where they are sequentially hydrogenated forming CH₄, with formates as reaction intermediates. The enhanced methanation capacity reported for DFM was then attributed to its larger CO₂ absorption capacity during the capture step.

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