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Overcoming Storage Limitations in SiO₂—Supported Dual Function Materials for CO₂ Capture and Methanation

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ABSTRACT

The role of the support for Dual Function Materials (DFMs) is critical in the overall activity of the materials, affecting both storage and conversion functions. Through microreactor and FT-IR investigation, the utilization of SiO₂ as support for the integrated CO₂ capture resulted in low CO₂ uptakes when using Ru- and Na- based DFMs, due to the weak protonic acidic nature of the support as well as its non-interacting nature. These properties cause the agglomeration of the Na-based sorbent, increasing its bulk basicity and lowering its effectively available amounts when higher Na loadings materials are prepared. On the other hand, higher efficiency of integrated CO₂ capture and conversion has been obtained by using segregated configurations, that is, physical mixtures of reducing/storage formulations, that in our conditions can overcome detrimental storage material-support interactions.

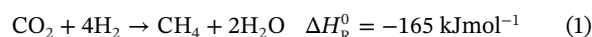
1 | Introduction

The increase of CO₂ levels in the atmosphere, roughly 150 ppm with respect to pre-industrialization, is strictly correlated with the worldwide temperature increase, and the scientific community is working to find effective solutions to mitigate its effects [1–3, 4].

CO₂ capture is valid alleviation method applied to point source emissions (after particulate, SO_x, and NO_x abatement), but it can be also extended to direct-air-capture (DAC) [3, 5]. Several technologies are nowadays proposed in the broad field of carbon capture [3, 6, 7], including absorption [8, 9], adsorption [10, 11], and membrane separation [12, 13]. Presently, absorption on amine-based compounds is the benchmark technology, but the high energy demand, due to the required temperature or pressure swings [3], results in high costs of the process. The separated

CO₂ can either be stored in deep geological reservoirs (CCS, Carbon Capture and Storage) or used (CCU, Carbon Capture and Utilization) along with green H₂ to produce valuable synthetic chemicals and e-fuels (i.e., methane [14], methanol [15], jet fuel [16], and syngas [17]).

The production of e-methane (CH₄) is particularly appealing thanks to its easy manufacture and to the possibility to use the pre-existing distribution grid. CO₂ methanation is a catalyzed reaction called after Paul Sabatier, which follows the stoichiometry of reaction (1) [15, 18]:



One of the drawbacks of e-methane production is related to the high separation costs of CO₂. In this respect, the reactive capture

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of CO₂, aimed at performing both capture and methanation in the same reactor, has gained attention. For this process, Dual Function Materials (DFMs) [19], where a CO₂ storage element (I or II group metals [20–23]) and a methanation metal catalyst (Ni, Ru, and Rh [24–26]) are dispersed over the same support, have been proposed. As a matter of fact, these materials are able both to capture and store CO₂ from a flue gas and convert it once green H₂ is introduced into the reactor. This enables the one-pot CO₂ abatement from point emissions followed by its conversion into methane using green H₂. Moreover, by tuning the catalysts formulations, other reactions can be carried out to valorize the captured CO₂ and convert it into different e-fuels, such as methanol [27] or syngas [28, 29]. The autothermal conduction of the cyclic methanation, that can be sustained thanks to the heat provided by the flue gas, as well as by the exothermic CO₂ adsorption and methanation reactions, represents an advantage over the traditional co-feed methanation, which needs a careful reactor design [5, 30, 31].

To date, there are still several open points on the development of DFMs, including the support effect. To the best of the authors' knowledge, mainly Al₂O₃-supported DFMs have been investigated in literature, with only few works investigating the utilization of other supports (i.e., CeO₂ [32], TiO₂ [33]). Following promising preliminary results [34], in this work SiO₂ is investigated as a support for DFMs for the integrated CO₂ capture and methanation. SiO₂ exhibits excellent textural properties, including high surface area [35], and well-defined porosity [36], which make it an attractive candidate for this application. Moreover, SiO₂ is morphologically stable even under harsh conditions, such as high temperature [37], high pressure, or in presence of steam [37]. Moreover, SiO₂ textural properties are tunable, and depending on the applied treatment, this allows to design micro-, meso- or macro-pores distribution on purpose for the final application [38]. Finally, SiO₂ could be obtained as by-product of several industrial production processes [39–41]. Therefore, the use of waste silica would simultaneously lead to a lower consumption of native natural resources and to the reduction of waste to be treated or stored in landfills, fulfilling the concepts of circular economy and sustainability.

Accordingly, in this work silica-based Ru catalysts, with different Na₂CO₃ loadings, have been prepared, characterized, and tested. The nature and the adsorption capability of the CO₂ storage sites, as well as the DFMs reactivity toward CO₂ methanation, have been assessed with microreactor experiments and FT-IR characterization. Finally, cyclic CO₂ capture and methanation experiments have been performed to study the reactivity of the material under working conditions and compared to physical mixtures of Ru/SiO₂ and Na₂CO₃/Al₂O₃. The final goal is to verify the applicability of SiO₂-supported DFMs in integrated CO₂ capture and methanation reaction.

2 | Results and Discussion

2.1 | Characterization Results

Characterization results have been carried out on the bare SiO₂ support and on the different Ru/xNa₂CO₃/SiO₂ active samples. As detailed in the experimental section, the active samples have

been prepared by impregnation of the SiO₂ support with an aqueous solution containing Na₂CO₃; after drying and calcination at 500°C, the obtained Na₂CO₃/SiO₂ has been impregnated with an aqueous solution of Ru nitrosyl nitrate and then dried at 100°C.

Results of the textural characterization of the Ru/xNa₂CO₃/SiO₂ samples are reported in Figures 1A and B, while BET surface area, pores volume and pores dimensions, calculated by BJH, are summarized in Table 1. The SiO₂-supported materials present type IV isotherms, similarly to the bare support (Figure 1A); however, the textural properties of the samples are strongly influenced by the presence of Na₂CO₃. Indeed, on increasing the Na₂CO₃ loading, a progressive and marked decrease of the surface area is observed, which is already detected for the lowest Na₂CO₃ content (Table 1). This evidence is accompanied by the decrease of the pores volume (Table 1), and the increase of the average pores' width (Table 1), suggesting the blocking of the smaller pores. The progressive surface coverage is evident starting from 10% Na₂CO₃ loading, and it becomes almost complete for the Ru/20Na₂CO₃/SiO₂ sample. Indeed, up to Na₂CO₃ loading of 5%, the distribution of the pore dimensions is very similar to that of the bare support, evidencing only a limited displacement of the maximum of the pores average toward higher values (Figure 1B). Above 10% Na₂CO₃, the pores' distribution curves broaden with maxima at 39 and 47 nm for 10% and 15% loadings, respectively. For the highest Na₂CO₃ loading, the sample becomes almost nonporous (Figure 1B), only a flat distribution of the pores dimensions is detected, and no maximum is present. Such a behavior could be explained with a progressive pore filling with Na₂CO₃, starting from the smaller ones, thus responsible for the large surface area decrease. In particular, for the samples with a Na₂CO₃ content equal to or higher than 10 wt.%, pores with diameter lower than 10 nm are no longer detected (Figure 1B), and the average pores dimensions is the results of the contribution of the empty pores only.

XRD results of the investigated samples are shown in Figure 1C. Amorphous–microcrystalline SiO₂ (ICSD 01-076-0941) is detected in each sample, regardless of the Na₂CO₃ loading. Instead, in the Ru/20Na₂CO₃/SiO₂ the reflections of trona, a dihydrate sodium carbonate—sodium bicarbonate double salt (Na₂CO₃·NaHCO₃·2H₂O) (ICSD: 98-019-2711), and of sodium nitrate (ICSD: 98-001-5332) are detected. The formation of these new phases is due to the preparation method adopted for the DFMs, as they become more evident upon increasing the Na₂CO₃ loading. Indeed, the double salt is reported to form via the interaction of the Na-containing species at the surface of the impregnated samples with moisture and CO₂ of the air [42], while sodium nitrate could be related to the preparation procedure, specifically the impregnation step (without a successive calcination) with the solution of Ru precursors.

FESEM images of the different samples are shown in Figure 2. The bare SiO₂ presents a flaky surface, deriving from the crushing and sieving of 300 μm SiO₂ pellets to obtain the desired 75–106 μm granulometry. In the presence of Na₂CO₃ the overall morphology of the support is maintained; furthermore, additional agglomerates are observed. The particles with smooth surfaces (Figure 2B, F, orange arrows) are consistent with Na nitrate, and their composition is confirmed by EDX mapping

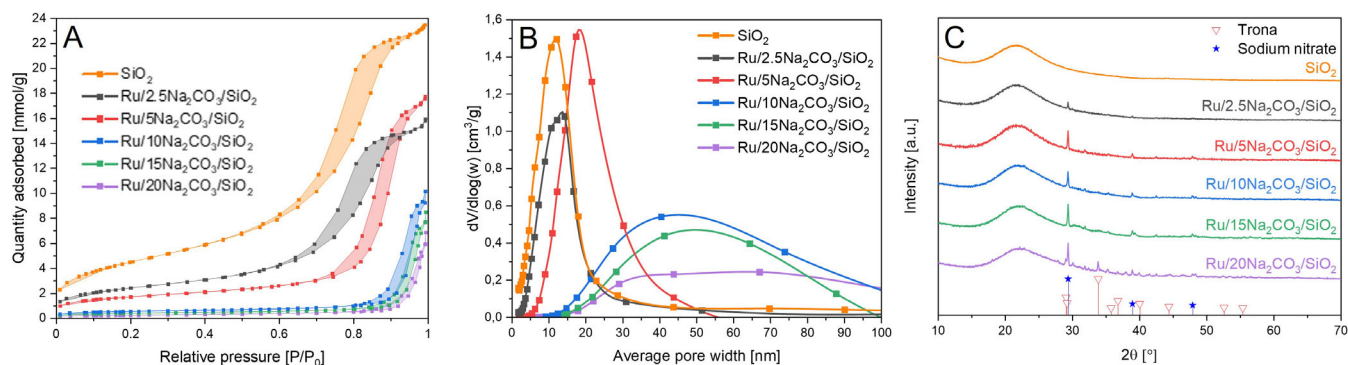


FIGURE 1 | Characterization results for SiO₂ and Ru/x Na₂CO₃/SiO₂ (x = 2.5, 5, 10, 15, 20): (A) N₂ adsorption–desorption isotherms, (B) Pore size distribution, and (C) X-ray diffraction patterns.

TABLE 1 | Nominal compositions and morphological characterization results.

Sample	Ru loading (wt.%)	Na ₂ CO ₃ loading (wt.%)	BET surface area (m ² /g)	BJH Pore volume (cm ³ /g)	BJH average pore width (nm)
SiO ₂	0	0	360	0.83	8
Ru/2.5 Na ₂ CO ₃ /SiO ₂	0.5	2.5	232	0.56	10
Ru/5 Na ₂ CO ₃ /SiO ₂	0.5	5	139	0.62	18
Ru/10 Na ₂ CO ₃ /SiO ₂	0.5	10	72	0.35	39
Ru/15 Na ₂ CO ₃ /SiO ₂	0.5	15	33	0.29	47
Ru/20 Na ₂ CO ₃ /SiO ₂	0.5	20	29	0.24	—

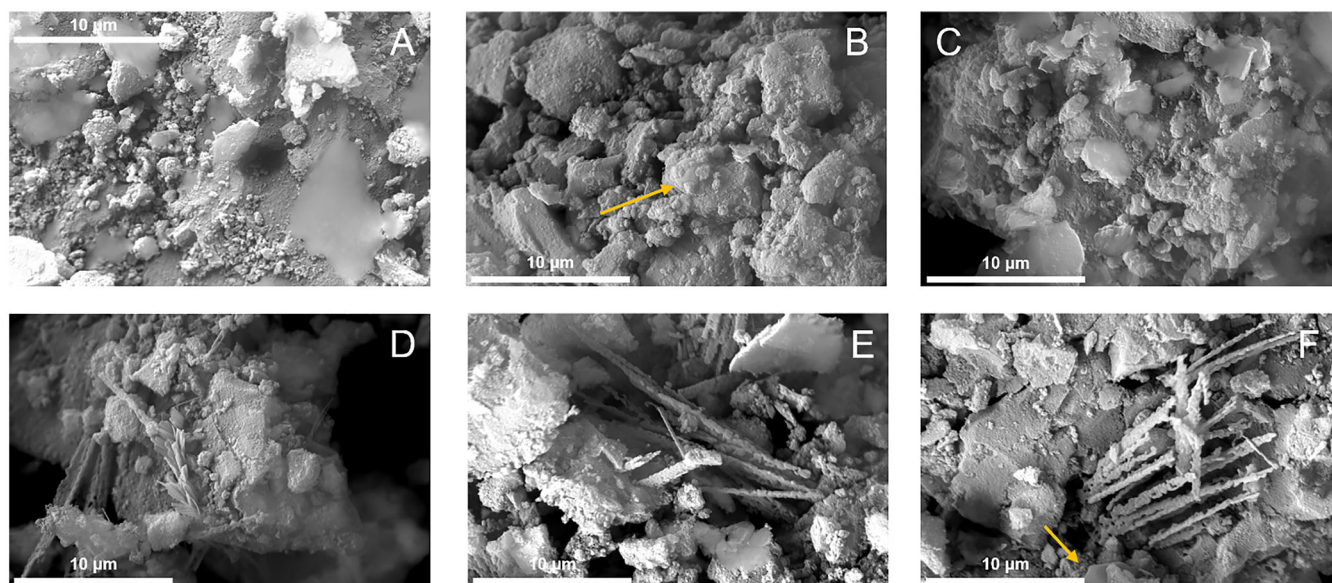


FIGURE 2 | Field emission scanning electron microscopy (FESEM) images of: (A) SiO₂; (B) Ru/2.5Na₂CO₃/SiO₂; (C) Ru/5Na₂CO₃/SiO₂; (D) Ru/10Na₂CO₃/SiO₂; (E) Ru/15Na₂CO₃/SiO₂; (F) Ru/20 Na₂CO₃/SiO₂. Orange arrows: sodium nitrate agglomerates.

(Figure S1). The sharp and elongated needles (Figure 2D–F), observed in the samples with Na₂CO₃ loadings higher than 10%, are consistent with the presence of crystalline trona [43], as confirmed by EDX mapping (see Figure S1 in Supporting Information). FESEM evidence confirms the XRD attribution.

ATR–FTIR skeletal spectra of the sodium-based DFMs prepared with both low (5 wt.%) and high (15 wt.%) Na₂CO₃ loadings are presented in Figure 3. Characteristic signals are visible at approximately 1050 (broad), 800, and 460 cm⁻¹. These bands are assigned to the fundamental IR-active vibrational modes of silica,

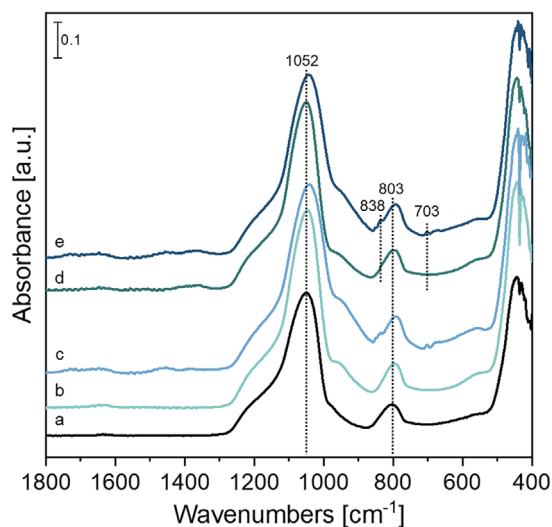


FIGURE 3 | ATR-FTIR spectra of (A) SiO_2 , (B) $5\text{Na}_2\text{CO}_3/\text{SiO}_2$, (C) $15\text{Na}_2\text{CO}_3/\text{SiO}_2$, (D) $\text{Ru}/5\text{Na}_2\text{CO}_3/\text{SiO}_2$ and, (E) $\text{Ru}/15\text{Na}_2\text{CO}_3/\text{SiO}_2$.

namely the asymmetric stretching, symmetric stretching, and bending vibrations of Si—O—Si bonds within the SiO_4 tetrahedral framework [44]. These spectra appear consistently across all silica-supported materials. In addition, a marked shoulder in the $980\text{--}930\text{ cm}^{-1}$ region, attributed to Si—OH vibrations, is observed. This feature is known to be sensitive to surface modifications [45], and its relatively strong intensity indicates the persistence of surface silanol groups even after the incorporation of Na_2CO_3 and Ru. The preparation route and the moderate calcination temperature (500°C) likely prevent these cations from diffusing substantially into the silica bulk.

Upon introducing 15 wt.% of Na_2CO_3 (Figure 3, spectra c), additional absorption bands emerge in the $1500\text{--}600\text{ cm}^{-1}$ region, particularly at 838 and 703 cm^{-1} , which are characteristic of bulk carbonate species [46]. Like for other materials [47], these findings imply that surface-exposed cations are accompanied by oxide anions, favoring the in-situ generation of carbonate species via CO_2 adsorption from the ambient environment and/or because of precursor decomposition during calcination. These carbonate-related features were detected for high Na-loading samples, irrespective of Ru presence (Figure 3, spectra c and e) suggesting that low Na-content limits the formation of bulk-like Na_2CO_3 species upon calcination.

After activation in vacuum at 500°C (see Figure S2 in Supporting Information), the Ru/Na-containing samples show the typical silanol feature at 3745 cm^{-1} that decreased in intensity at increasing sodium content (commercial silica spectrum reported as comparison) [48]. This trend points to a surface perturbation induced by oxide species, which both reduces the density of accessible silanols and introduces heterogeneity among surface hydroxyl groups.

As noted earlier, bands corresponding to surface and bulk carbonate species are only evident in the sample with high sodium loading, appearing in the $1600\text{--}1300\text{ cm}^{-1}$ region. Their presence highlights the basic character of the modified surface and confirms that sodium-derived bulk carbonate species remain stable even after high-temperature activation under vacuum.

Reducibility of the samples has been assessed through H_2 -TPR on the fresh materials, and the results are shown in Figure S3. In the case of the Ru/SiO_2 sample, the onset for H_2 consumption (due to the reduction of Ru) is observed at 125°C . The presence of Na progressively shifts to higher temperatures the onset for H_2 consumption, suggesting that Na inhibits the reducibility of Ru. Besides, in the Na-containing samples higher amounts of H_2 are also consumed, likely related to the reduction of sodium nitrates and carbonates. Over the high-loaded Na sample ($\text{Ru}/15\text{Na}_2\text{CO}_3/\text{SiO}_2$) a high-temperature reduction peak centered at 450°C is also observed, likely associated with bulk Na carbonates.

The nature of the Ru species has also been characterized through room-temperature FT-IR CO-adsorption experiments (see Figure S4 in Supporting Information), carried out on the pre-reduced Ru/SiO_2 samples containing low and high Na_2CO_3 loadings (respectively, 5 and 15 wt.%). In both cases a broad band centered at 2036 cm^{-1} was detected, accompanied by broad shoulders at higher and lower wavenumber range extending across the $2080\text{--}1950\text{ cm}^{-1}$ region. This feature is typically associated with bridging carbonyl species and has also been assigned by several authors to linearly coordinated carbonyls on reduced or metallic Ru particles [49]. Upon outgassing and increasing temperature, this band shifted, consistent with carbonyls adsorbed on extended metal particles whose vibrational frequency decreases at lower CO coverage due to well-known coupling effects [50, 51]. The shoulder at higher wavenumbers is assigned to characteristic carbonyl groups coordinated to partially oxidized Ru species and on Ru ions [51]. The absence of high-frequency bands above 2100 cm^{-1} , typically attributed to $\text{Ru}^{\text{n+}}(\text{CO})_{2-4}$ species, suggests that CO did not induce Ru oxidation in the $\text{Na}_2\text{CO}_3/\text{SiO}_2$ -based catalysts, even at high temperatures. Therefore FT-IR CO-adsorption experiments indicate that no clear differences can be pointed out by comparing the temperature evolution of the carbonyl species arising from the interaction of CO with Ru in the samples with low and high Na content.

Additional information about the different redox behavior of Ru can be assessed by performing H_2 -TPR of the pre-reduced and oxidized samples. This approach allows to isolate the H_2 consumption related to the reduction of Ru oxides from that of the carbonate hydrogenation, and results are shown in Figure S5. In the case of Ru/SiO_2 , the temperature onset for the reduction is observed at 125°C , like for the fresh sample. Then the H_2 consumption shows a distinct behavior with respect to the fresh sample, possibly due to some modification on Ru induced by the thermal treatment. In any case, also these experiments confirm the shift toward high temperature of the H_2 consumption in the case of the Na-containing samples, confirming the inhibition of Na on Ru reduction.

2.2 | CO_2 Adsorption-Desorption and Reaction

CO_2 Temperature Programmed Desorption (CO_2 -TPD)

The interaction of CO_2 with the catalyst surface has been investigated by Temperature Programmed Desorption (CO_2 -TPD) both in microreactor and in the IR cell in static conditions, to assess the stability of the stored CO_2 over the surface basic sites.

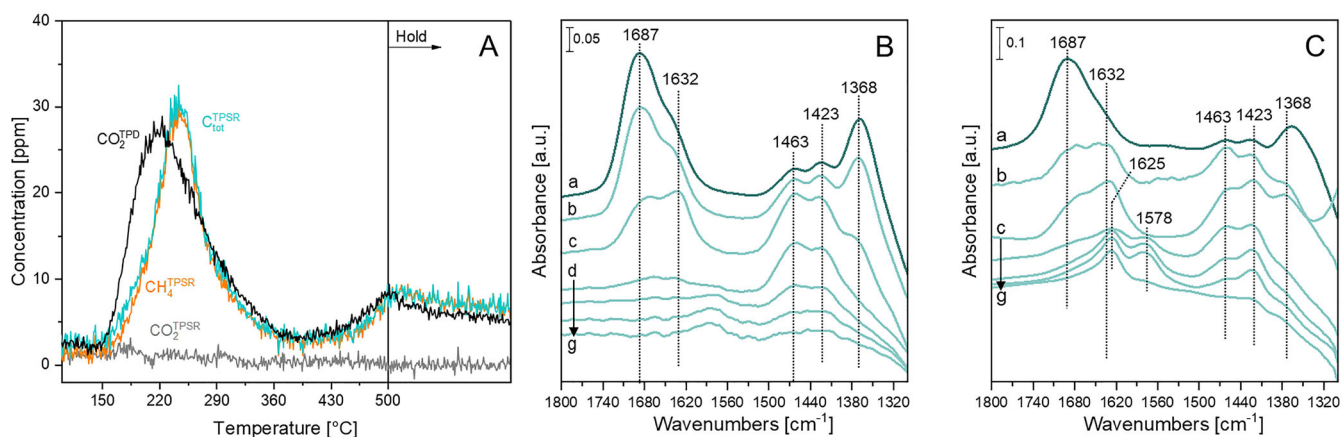


FIGURE 4 | CO₂-TPD and H₂-TPSR results for Ru/5Na₂CO₃/SiO₂ obtained with microreactor (panel A) and FT-IR (panel B: CO₂-TPD; panel C: H₂-TPSR) experiments. The spectrum of the activated surface was subtracted for (A) in the presence of 18 Torr CO₂ and (B) outgassing for 2 min and (C) for 1 h at R.T.; outgassing (CO₂-TPD) or in 140 Torr of H₂ (H₂-TPSR) at increasing temperature from 150°C to 300°C (step: 50°C, spectra d-g).

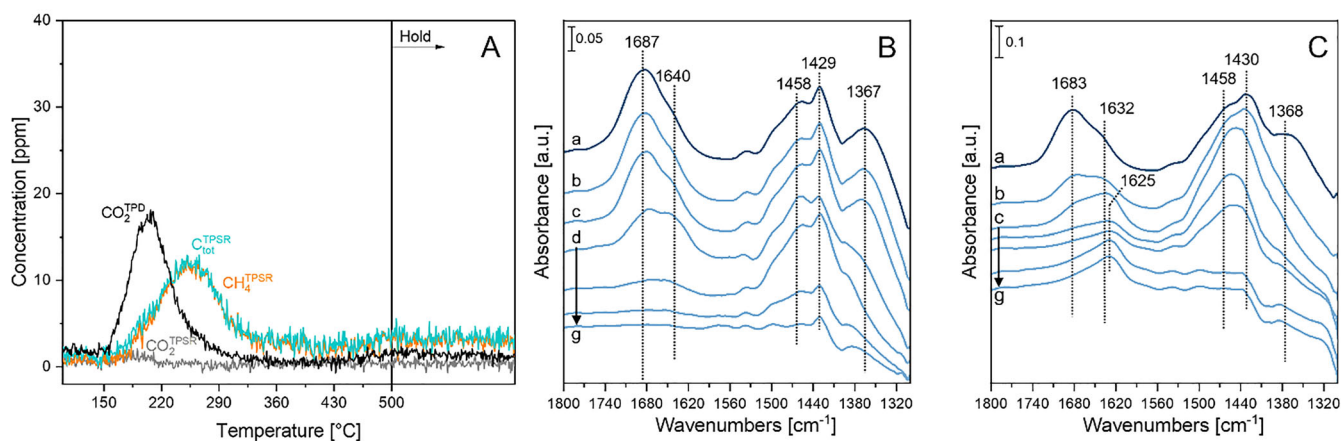


FIGURE 5 | CO₂-TPD and H₂-TPSR results for Ru/15Na₂CO₃/SiO₂ obtained with microreactor experiments (panel A) and FT-IR (panel B: CO₂-TPD; panel C: H₂-TPSR). The spectrum of the activated surface was subtracted for (A) in the presence of 18 Torr CO₂ and (B) outgassing for 2 min and (C) for 1 h at R.T.; outgassing (CO₂-TPD) or in 140 Torr of H₂ (H₂-TPSR) at increasing temperature from 150°C to 300°C (step: 50°C, spectra d-g).

The results of these experiments are shown in Figures 4 and 5 for Ru/5Na₂CO₃/SiO₂ and Ru/15Na₂CO₃/SiO₂, respectively, taken as examples, and in Figure S6 of the supplementary material for the other materials (only microreactor experiments). Note that the figures show the traces of CO₂ desorbed during the TPD experiments (CO₂^{TPD}), and those of CO₂, CH₄ and C_{TOT} (i.e., CO₂ + CH₄) during the H₂-TPSR experiments (CO₂^{TPSR}, CH₄^{TPSR}, and C_{TOT}^{TPSR}) that will be discussed later on. In the case of the Ru/2.5Na₂CO₃/SiO₂ catalyst, CO₂ desorption is observed as soon as the reactor temperature is increased and presents a single peak at 220°C (Figure S6A). No gas phase evolution of CO₂ is observed above 400°C. The quantitative analysis reported in Figure 6 shows that 21.6 μmolCO₂/g_{DFM} are stored on this sample resulting in a poor CO₂ adsorption capacity if compared with similar Na-containing catalysts supported on Al₂O₃ [20, 52], possibly associated with the prevailing weak protonic acidic nature of SiO₂ silica support.

Upon increasing the Na₂CO₃ content (Ru/5Na₂CO₃/SiO₂ sample, Figure 4A), an increase in the amounts of CO₂ desorbed at low

temperature is observed, together with a new desorption peak at 500°C, which reaches a maximum at the end of the temperature ramp. This high temperature desorption peak is associated with strong basicity of the CO₂ adsorption sites, while the increased CO₂ desorption with respect to the previous material is consistent with the increased content of storage element in the material.

When the Na₂CO₃ content is equal to 10 wt.% (Ru/10Na₂CO₃/SiO₂ catalyst, Figure S6B), CO₂ is still desorbed as soon as the catalyst is heated, but the shape of the desorption peak appears narrower than in the previous cases. Moreover, a low but steady CO₂ desorption is observed during the whole temperature ramp, in the absence of a sharp high temperature peak of desorption. The reasons behind this different behavior of this sample can be ascribed to both the modified basicity of the storage element and to morphological properties of the material: the higher content of basic Na₂CO₃ leads to an increased basicity of the surface and lowers the available surface area of the material, as observed from BET results. Consequently, less storage sites are available, and those available show an increased basic nature.

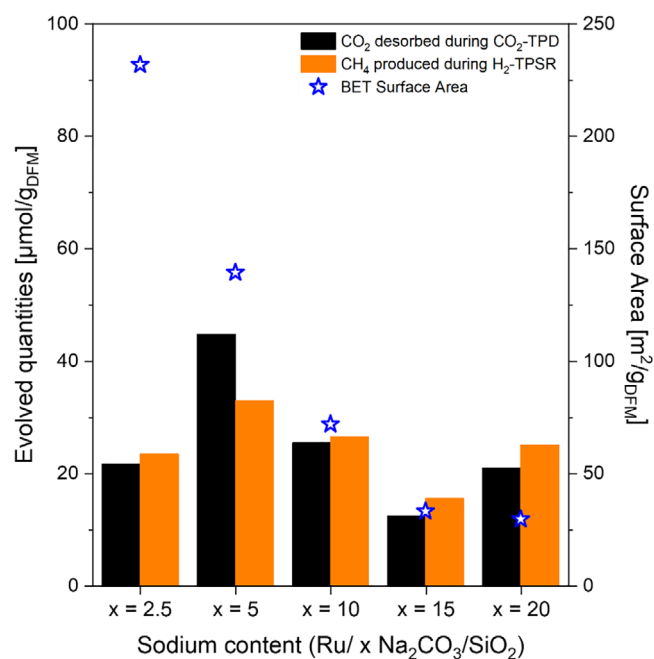


FIGURE 6 | Quantitative CO₂-TPD and H₂-TPSR results (left axis) and BET surface area (right axis) for Ru/x Na₂CO₃/SiO₂ as a function of Sodium content. Black columns: CO₂ desorbed during purge; orange columns: CH₄ produced during TPSR. Stars: BET surface area.

Upon further increasing of the Na₂CO₃ content (Ru/15Na₂CO₃/SiO₂ sample, Figure 5A), the low temperature CO₂ desorption peak is furthermore decreased, and in general the amount of desorbed CO₂ is lower than every sample previously reported.

Finally, in the Ru/20Na₂CO₃/SiO₂ sample (Figure S6C) the low temperature peak is even weaker, while at higher temperatures some CO₂ desorption is observed.

TPD experiments results highlight the poor CO₂ capacity of SiO₂-supported DFMs even when the content of Na₂CO₃ is high. Comparing the amounts of desorbed CO₂ (Figure 6, black columns), in the best case (Ru/5Na₂CO₃/SiO₂: 42 μmol/g_{DFM}) the uptake is one order of magnitude lower with respect to typical Al₂O₃-supported DFMs reported in literature [20, 52], pointing out that the role of the support for the CO₂ storage capacity is crucial. The low interactive nature of SiO₂, that has been reported with respect to Ru/SiO₂ methanation catalysts [36], could also play a role for the dispersion of the Na₂CO₃: at low loadings Na appears to be homogeneously dispersed, while at higher loadings the loss in surface area and the increased basicity of the CO₂ adsorption sites suggest that larger Na-containing particles are formed, thus introducing increased contents of bulk carbonates species with high thermal stability [53].

The nature and thermal stability of the surface species formed upon CO₂ adsorption were investigated with FT-IR spectroscopy for the samples with 5 and 15 wt.% Na₂CO₃ loadings, and results are shown in Figures 4B and 5B, respectively. Before adsorption, the samples were activated under vacuum and subsequently satu-

rated with CO₂ at room temperature to ensure maximum surface coverage. The samples were then subjected to stepwise outgassing between 150°C and 300°C, with temperature increments of 50°C.

The CO₂ adsorption-desorption FT-IR experiments performed on samples with low and high Na loadings reveal the formation of a complex array of carbonate-related surface species within the 1800–1320 cm⁻¹ region. For the low Na-loading sample, Ru/5Na₂CO₃/SiO₂ (Figure 4B), distinct bands were observed at 1687 cm⁻¹ (ν_{3as}) + 1368 cm⁻¹ (ν_{3s}) and 1632 cm⁻¹ (ν_{3as}), corresponding to O–C–O stretching vibrations. These features are associated with two different bidentate carbonate species [54] formed upon CO₂ exposure at room temperature. Both bands disappeared upon outgassing at 150°C, indicating their relatively low thermal stability as observed previously at CO₂-TPD microreactor test. Additional bands centered at 1463 and 1423 cm⁻¹ were detected and assigned to polydentate carbonate species [46, 54]; and strongly bonded bidentate chelating carbonates [55–57] formed on Na oxide, respectively. The 1463 cm⁻¹ band persisted upon heating up to 250°C, whereas the 1423 cm⁻¹ band remained visible up to 300°C. This effect indicates that these carbonate species are not desorbed until the medium-to-high temperature range, highlighting their enhanced thermal stability compared to the bidentate species formed at room temperature. Similar results were also reported by Keturakis et al. [54] and Proaño et al. [58] for sodium-based materials supported over alumina.

A similar population and evolution of carbonate species were observed during the CO₂-TPD FT-IR test for the sample with a higher Na₂CO₃ loading (15 wt.%), e.g., Ru/15Na₂CO₃/SiO₂ (Figure 5B). As in the low-loading sample, bands associated with bidentate carbonate species were detected at 1387 and 1367 cm⁻¹, along with a signal at 1640 cm⁻¹. These features progressively decreased in intensity and disappeared upon outgassing at 150°C, indicating their limited thermal stability. In contrast, the bands at 1458 and 1429 cm⁻¹, corresponding to thermally more stable polydentate and bidentate chelating carbonate species, exhibited higher relative intensities compared to the low Na-loading sample. This suggests that increasing the Na content promotes the formation of more strongly bonded carbonate species, requiring evacuation temperatures of approximately 300°C for polydentate carbonates and above 350°C for bidentate chelating species to achieve complete desorption.

As expected, the substantial increase in sodium loading, while keeping the Ru phase concentration constant, enhanced the CO₂ retention capacity of the silica-supported materials as was reported in literature [20, 59, 60], however, as observed in CO₂-TPD microreactor tests, the increase of Na loading exceeding 10 wt.% over SiO₂ led to a reduction of the overall CO₂ retention capacity, likely due to the presence of larger Na₂CO₃ particles that provokes a decreasing of the specific surface area, resulting in reduced availability of the active storage sites. Although the chemical nature of the adsorbed species remained similar, the overall carbonate population shifted toward carbonate species with higher thermal stability. Similar trends were reported by Keturakis et al. [54] for CO₂ adsorption-desorption experiments performed on alumina-supported samples with varying Na₂O loadings.

H₂ Temperature Programmed Surface Reduction (H₂-TPSR)

Temperature Programmed Surface Reduction with H₂ (H₂-TPSR) experiments have been performed to study the reactivity of the surface carbonates in presence of H₂. Results of H₂-TPSR experiments are shown in Figure 4 for Ru/5Na₂CO₃/SiO₂, Figure 5 for Ru/15Na₂CO₃/SiO₂, and in Figure S6 of the supplementary material for the other materials. Quantitative results are reported in Figure 6.

After saturation with CO₂, Ru/2.5Na₂CO₃/SiO₂ is exposed to H₂ (4% H₂/He v/v) and heated to 500°C (heating rate: 10°C/min). As soon as the temperature is increased, the signal of CH₄ starts to increase reaching a maximum at 280°C. After this temperature, the concentration rapidly decreases until approaching zero by the temperature of 400°C. Comparing the evolution of gas phase species during the TPD and TPSR experiments, it is observed that the peak of CO₂ desorption during TPD (i.e., CO₂^{TPD}) is detected at lower temperatures with respect to the evolution of the carbonaceous species (mainly CH₄) during the TPSR run. It is suggested that during the TPSR run, at low temperatures CO₂ is converted to CO, that remains adsorbed on reduced Ru sites as a Ru-carbonyl [61] and this explains the observed delay in the evolution of C-species in the TPSR run with respect to the TPD experiment. Although CO is not observed in the microreactor experiments, FT-IR studies of carbonate hydrogenation in static conditions evidenced very weak features at 2042 cm⁻¹ and in the range 2000–1950 cm⁻¹, associated with bridging carbonyl species over Ru particles [50, 62] (see Figure S7 in Supporting Information).

Similar conclusions can be drawn for Ru/5Na₂CO₃/SiO₂, where only a small shift to higher temperatures for the onset of methane formation is observed with respect to CO₂ evolution during the TPD experiment.

At variance, for Ru/10Na₂CO₃/SiO₂, a CO₂ desorption peak is observed before the CH₄ production peak during TPSR, indicating that Ru starts to be active toward CO₂ activation at slightly higher temperatures. Moreover, the temperature difference between the peak of CO₂ desorption during TPD and CH₄ formation in TPSR appears to be greater with respect to the previous samples. Along similar lines, in the Ru/15Na₂CO₃/SiO₂ and Ru/20Na₂CO₃/SiO₂ samples having the highest Na content, methane formation is further delayed, and this is particularly evident for the latter sample: CH₄ starts to be produced only above 200°C, with a peak at 500°C.

These data indicates that at low Na₂CO₃ loadings, the high surface area of the silica support ensures an appreciable dispersion of the alkali component. As the Na₂CO₃ loading increases, a higher amount of sodium agglomerates forms, which consequently reduces the number of accessible CO₂ storage active sites. Besides, an inhibition effect is observed of the alkali component on the methanation reactivity.

The reduction of the adsorbed CO₂ was further examined by in situ FT-IR spectroscopy for the Ru/5Na₂CO₃/SiO₂ (Figure 4C) and Ru/15Na₂CO₃/SiO₂ (Figure 5C) samples. In this set of experiments, after saturation with CO₂ at room temperature to

ensure maximum coverage of the surface, the sample was first subjected to prolonged outgassing at room temperature, followed by a stepwise temperature ramp from 150°C to 300°C under H₂ atmosphere.

As for the lowest Na concentration (Figure 4C), the main bands of the spectra are due to carbonate species, whose intensities evolve upon exposure to hydrogen. No additional features associated with formate species typically observed during CO₂ methanation over Ru/Al₂O₃ or Na-based dual-function materials [58, 63–65], could be clearly identified. In agreement with the microreactor analysis (Figure 4A), a rapid and marked decrease in carbonate band intensity was observed as the temperature increased under hydrogen, indicating the progressive reduction of these species.

The peak at 1625 cm⁻¹ was detected starting at 200°C and is attributed to the presence of molecularly adsorbed water on the surface [66]. The appearance of water as a reaction product is linked to the reduction of carbonate species to methane (see gas-phase signal in Figure S8A) through the methanation process, as confirmed by microreactor tests. As observed, the thermally stable carbonate species, namely polydentate carbonates (1463 cm⁻¹) and strongly bonded bidentate chelating carbonates (1423 cm⁻¹), were not perturbed until 200°C. Instead, a sequential reduction occurs: the band at 1463 cm⁻¹ decreases first and completely disappears at 250°C, followed by the progressive reduction of the 1423 cm⁻¹ band. This latter reduction occurs concurrently with the emergence of a new band at 1578 cm⁻¹, assigned to bidentate bridged carbonates [46], which are fully reduced to methane at 300°C. This phenomenon suggests that bidentate chelating carbonates are converted to methane through two parallel pathways: (i) direct carbonate reduction at isolated Na sites, and (ii) conversion to thermally stable bridging bidentate carbonates (at neighboring Na sites), which are subsequently reduced to methane at higher temperatures.

An increase in the Na₂CO₃ loading of the catalyst led to a similar overall evolution of surface species (Figure 5C), albeit with some differences in their behavior upon heating in hydrogen atmosphere after CO₂ capture phase. As revealed by the analysis of gas phase species in the IR cell, the presence of more thermally stable carbonates on the catalyst surface following CO₂ capture resulted in a shift of their reduction to CH₄ toward higher temperatures. In the gas phase (Figure S8B), methane formation was not detected below 250°C, indicating that polydentate (~1460 cm⁻¹) and bidentate chelating (~1430 cm⁻¹) carbonates exhibit greater thermal resistance in the presence of hydrogen. The excess Na₂CO₃ loading in the silica-supported dual-function materials possibly promotes a high dispersion of Ru species on the surface, which ultimately reduces the surface regeneration capacity through the H₂ spillover mechanism.

To summarize, the amounts of CO₂ desorbed during CO₂-TPD runs and the C-containing species (CO₂, CH₄) evolved during H₂-TPSR experiments are shown in Figure 6, along with their respective BET surface area value. The amounts of desorbed species per gram of catalyst appears to present a maximum for Ru/5Na₂CO₃/SiO₂, indicating that no beneficial effect is obtained by further increases of the Na₂CO₃ contents. As already discussed for CO₂-TPD, the increases of Na₂CO₃ loading are not accompanied by a correspondent increase of the CO₂ storage

capacity due to agglomeration of the alkali component, and thus of the CH_4 production. Similar results were reported by Bahrami et al. [67]. They revealed that the increase of Na-loading for Ru-Na based DFMs supported on $\text{CeO}_2\text{-Al}_2\text{O}_3$ did not result in a linear increase of CO_2 -uptake capacity along with CH_4 -production during H_2 -TPSR. This can be due to the increase in the loading of Na-containing species which leads to differences in the formation of Na-oxide due to the precursor reducibility because of Na-agglomeration on the support. Moreover, while medium basic sites increase by increasing the loading of the absorbent, the catalytic material should also be sufficiently available with a higher surface area to convert this adsorbed CO_2 .

2.3 | Reactivity During $\text{CO}_2\text{-H}_2$ Co-Feed

$\text{CO}_2\text{-H}_2$ co-feed experiments have been performed to determine the activity of the catalyst toward the methanation of CO_2 . Experiments have been performed by feeding CO_2 and H_2 in stoichiometric amounts (ratio 1:4) while increasing the temperature to 400°C , and the results are shown in Figure S9 of the supplementary material.

As for Ru/ SiO_2 catalyst (Figure S9A), which has been used as reference, it is possible to observe that CO_2 is converted starting from 125°C . From this temperature onward, CH_4 is initially produced, followed by CO production. Upon increasing the temperature, CO selectivity increases at the expense of CH_4 , coherently with thermodynamic constraints [68]. Once 400°C are reached, CO_2 conversion reaches a plateau while the selectivity toward CO and CH_4 slightly change over time, progressively favoring CO production.

The doping of the SiO_2 support with small amounts of Na_2CO_3 (Figure S9B: 2.5 wt.% and Figure S9C: 5 wt.%) leads to a change in selectivity of the DFM: once CO_2 is starting to be converted, CO is the first observed reduction product. After a small delay, CH_4 starts to be produced, and its selectivity steadily increases until the reaching of 400°C . Although less methane is produced with respect to the Ru/ SiO_2 case, CH_4 selectivity is greater than 20% for both Ru/ $2.5\text{Na}_2\text{CO}_3/\text{SiO}_2$ and Ru/ $5\text{Na}_2\text{CO}_3/\text{SiO}_2$, indicating a mild inhibition of the methanation reaction in the presence of Na.

Notably, a lower CH_4 selectivity is observed during the $\text{CO}_2\text{-H}_2$ co-feed experiments if compared to the $\text{H}_2\text{-TPSR}$ runs. This is likely related to the different $\text{H}_2\text{-CO}_2$ ratios that is attained on the catalyst surface during these two sets of experiments. In fact, during $\text{H}_2\text{-TPSR}$, a feed of H_2 is sent to the carbonated sample and under these conditions we expect a very high $\text{H}_2\text{-CO}_2$ ratio on the surface in view of the slow CO_2 release/desorption from the surface. At variance, when performing CO_2 and H_2 co-feeding experiments, the $\text{H}_2\text{-CO}_2$ ratio on the surface is significantly lower since CO_2 is continuously fed, and under these conditions an increase in the CO selectivity is observed at the expenses of CH_4 .

For further increases of the amounts of Na_2CO_3 (Figure S9D: 10 wt.%, Figure S9E: 15 wt.%, and Figure S9F: 20 wt.%), CH_4 selectivity is further inhibited, with values always below 10%. CO is the main product of CO_2 reduction, pointing out that the inhibition of the alkali component on the methanation reaction.

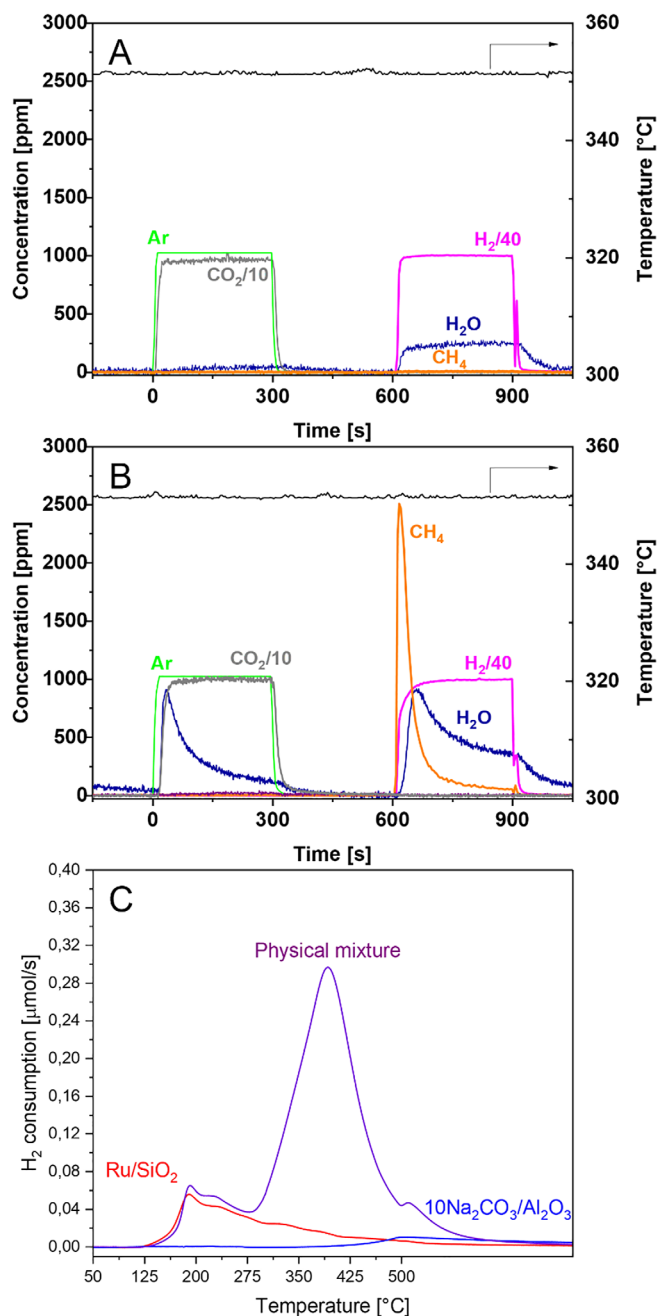


FIGURE 7 | Panels A, B: Results of isothermal cycles performed under model conditions at 350°C (adsorption: 1% CO_2/He , 5 min; reduction: 4% H_2/He , 5 min) for Ru/ $10\text{Na}_2\text{CO}_3/\text{SiO}_2$ sample (panel A) and for the physical mixture of Ru/ SiO_2 and $10\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ and (panel B); panel C: results of $\text{H}_2\text{-TPR}$ experiments for Ru/ SiO_2 (red line), $10\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ (blue line) and their physical mixture (purple line). After reaching 500°C , temperature was kept constant.

2.4 | Isothermal CO_2 Capture and Methanation Cycles

The application of SiO_2 -supported DFMs for the cyclic capture and methanation of CO_2 has been investigated through alternating cyclic experiments, and the resulting cycles in model conditions (i.e., only CO_2 during the adsorption phase) are reported in Figure 7.

When exposing Ru/10Na₂CO₃/SiO₂ (Figure 7A) to a CO₂ containing atmosphere (i.e., $t = 0$ s), the signal of the CO₂ and the signal of the tracer (Ar) are detected at the same time, indicating the absence of a breakthrough time. Then, the CO₂ signal is evolving slower than the evolution of the tracer, indicating that some degree of CO₂ adsorption is taking place. When CO₂ is removed to start the purge phase (i.e., $t = 300$ s), the majority of the just stored CO₂ is desorbed, indicating a low stability of the adsorbed species, leading to negligible CH₄ yields during the successive reduction phase ($t = 600$ – 900 s).

Confirming what reported in the previous paragraphs, Ru/Na formulations evidenced limited CO₂ capture capacity when supported over SiO₂. On the other hand, Ru/SiO₂ itself shows activity in CO₂ methanation [69–71], suggesting the utilization of an alternative approach: separating the adsorption functionality from the methanation one, possibly by using different supports for each component. In this sense, we tested a physical mixture of a methanation catalyst (i.e., Ru/SiO₂) and a CO₂ sorbent (i.e., Na₂CO₃/Al₂O₃, 10 wt.%) to overcome the limitations concerning the CO₂ storage capacity of the SiO₂-based systems [52]. Cycles of CO₂ adsorption and methanation have been performed (Figure 7B) and compared with the ternary configuration of Ru/10Na₂CO₃/SiO₂ previously discussed. Note that equivalent amounts of Ru and Na₂CO₃ are present in the two catalytic systems, differing only for their relative support.

The results of model cycles for the mechanical mixture of Ru/SiO₂ and Na₂CO₃/Al₂O₃ (Figure 7B) show that after CO₂ admission to the reactor, a dead time is observed before it is detected in the gas phase, indicating complete CO₂ adsorption. After the breakthrough time, CO₂ is rapidly evolving in the gas phase until reaching its steady state value, indicating the saturation of the catalyst. After CO₂ switch-off (i.e., at 300 s), during the purge in He, CO₂ concentration decreases, indicating partial desorption of the stored CO₂. Finally, when H₂ is fed ($t = 900$ s) a sharp evolution of the CH₄ peak is observed, along with a consumption of H₂, indicating that the methanation of the previously stored CO₂ is taking place. In this condition the catalyst is able to produce 71 $\mu\text{mol/g}_{\text{PM}}$ of CH₄ with complete selectivity.

Noticeably, a delay with respect to CH₄ evolution, a peak of H₂O is also detected, likely associated to the desorption of H₂O produced from the methanation and previously adsorbed (in agreement with IR data in the previous paragraphs). By comparing the results of the ternary catalyst with the mechanical mixture, the advantage of using the latter is evident.

Similar behavior is observed when testing the catalysts under simulated flue gas conditions, that is, in the presence of CO₂, O₂ and H₂O (Figure S10): Ru/10Na₂CO₃/SiO₂ still captures low CO₂ amounts and consequently produces negligible CH₄ quantities (Figure S10A). On the other hand, the physical mixture (Figure S10A) captures a lower amount of CO₂ with respect to the model case (i.e., only CO₂ during adsorption phase) due to the competitive adsorption mechanism between CO₂ and H₂O for the same Na adsorption sites, translating to a lower CH₄ production (37 $\mu\text{mol/g}_{\text{PM}}$) during the reduction phase. Apparently, since the methane peak does not appear with a delay with respect to the injection of H₂, the presence of O₂ seems to not induce

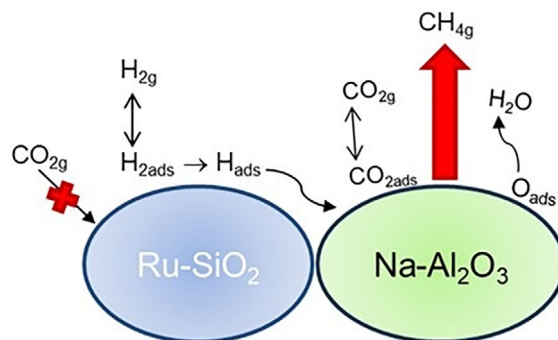


FIGURE 8 | Scheme of methanation reaction on Ru/SiO₂-Na/Al₂O₃ physical mixture.

any modification of the Ru activity during the reduction phase, indicating a good reducibility of Ru.

The results of these experiments point out that physical mixtures are able to effectively produce CH₄ during cyclic operations. The obtained CH₄ yield is similar to the ones reported in the literature in the same conditions with other physical mixtures formulations (Table S1), indicating the effectiveness of this configuration. The mechanisms behind the activity of the physical mixture are still under discussion and could be related to thermal effects [74] due to the exothermicity of CO₂ methanation, leading to CO₂ desorption and methanation, and/or to the spillover of activated hydrogen from Ru to the sorbent [75]. In contrast with traditional DFMs, where superficial intra-particle spillover has been recognized to enhance the catalytic activity [72, 73], in the case of physical mixtures the spillover should be inter-particle [76] due to the segregation of the methanation and storage functions. Likely, in this case the inter-particle H-spillover occurs when H₂ is activated on Ru/SiO₂ and is then transported to Na₂CO₃/Al₂O₃ particles to allow the CO₂ reduction, as depicted in the Figure 8. This mechanism is supported by H₂-TPR experiments performed over Ru/SiO₂, Na₂CO₃/Al₂O₃ and Ru/SiO₂-Na₂CO₃/Al₂O₃ physical mixture (Figure 7C). The H₂ consumption measured for the physical mixture (243 μmol) is significantly higher than that of the Ru/SiO₂ and Na₂CO₃/Al₂O₃ samples (52 and 14 μmol , respectively). This indicates that in the physical mixtures H₂ activated over Ru is able to spill to Na₂CO₃/Al₂O₃ where it is consumed in the reduction of the carbonates, as sketched in Figure 8.

The presence of the interparticle spillover in the physical mixture allows to overcome the limitations given by unwanted interactions between the hydrogenation metal and the storage element, when dispersed over the same support. Once the H₂ transfer is guaranteed from the hydrogenation metal to the adsorbed CO₂, the optimization of the individual reactivity of the methanation and storage functions is also possible.

3 | Conclusions

In this work, the utilization of SiO₂ supported DFMs for the integrated capture and methanation of CO₂ has been investigated. The interactions between SiO₂ and Na lead to limited CO₂ uptakes, which do not change even when increasing the amounts

of Na in the material. The reasons behind this inhibition rely on the drastic reduction of the surface area of the materials following Na doping, as well as due weak protonic acidic nature of SiO₂. Moreover, FT-IR spectroscopic investigation evidenced the high stability of carbonate species formed following CO₂ adsorption that limits CO₂ desorption ability even at high temperatures. On the other side, physical mixtures of Ru/SiO₂ and Na₂CO₃/Al₂O₃ have been used under cyclic CO₂ capture and reduction conditions, leading to interestingly good results if compared to the ternary Ru/Na/Silica formulations. This is related to the presence of H₂-interparticle spillover that guarantees the H₂ transfer from the hydrogenation metal to the adsorbed CO₂, opening the way toward the optimization of the individual reactivity of the methanation and storage functions.

4 | Experimental Section

4.1 | Catalyst Preparation

Commercial SiO₂ (BASF, crushed and sieved to 75–106 μm particles) was used as support to prepare different catalysts, whereas commercial γ-Al₂O₃ (Sasol Puralox, 75–106 μm) was employed to prepare a reference sample.

The Si-based catalysts were prepared via incipient wetness impregnation method [52]. The supports were impregnated with Na₂CO₃ aqueous solutions (final loading 2.5–20 wt.% Na₂CO₃), dried at 110°C for 12 h, and calcined at 500°C for 5 h (heating rate 2°C/min). The obtained samples were then impregnated with an aqueous solution of Ru nitrosyl nitrate (Ru(NO)(NO₃)_x(OH)_y, x + y = 3, Alfa Aesar, 15.5 mg_{Ru}/mL) to obtain a final loading 0.5 wt.% Ru, and then dried at 110°C for 12 h; these dried samples were thus characterized and tested. The prepared samples Ru/xNa₂CO₃/SiO₂, where x is the Na₂CO₃ weight percentage, are identified in the text with acronyms indicating the composition and the Na content; for example, Ru/2.5Na₂CO₃/SiO₂ identifies the sample containing 2.5 wt.% of Na₂CO₃. Using the same procedure, a Ru/SiO₂ sample, nominal Ru loading equal to 0.5 wt.%, was also prepared and subjected to the same drying treatment (100°C, 12 h).

The reference Al-based sample (Na₂CO₃/Al₂O₃, hereafter) was obtained by impregnation of the support to reach a nominal Na₂CO₃ loading of 10 wt.%. The sample was dried at 110°C for 12 h and calcined at 500°C for 5 h (heating rate: 2°C/min).

Finally, a physical mixture of Ru/SiO₂ and Na₂CO₃/Al₂O₃ was obtained by thoroughly mixing the same weighted amount of both samples.

4.2 | Catalyst Characterization

Specific surface area and pore volume of the prepared samples were measured by adsorption-desorption of nitrogen (N₂) at -196°C using a Micrometrics Tristar 300 instrument. Prior to the measurement, the samples were outgassed under vacuum at 120°C for 3 h. Brunauer–Emmett–Teller (BET) surface area and pore volume were determined by the Barrett–Joyner–Halenda (BJH) method, using the adsorption branch of the isotherm.

X-ray diffraction (XRD) patterns were collected using a Panalytical diffractometer (Empyrean model) in Bragg–Brentano geometry fitted with a copper tube (Cu Kα radiation). The data sets were acquired in continuous scanning mode over the 2θ range 5°–70°, using a step interval of 0.0260° and step time of 110 s. Inorganic Crystalline Structure Database (ICSD) has been used to identify the crystalline phases.

Sample morphology and the distribution of the active elements were assessed by a Field Emission Scanning Electron Microscope (FESEM, Zeiss Sigma 500) equipped with an energy dispersive X-ray detector (EDX, Oxford Ultimex 65).

Skeletal Fourier-transform infrared (FT-IR) spectra of catalyst powders were recorded in a FT-Instrument (ThermoNicolet) equipped with an ATR accessory (diamond window), collecting 100 scans with a resolution of 4 cm⁻¹ and background air (DTGS detector and OMNIC software).

Adsorption and desorption of probe molecules FT-IR experiments were carried out in transmission mode over pure powder disks (25 mg average disks weight) directly in an IR cell connected to a conventional gas manipulation apparatus. Before each adsorption experiment, samples were activated in vacuum (10⁻³ Torr) for 1 h at 500°C or reduced at the same temperature in hydrogen and subsequently outgassed at 500°C. CO adsorption and desorption tests were carried out over the pre-reduced samples (400 Torr of H₂ during 1 h at 500°C and subsequent outgassing for 1 h) at R.T., and spectra were recorded upon outgassing and warming in the temperature range from R.T. up to 300°C (50°C/step).

Reducibility of the materials has been assessed through H₂-TPR experiments, carried out using a TPDRO 1100 instrument (ThermoFisher) by feeding 5% H₂/Ar and heating from room temperature to 500°C (heating rate: 10°C/min). Reducibility of Ru has been assessed by repeating H₂-TPR experiments after sequential H₂-TPR (to remove carbonates) and temperature programmed oxidation (TPO), performed by feeding 2% O₂/Ar and heating from room temperature to 500°C (heating rate: 10°C/min).

4.3 | In-Flow Characterization and Testing Experiments

Catalytic in-flow characterization and testing were performed through microreactor and FT-IR setups. Microreactor experiments have been carried out by loading 60 mg of catalyst in a quartz microreactor (internal diameter 8 mm). The catalytic bed has been packed in the reactor using quartz wool and the rest of the reactor volume has been filled with quartz granules to reduce the void volume, ensuring a proper mixing of the feed gases. Temperature has been monitored using a K-type thermocouple placed in the center of the catalytic bed.

Every microreactor experiment has been performed using a constant gas flow rate of 100 mL(STP)/min, corresponding to 100 L(STP)/h/g_{cat}. Gases have been dosed using Brooks mass flow controllers and sent to two 4-way-valves, allowing to stepwise change the feed composition when switching the position of the valve. In this direction, in each valve two identical gas

flow rates are fed, consisting in a reagent (i.e., CO₂ or H₂) and an equal flow rate of He, which has also been used as carrier gas, allowing to change the gas phase composition without affecting the total gas flow rate. The composition of the gases at the outlet of the reactor have been monitored using a Mass Spectrometer (Pfeiffer Vacuum, analysis every 4 s) and a micro-gas Chromatograph (Agilent, analysis every 180 s) equipped with two different chromatographic columns.

Each catalyst has been pre-treated in H₂ atmosphere (4% H₂/He v/v) at high temperature (500°C, heating rate: 10°C/min) to decompose the precursor of Ru and reduce it to its metallic form. The same pretreatment has been repeated before each experiment, to remove any adsorbed species that could have been adsorbed from air (i.e., CO₂, H₂O).

The stability and reactivity of the adsorbed CO₂ have been gathered respectively from Temperature Programmed Desorption of CO₂ (CO₂-TPD) and Temperature Programmed Surface Reduction with H₂ (H₂-TPSR) experiments, respectively. After CO₂ saturation at 150°C, the catalyst was heated to 500°C (heating rate: 10°C/min) in inert atmosphere (He) to perform CO₂-TPD or reducing atmosphere (4% H₂/He v/v) to perform H₂-TPSR.

Similarly, CO₂-TPD experiments were performed in the FT-IR setup by introducing into the IR cell 18 Torr of pure CO₂ at room temperature and then outgassing at R.T. for 1 h. Subsequently, spectra of the surface species were recorded at each desorption T-step in the range 150–300°C. Differently, to perform H₂-TPSR after CO₂ adsorption phase and outgassing at room temperature, 140 Torr of pure H₂ were introduced in the IR cell at room temperature, and then spectra of the surface species and gas phase were recorded at each temperature in the range 150–300°C maintaining H₂-atmosphere.

Reactivity under stoichiometric amounts of CO₂ and H₂ (CO₂:H₂ = 1:4) for the Sabatier reaction was investigated in the microreactor setup by co-feeding CO₂ and H₂ (1% CO₂ + 4% H₂ v/v in He) while increasing the temperature up to 400°C (heating rate: 10°C/min). After 30 min, the temperature was decreased (heating rate: -10°C/min) still in presence of CO₂ and H₂ until R.T. was reached.

Reactivity under adsorption and reduction isothermal cycles has been performed at 350°C in microreactors. Cycles are performed by alternating an adsorption phase (5 min, 1% CO₂/He v/v) and a reduction phase (5 min, 4% H₂/He v/v) spaced out by a purge in inert (5 min, He). Three cycles were performed for each experiment to obtain reproducible results. To conclude the experiment, the catalyst is heated to 500°C (heating rate: 10°C/min) in H₂ (4% H₂/He) to desorb eventual unreacted adsorbed species. Cyclic experiments have been performed in model conditions (adsorption phase: 1% CO₂/He v/v) or in simulated flue gas conditions (adsorption phase: 1% CO₂ + 3% O₂ + 2% H₂O in He v/v) to observe the influence of such conditions on the reactivity. For the physical mixture, equivalent amounts of active phases (i.e., Ru and Na₂CO₃) have been used, thus loading twice the amount of catalyst (i.e., 60 mg Ru/SiO₂ + 60 mg 10Na₂CO₃/Al₂O₃). A different quartz microreactor has been used (internal diameter 11 mm) to maintain the same height of the catalytic bed. For the quantitative calculations, moles of evolving

species (i.e., CO₂, CH₄) have been divided by 60 mg for DFMs (i.e., μmol/g_{DFM}) and 120 mg for physical mixtures (i.e., μmol/g_{PM}).

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

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