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Enhanced H₂ recovery by coupling the water–gas shift reaction with *in situ* CO₂ capture and mineralization using earth abundant Ca- and Mg-silicates and hydroxides†

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Decarbonization of clean energy carriers such as H₂ by coherent integration of multiphase chemical pathways with inherent carbon mineralization is a thermodynamically downhill pathway designed for a sustainable climate, energy, and environmental future. In this effort, a low-temperature water–gas shift reaction (WGSR) with Pt/Al₂O₃ catalysts is integrated with *in situ* carbon mineralization in a multiphase reaction environment. The hypothesis that Pt-based catalysts favor selective formation of H₂ over CH₄ has been investigated. H₂ yields increased by 30.8%, 9.5%, 8.3%, and 1.7% in the presence of Ca(OH)₂, Mg(OH)₂, Mg₂SiO₄, and CaSiO₃ relative to the blank experiment without the sorbent at constant experimental conditions of 250 °C and reaction time of 12 hours in the presence of Pt/Al₂O₃ catalyst with initial CO and N₂ pressures of 8 bar and 12 bar, respectively. These studies unlock the feasibility of advancing single-step multiphase pathways for enhancing H₂ yields with inherent CO₂ capture and mineralization for a low carbon and sustainable energy and resource future.

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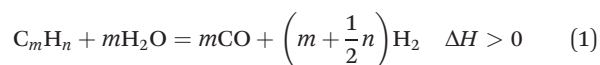
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1. Introduction

Demand for low-cost and abundant fossil energy resources has exacerbated greenhouse gas emissions (GHGs) leading to detrimental impacts on climate and the environment.¹ To mitigate the detrimental impacts of GHG emissions and realize a carbon-neutral future, it is essential to develop novel chemical pathways to produce clean energy carriers such as H₂ while capturing and storing CO₂ emissions.^{2,3} As an alternative to conventional multi-step processes to capture, compress, and store CO₂ emissions, intensified approaches that simultaneously inherently capture and store CO₂ emissions in a single step *via* reactive separation are needed.^{4,5} The abundance of renewable energy resources such as biomethane serves as a viable feedstock for H₂ production as an alternative to fossil-derived methane. H₂ has emerged as a preferred energy carrier given the high energy density of H₂ (122 MJ kg⁻¹) compared to alternative fossil fuel-derived resources⁵ and the absence of CO₂ emissions on combustion.⁶

Current commercial H₂ production involves energy-intensive hydrocarbon reforming, by which the non-renewable hydrocarbon fuel is reformed into carbon monoxide (CO) to release H₂ over metal catalysts.⁷ As one of the primary reforming techniques, steam reforming (SR) is widely studied due to its relatively low operating temperature and high purity of the H₂ product.⁸ The general reaction for steam reforming can be represented as follows:



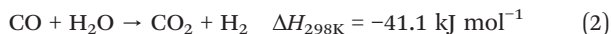
In this expression, when $m = 1$ and $n = 4$, the reforming reaction corresponds to steam methane reforming (SMR), which is the most extensively applied approach for industrial H₂ production with thermal efficiencies of up to 85%.⁸ SMR is typically coupled with subsequent water–gas shift reaction (WGSR) and methanation to further enhance H₂ yield and purity.⁹ As an effective supplement to SMR, the WGSR generates additional H₂ while simultaneously reducing the concentrations of CO at intermediate temperatures (200–450 °C).¹⁰ The literature review by Wagner on catalytic advancements¹¹ and fundamental insights on kinetic rates and challenges towards water gas shift are pioneering studies focused on optimizing this reaction.^{9,12} Thermodynamically, WGSR is favored at low temperatures because it is a reversible exothermic process using steam as the hydrogen source as eqn (2) indicates:

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However, in the low-temperature regime, WGS is challenged by sluggish kinetics and low CO conversions. The limiting kinetics of WGS can be overcome by harnessing catalysts to enhance CO conversion kinetics and yields at low temperatures, for which various noble (Pt, Pd, Ru) and non-metal (Cu, Zn, Fe, Cr)-based supported catalysts have been reported in precedent literature.^{13–15} Especially, Pt-based materials have been reported to be promising metals for WGS in the medium to low temperature (250–350 °C) regime due to their high stability in oxidizing environments.¹⁶

Even though steam methane reforming and WGS are widely deployed for H₂ production, challenges associated with producing high-purity H₂ and achieving high selectivity remain.¹⁷ The competing co-presence of CO and CO₂ along with H₂ from gasification and WGS at the effluent limits H₂ selectivity and its yield. Consequently, the reactor effluent gases must be purified by the pressure swing adsorption process operating at high pressures (1 MPa) to produce a significant amount of high-purity H₂.

This challenge necessitates the development of sustainable multiphase chemical pathways for selective and energy-efficient reactive separation of H₂ from CO₂ and CO. Harnessing alkaline materials such as Ca- and Mg-bearing hydroxides and silicates is a thermodynamically favorable pathway to enhance H₂ yield. The proposed enhanced WGS concept works based on the Le Chatelier's principle, in which the reversible gas phase WGS when integrated with a slurry bearing Ca- and Mg-bearing hydroxides and silicates enhances H₂ yield *via in situ* CO₂ capture and mineralization.¹⁸ This integrated concept has the potential to significantly improve reaction efficiencies, minimize capital cost, and simplify the process configuration from the two-step conventional catalytic process to a single – step process. This approach also circumvents the thermodynamic limitations of conventional WGS thereby enhancing the rate

of forward reaction for H₂ generation, driving the reaction towards the product side by shifting the equilibrium, and allowing high conversions of CO and steam to H₂ and solid carbonates.

The approach of coupling carbon mineralization as a pathway to capture and crystallize CO₂ emissions as solid carbonates is a significant departure from conventional carbon capture and storage (CCS) technologies in which CO₂ is first captured using solvents, sorbents, and membranes and is then injected into geologic reservoirs for storage.^{19–23} The permanence and stability of solid Ca- and Mg-bearing carbonates²⁴ motivate the coupling of carbon mineralization as a pathway to separate CO₂ emissions and enhance H₂ yields. Table 1 summarizes the state-of-the-art literature reports focused on the enhancement towards WGS performance and H₂ yields.^{18,25–33}

Carbon mineralization involves the reaction between silicate, hydroxide, and oxide minerals bearing divalent cations (*e.g.*, Ca²⁺, Mg²⁺ ions) and CO₂ to produce the respective carbonates. The negative free energy change of the reaction indicates the spontaneity of the process and the chemical stability of the carbonate products.³⁴ Apart from the spontaneity of the reaction, carbon mineralization has several advantages. First, the natural abundance of starting materials guarantees easy accessibility and affordable prices. Besides, the alkaline minerals have a large CO₂ storage capacity, providing an enormous CO₂ storage potential worldwide. Additionally, the typical products from carbon mineralization, including silica, carbonates, and metal oxides, usually have multiple industrial applications after purification.

For carbon mineralization, the starting materials could be magnesium silicate minerals such as (Mg,Fe)₂SiO₄ (olivine), Mg₂SiO₄ (forsterite), MgO (periclase), CaO (lime), CaSiO₃ (wollastonite), and Ca²⁺- and Fe²⁺-rich silicates (*e.g.*, larnite). These minerals are known to spontaneously react with atmospheric CO₂ to produce solid carbonates.^{35–37} These geoinspired mineralization pathways motivated advances in

Table 1 Comparative table of enhanced WGS with different sorbents and catalytic systems

Feedstock	Sorbents	Catalyst	Temperature [°C]	Pressure [bar]	Sorbents amount [g]	Catalyst amount [g]	H ₂ yields [%]	CO _x yields [%]	Ref.
CO ₂ , CO, steam, H ₂ , N ₂	LDHs	Iron–chromium	400	28	891	434	99.83	0.17%	18
CO, steam, Ar	LDHs	Cu/ZnO/Al ₂ O ₃	400	1	48.45	48.45	99.99	0.01%	25
CO, steam, N ₂	CaO/Al ₂ O ₃	Ni nanoparticle	400	NA	0.25	0.0075	76–98	NA	26
CO, steam, N ₂	CaO/Al ₂ O ₃	Pt/Al ₂ O ₃	350	NA	NA	NA	High purity	NA	27
CO, steam, Ar	CaO/Ca ₁₂ Al ₁₄ O ₃₃	Fe/Mn	400–700	1	0.88	0.12	88–95	5–12	28
CO, steam	CaO-based	Pd/Ni/Co	425–550	1	20	1	98–99	0.35	29
CO, steam, H ₂ , He	CaO/NaOH	Pt/ZDC	300–600	1–11	NA	NA	51–100	0–49	30
CO, steam	AMS/MgO/CaCO ₃	Cu/Ce _{0.6} Zr _{0.4} O ₂	275–375	12	2.625	2.625	86–99	1–14	31
H ₂ , CO, steam, N ₂	Na–Mg based	Cu/ZnO/Al ₂ O ₃	375	1	5	5	High purity	NA	32
CO ₂ , N ₂ , H ₂	CaO	MO _x (Al, Ce, Ti, Zr)	600–750	NA	0.2	0.1	NA	NA	33
H ₂ , CO, N ₂	Mg/Ca hydroxide and silicate	Pt/Al ₂ O ₃	250–300	20	3	3	72.67	27.33	This work



engineered analogs to accelerate mineralization.^{34,38} Prior work by Gadikota and co-workers showed that olivine carbon mineralization extents as high as 85% are achieved at 185 °C, $p\text{CO}_2$ of 139 atm, reaction time of 3 hours, and in 1.0 M NaCl and 0.64 M NaHCO_3 solution with particle sizes of 30 μm or less.^{39–41} The observed high extents of carbon mineralization at the temperature conditions that are similar to that of the water gas shift reaction motivated the coupling of this mineralization pathway.

As an alternative to these hydrothermal routes, direct gas – solid mineralization routes^{42,43} are explored but challenged by slow kinetics when Mg- or Ca-bearing silicates are used. In this context, sorbent-enhanced water gas shift reactions (WGSR) in direct gas–solid modes were extensively studied.^{44–47} Compared with the widely used membrane separation approach to separate CO_2 in WGSR, the sorbent-enhanced WGSR possesses multiple advantages, including more favorable and uniform kinetics, greater material durability, and larger CO_2 capture capacity.^{30,48} Conventional sorbent-enhanced water–gas shift reactions occur in fluidized bed reactors with steam-saturated CO_2 flow.^{32,49} The selected sorbents are typically metal oxides (e.g., CaO) or layered double hydroxide (LDH) (e.g., hydrotalcite) with high CO_2 capture capacity.^{18,25,26} However, direct gas–solid carbonation is very kinetically limited and tends to be greatly enhanced with the participation of aqueous media, which dissolves the alkaline resource to release metal cations that capture CO_2 to form carbonate species.^{43,50–52}

While Ca-bearing oxides have been reported to be effective for enhanced water gas shift reaction in a direct gas–solid reaction mode,^{27,29,30} the direct use of earth abundant Mg- and Ca-bearing silicates in this mode is significantly challenged by mass transfer limitations and slow kinetics of reaction.^{39–41} The direct use of Mg- and Ca-bearing silicates circumvents the need to use additional reagents to produce more reactive Ca- and Mg-bearing hydroxides. To accelerate mass transfer and the kinetics of CO_2 capture using earth-abundant Mg- and Ca-bearing silicates, aqueous routes which involve the dissolution of silicates to release Mg^{2+} or Ca^{2+} ions for capturing CO_2 produced from the WGSR to produce the respective carbonates are investigated in this work.⁵³ Prior studies have reported that the dissolution of silicate minerals facilitates more robust mass transfer and accelerates carbon mineralization.^{54–56} Prior studies have demonstrated enhanced H_2 production using $\text{Mg}(\text{OH})_2$ for *in situ* CO_2 capture and mineralization.⁵⁷ However, the influence of directly using of Mg- and Ca-bearing silicates for the enhanced water gas shift reaction has not been reported to date. The conventional hypothesis is that silica precipitated as Mg- and Ca-bearing silicates limit mass transfer and thus lower reactivity with CO_2 to produce the respective Ca- and Mg-bearing carbonates. However, this hypothesis has not been evaluated in the context of harnessing earth-abundant Ca- and Mg-bearing silicates to enhance the WGSR with *in situ* CO_2 capture and

mineralization, and is therefore, the focus of the proposed investigations.

Several favorable multiphase chemical interactions are necessary for this approach to be feasible. First, the reactivity of CO and steam in the presence of Pt/ Al_2O_3 catalyst needs to be robust in producing CO_2 and H_2 as the products in sufficient quantities. Second, CO_2 needs to be soluble in the aqueous phase to facilitate the forward WGSR for enhancing H_2 production. Third, the dissolved CO_2 needs to react with Mg- and Ca-bearing silicates to produce the respective carbonates. Fourth, the precipitated silica should not limit mass transfer and the subsequent carbon mineralization behavior. To unlock the full potential of enhanced H_2 production coupled with carbon mineralization, it is essential to identify the rate limiting factor and advance strategies to overcome these limitations. To this end, the multiphase reaction pathways are assembled such that the gas phase catalytic WGSR is coupled with slurry phase carbon mineralization as shown in Fig. 1. The associated CO_2 from WGSR reacts with water to produce carbonate species, which subsequently react with dissolved calcium or magnesium ions obtained from the sorbents for *in situ* carbon mineralization. To identify and address the factors limiting H_2 production coupled with carbon mineralization, several key research questions are addressed: (i) what are the chemical mechanisms underlying enhanced H_2 conversion with *in situ* carbon mineralization using Mg- and Ca-bearing

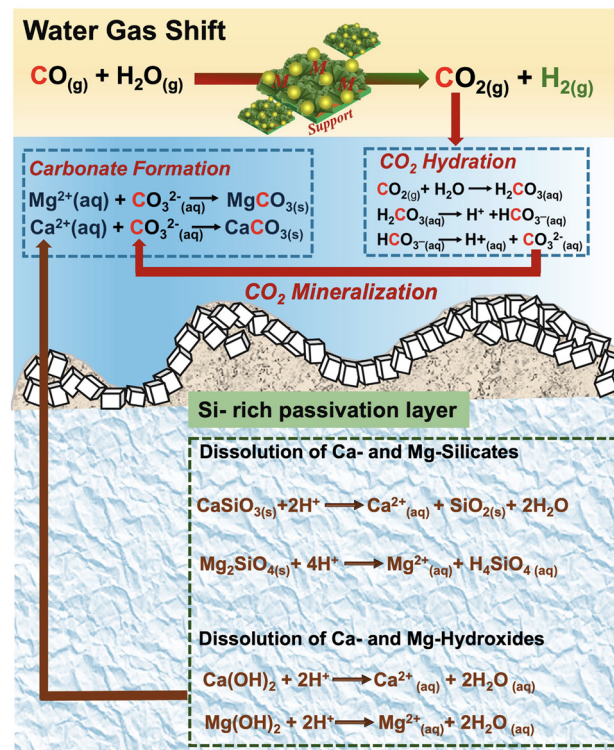


Fig. 1 Schematic representation of the pathway to enhance H_2 conversion by integrating the water gas shift reaction integrated with carbon mineralization of Ca- and Mg-bearing hydroxides and silicates.



hydroxides and silicates? (ii) What is the influence of the silicate vs. hydroxide reactivity on enhancing H₂ production with carbon mineralization? (iii) In this multi-step reaction pathway, what is the rate limiting step and how can this step be accelerated?

Addressing these questions unlock new insights into the mechanisms and the scientific feasibility of enhancing H₂ conversion with *in situ* CO₂ capture and mineralization using Mg- and Ca-bearing silicates and contrasting with that of the respective hydroxides.

2. Experimental methods

2.1 Materials and methods

All experiments to investigate enhancement in H₂ conversion with the WGSR coupled with *in situ* CO₂ capture and mineralization are conducted in the presence of platinum on alumina support (Pt/Al₂O₃) catalyst.²⁷ The Pt/Al₂O₃ catalyst is selected due to its high activity, superior thermal stability, and high product specificity to H₂ and CO₂.^{58–60} Specifically, Pt/Al₂O₃ catalyst is sized as 3.2 mm pellets with a composition of 0.5 wt% Pt and is procured from Sigma Aldrich, USA. Mg-bearing hydroxide (brucite (Mg(OH)₂)) and silicate (forsterite (Mg₂SiO₄)) used for *in situ* CO₂ capture and mineralization are obtained from Fisher Chemical and Xi'An Function Material Group Co. Ltd, respectively. Ca-bearing hydroxide (portlandite (Ca(OH)₂)) and silicate (wollastonite (CaSiO₃)) also used for *in situ* CO₂ capture and mineralization are acquired from Thermo Fischer Scientific Co., USA. These Mg- and Ca-bearing silicates and hydroxides are ball-milled in a bench-top mixer mill (8000 M Mixer/Mill® by SPEX® Sample Prep) to obtain raw materials with comparable mean particle sizes (5.57 μm to 10.38 μm). The particle sizes of the milled samples are determined using laser diffraction

particle size analyzer (Anton Paar). Deionized water (18.2 MΩ cm, Millipore) is used throughout all the experiments as required. Ultra-high purity CO gas (99.999% purity) is supplied by Airgas Co., USA.

2.2 Experimental setup for enhanced WGSR and carbon mineralization

Experiments to investigate enhanced H₂ conversion with *in situ* CO₂ capture and mineralization are conducted in a 50 mL stainless steel high-pressure stirred reactor (Micro Bench Top Reactor, Parr Instruments Co., USA) in a multiphase reaction environment. A schematic representation of the experimental setup is shown in Fig. 2. The reactor is a stirred cylindrical system with an inner diameter of 33 mm and a height of 57 mm. It features a 4-blade Rushton turbine stirrer with a 20 mm diameter, positioned 9 mm above the bottom along the central axis of the reactor. Given the stirring rate and the dimensions of the stirrer, efficient mixing and mass transfer in the aqueous phase is expected during the reaction. Simultaneously, CO and N₂ are introduced through a gas inlet pipe (inner diameter of 3 mm) into the headspace for gas-phase reactions and to build internal pressure. Elevated internal pressures are preferred for these multiphase reactions, as the increased CO partial pressure shifts the equilibrium of the WGSR towards higher H₂ and CO₂ production, enhancing the subsequent dissolution and diffusion of CO₂. Catalytic conversion of CO and steam occurs in the gas phase in the presence of Pt/Al₂O₃ catalyst. The surface area, pore volume, and average pore diameter of Pt/Al₂O₃ catalyst are 163.13 m² g⁻¹, 0.303 cc g⁻¹, and 6.282 nm, respectively (see Table S1 in ESI†). Prior to CO gas injection, 3 g (0.5 wt%) of the commercial Pt/Al₂O₃ catalyst is placed in an aluminum basket and suspended in the

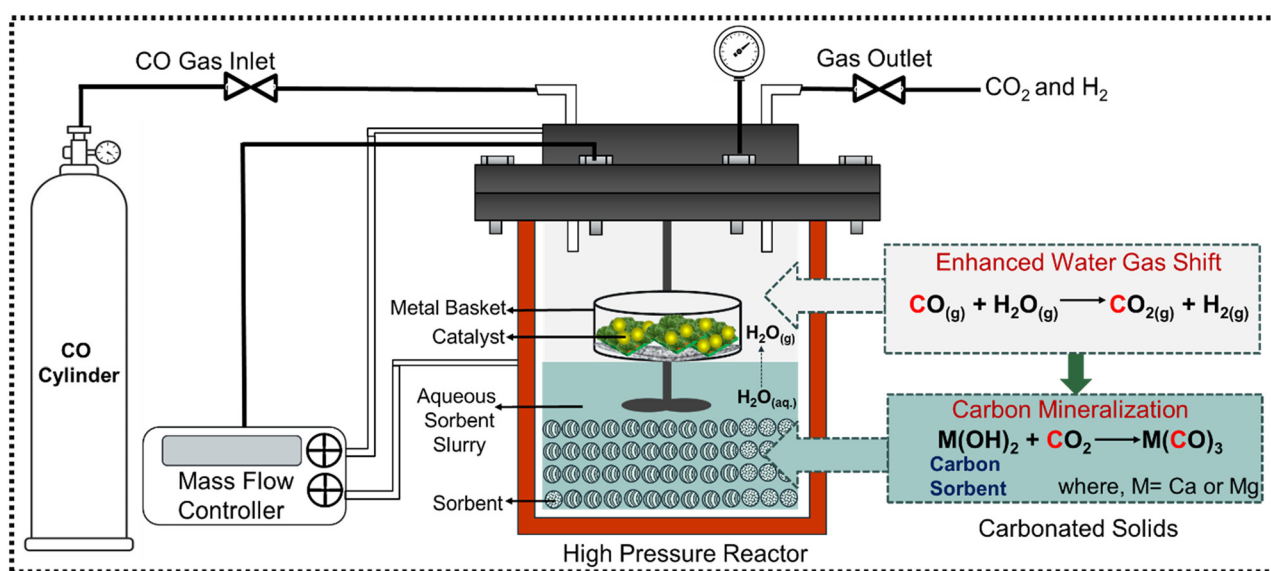


Fig. 2 Schematic representation of the experimental setup for coupling the water gas shift reaction (WGSR) with *in situ* CO₂ capture and mineralization for enhanced H₂ conversion.



headspace of the reactor ensuring the basket is not in contact with the sorbent slurry. CO flow rate from the cylinder is controlled by using a mass flow controller (MFC). CO₂ capture and mineralization occurs in a slurry phase bearing 3 g of Mg- and Ca-bearing hydroxides and silicates, mixed with 10 mL of deionized water. The initial solid-to-liquid weight ratio is set at 3:10, resulting in mole percentages of 8.48% for Mg(OH)₂, 3.70% for Mg₂SiO₄, 6.80% for Ca(OH)₂, and 4.45% for CaSiO₃, respectively. The sorbent-to-catalyst ratio is maintained at a consistent weight ratio of 1:1 across all cases.

The headspace of the reactor is purged with CO gas for 15 minutes to evacuate gaseous impurities before it is pressurized and sealed tightly. After reaching the desired pressure set point for CO at 20 bar, the heater is switched on to achieve a setpoint of 250 °C with a constant stirring rate of 300 rpm, signaling the start of the experiment. Steam is generated by the vaporization of water in the slurry. The corresponding partial pressure of steam is determined by the temperature in the steam table (Table S2.1 and 2.2[†]). The reactor outlet is sealed with heating tape to avoid the possibility of steam condensation and is connected directly to a gas chromatograph to analyze the concentrations of gaseous products. The pH of the slurry increased to 9.95 for Mg(OH)₂, 8.69 for Mg₂SiO₄, 12.37 for Ca(OH)₂, and 8.98 for CaSiO₃, respectively. The experiments are performed at different reaction times ranging from 3 to 12 hours. After the completion of the reaction, the reactor is cooled down to ambient temperature. Following this, the outlet valve is slowly opened to purge the gaseous products in the micro-GC and the carbonate-bearing solid products are collected for further analysis and characterization. Additionally, enhancement in H₂ yield resulting from CO₂ capture and mineralization is investigated as a function of reaction time and the alkaline sorbent type.

Additional experiments are conducted to determine the exact moles of each gas in the reactor. The experimental setup is the same as described previously. In this approach, 8 bar of CO is injected into the reactor with 12 bar of N₂. N₂ is used as a reference due to its inert nature and unchanged pressure over the course of the reaction. This approach enables the calculation of the moles for the other gaseous components based on the initial N₂ content. The temperature is increased to a setpoint of 300 °C, and the reaction is performed for 12 hours, while keeping other reaction conditions unchanged, to investigate the influence of Mg- and Ca-bearing hydroxides and silicates on enhancing H₂ conversions.

2.3 Product analysis and characterization

After the reaction, the compositions of effluent gases are analyzed by micro gas chromatography (GC) with the calibration data shown in Fig. S1.[†] The changes in the composition and structure of the Mg- and Ca-bearing hydroxides and silicates are investigated using infrared (IR)

spectroscopy collected in an attenuated total reflection (ATR) mode using an attenuated total reflection-Fourier transform infrared spectrometer (ATR-FTIR, Nicolet™ iS50, Waltham, MA), and X-ray diffractometry (XRD, Bruker D8 Advance ECO powder diffractometer, Bruker), respectively. Furthermore, the morphology and particle sizes are determined using the field emission scanning electron microscope (FESEM, LEO 1550 FESEM, Bruker) and particle size analyzer (Anton Paar). The surface area and the pore size distributions of the sorbents before and after the experiments were determined by N₂ adsorption-desorption isotherms using the Brunauer-Emmett-Teller technique (BET) (Quantachrome Autosorb iQ Analyzer, Boynton Beach, FL) with the BJH model. Prior to measuring the adsorption-desorption isotherms, the samples were outgassed at 140 °C for 12 hours. A ±5% BET instrument error was accounted for all the analysed samples. The concentration of formate in the aqueous phase was measured using a 500 MHz ¹H NMR spectrometer (Bruker AVIII 500) using a solvent suppression method. The calibration line for formate concentration and its corresponding slope, determined using DMSO as internal standards, are shown in Fig. S2.[†]

3. Results and discussion

3.1 Reaction pathways involved in coupled WGSR with *in situ* CO₂ capture and mineralization for enhanced H₂ conversion

The multiphase reactions involved in coupling the WGSR with *in situ* CO₂ capture and mineralization for enhanced H₂ conversion include: (i) low-temperature conversion of CO and steam over Pt/Al₂O₃ catalyst to produce CO₂ and H₂; (ii) dissolution of Mg- and Ca-bearing hydroxides and silicates to release Mg²⁺ and Ca²⁺ ions, respectively and promote alkalinity; (iii) dissolution of the produced gaseous CO₂ in the alkaline aqueous phase; (iv) reactivity of the hydrated CO₂ with Mg²⁺ and Ca²⁺ ions to mineralize into Mg and Ca-carbonates; and (v) generation of high-purity H₂ due to equilibrium shift due to CO₂ capture and mineralization.

The motivation for using Pt/Al₂O₃ catalyst stems from the need to direct the formation of H₂ as opposed to CH₄.⁶¹ Prior analogous studies showed that Pt or Ni/Al₂O₃ catalysts are effective in reforming aqueous biomass oxygenates such as ethylene glycol and glycerol to produce H₂ and CO₂ preferentially over CH₄.⁶² Therefore, in this study, Pt/Al₂O₃ catalysts are used to lower the activation energy barrier, accelerate reaction kinetics, suppress the formation of CH₄, and promote the formation of H₂ and CO₂. Furthermore, the *in situ* capture and conversion of gaseous CO₂ in the presence of alkaline Mg- and Ca-bearing hydroxides and silicates to produce the respective carbonates favors the forward equilibrium shift towards more CO conversion and H₂. Dissolution of Mg- or Ca- bearing hydroxides and silicates releases Mg²⁺ and Ca²⁺ cations which capture and solubilize CO₂ to produce the respective solid carbonates. For example, in this work, the pH of the alkaline slurry is observed to be in the range of 8.69–12.37 for the Mg- and Ca-bearing



hydroxides and silicates. This pH is ideal to capture and solubilize CO₂ from the gas phase to produce the respective (bi)carbonate species.

To probe the mechanisms underlying enhanced H₂ conversion by coupling the WGSR with *in situ* CO₂ capture and mineralization, the first set of experiments are conducted by injecting CO gas. Steam required for the WGSR is provided by the slurry. The ratio of CO to steam is calculated and quantified from the steam table (Table S2.1 and 2.2, ESI†). In this approach, the effluent gas compositions are measured using micro gas chromatography (GC), and the molar percentage of each phase is normalized by the total amount of H₂, CO, and CO₂. This approach provides insights into the relative abundance of the gas phase compositions. In this scenario, the relative gas phase composition of H₂ can be elevated if CO₂ is absorbed by the liquid phase, even if CO conversion is unchanged. Therefore, CO conversion is determined for quantifying the enhancement in WGSR using the following expression:

$$R_{\text{CO}} = \frac{M\%_{\text{H}_2}}{M\%_{\text{H}_2} + M\%_{\text{CO}}} \quad (3)$$

In this expression, R_{CO} is the conversion of CO, $M\%_{\text{H}_2}$, and $M\%_{\text{CO}}$ are the mole percentages of H₂ and CO in the measured gas samples, respectively. In this equation, the mole percentage of H₂ is applied as the substitute for the mole percentage of CO₂ because a large amount of generated CO₂ partitions into the aqueous phase as the reactant for carbon mineralization, making it inaccurate to quantify CO₂ only based on the gas phase compositions.

Additionally, the exact number of moles of each gas is necessary to determine the theoretical maximum yield of H₂ and gaseous CO₂ compositions. To this end, additional experiments are conducted with a moderate amount of N₂ in the system as the baseline. In this approach, the absolute number of moles of N₂ is constant throughout the experiment.

This approach enables the determination of the exact moles of H₂, CO, and CO₂ by the van der Waals equation (as shown below) from the normalized mole percentages after the multi-step reactions.

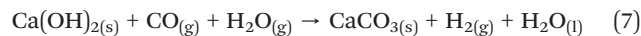
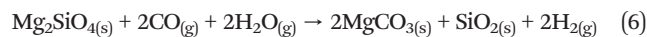
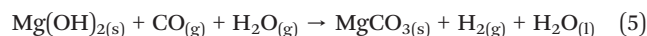
$$\left(P + \frac{n^2 \cdot a}{V^2}\right)(V - n \cdot b) = n \cdot R \cdot T \quad (4)$$

In the expression above, P = pressure, V = volume, a , b = van der Waal's constants, n = number of moles, R = universal gas constant, T = temperature.

3.2 Thermodynamic considerations for enhanced H₂ conversion by coupling the WGSR with *in situ* CO₂ capture and mineralization

The reaction conditions for enhanced H₂ conversion by coupling the WGSR with *in situ* CO₂ capture and mineralization is equilibrium-limited and dictated by the thermodynamics for WGSR to form CO₂ and H₂ and CO₂

capture and mineralization to form Mg- and Ca-carbonates.⁴⁸ The detailed reactions associated with coupling the WGSR with *in situ* CO₂ capture and mineralization are below:



The overall reaction functions reveal the stoichiometric ratio of the reactants and products, indicating a correlation between equilibrium constants (K_{eq}) and gas species partial pressure (P) at the equilibrium state, respectively:

$$K_{\text{eq}}(\text{Mg}(\text{OH})_2) = \frac{P_{\text{H}_2}}{P_{\text{CO}} \times P_{\text{H}_2\text{O}}} \quad (9)$$

$$K_{\text{eq}}(\text{Mg}_2\text{SiO}_4) = \frac{P_{\text{H}_2}^2}{P_{\text{CO}}^2 \times P_{\text{H}_2\text{O}}^2} \quad (10)$$

$$K_{\text{eq}}(\text{Ca}(\text{OH})_2) = \frac{P_{\text{H}_2}}{P_{\text{CO}} \times P_{\text{H}_2\text{O}}} \quad (11)$$

$$K_{\text{eq}}(\text{CaSiO}_3) = \frac{P_{\text{H}_2}}{P_{\text{CO}} \times P_{\text{H}_2\text{O}}} \quad (12)$$

The concentration of the different components involved in enhancing H₂ conversion coupled with *in situ* CO₂ capture and mineralization can be determined by their equilibrium constants using thermodynamic properties and relationships as shown by the equation below:⁶³

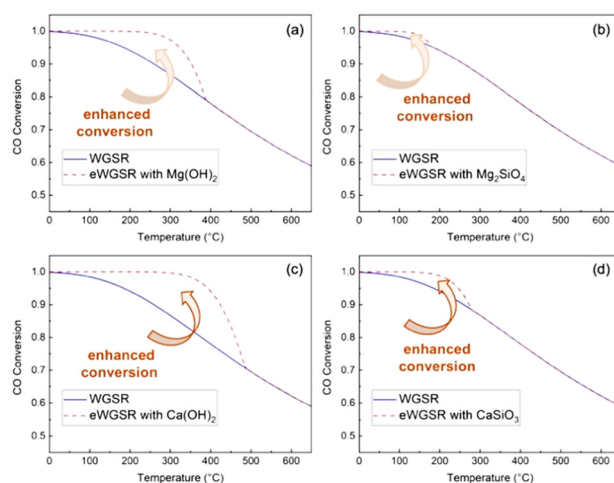


Fig. 3 Enhancement in WGSR as determined from CO conversions based on thermodynamic evaluations in gas–solid reaction mode using (a) Mg(OH)₂, (b) Mg₂SiO₄, (c) Ca(OH)₂, and (d) CaSiO₃ for the *in situ* CO₂ capture. The initial steam-to-CO ratio is 1:1 with adequate sorbents for carbon mineralization. Results for Mg(OH)₂ agree with prior studies.⁶⁴



$$K_{\text{eq}} = \exp\left(\frac{5693.5}{T} + 1.077 \ln T + 5.44 \times 10^{-4} T - 1.125 \times 10^{-7} T^2 - \frac{49170}{T^2} - 13.148\right) \quad (13)$$

The equilibrium constants determined using expression (13) are used to calculate the theoretical CO conversions as a function of temperature using expressions (9)–(12). Thermodynamic simulations with steam-to-CO ratio of 1:1 are used to determine theoretical CO conversions using Mg(OH)₂, Mg₂SiO₄, Ca(OH)₂, and CaSiO₃ as alkaline sources (Fig. 3).

Notably, the WGSR and enhanced WGSR (or eWGSR) conversions define the theoretical percentage of CO converted to CO₂ at the equilibrium. CO₂ conversions are calculated from the partial pressure of H₂, CO, and steam. The theoretical CO conversion of Mg(OH)₂ confirms prior reported calculations.⁶⁴ CO conversions at equilibrium decrease with increasing temperature due to the exothermic nature of the reactions (Fig. 3). Compared with conventional WGSR, a significant enhancement in CO conversion is noted at temperatures below 350 °C, indicating that Mg- and Ca-bearing hydroxides and silicates are effective in aiding CO (and H₂) conversion by capturing CO₂. It is interesting to note that at temperatures below 350 °C, Mg(OH)₂ and Ca(OH)₂ enhance CO conversion at 250 °C and 300 °C due to *in situ* capture of gaseous CO₂.

In contrast, the enhancement in CO conversion realized using Mg- and Ca-bearing silicates is achieved below 200 °C. Based on these thermodynamic analyses, it is evident that CO conversion can be enhanced using Ca- and Mg-bearing silicates in gas–solid reaction modes. To overcome the mass transfer limitations associated with gas–solid reactions, multiphase gas–liquid–solid reactions are proposed to accelerate the kinetics of WGSR when coupled with aqueous CO₂ capture and mineralization pathways at temperatures below 300 °C. These experimental conditions are a significant departure from conventional sorbent-enhanced WGSR operating in a gas–solid mode to capture CO₂.

3.3 Enhancement in WGSR using Mg(OH)₂ and Mg₂SiO₄

To enhance H₂ conversion with *in situ* CO₂ capture, it is essential to use a suitable catalyst that will convert CO and steam to produce H₂ and CO₂ and an alkaline source to capture CO₂.⁶⁵ Prior studies have reported enhancement in H₂ conversion *via* sorbent – enhanced WGSR using Ca-bearing sorbents.⁴⁶ Enhancement in H₂ yields were also reported by coupling the WGSR with slurry phase CO₂ capture and mineralization using Mg(OH)₂.⁶⁶ However, Mg(OH)₂ needs to be directly mined or extracted from earth – abundant Mg-silicates. Eliminating this additional mining or extraction step and directly using earth – abundant Mg-silicate minerals for enhancing H₂ conversion while capturing CO₂ is less explored but highly transformative. To address this knowledge gap, experiments are conducted to contrast the influence of Mg(OH)₂ vs. Mg₂SiO₄ on enhancing

H₂ yield with *in situ* CO₂ capture. The abundance of olivine (Mg,Fe)₂SiO₄ bearing forsterite (Mg₂SiO₄) in the natural environment motivates the direct use of these materials for CO₂ capture.³⁹ To investigate the enhancement in H₂ yield with CO₂ capture, the gaseous products at the effluent are analyzed. Following this, the structures and morphologies of the carbonate-bearing products are characterized separately.

Initially, a blank experiment is performed by considering only the WGSR over Pt/Al₂O₃ catalyst, to investigate its catalytic activity in the low-temperature regime. Fig. 4(a) represents the gas mole percentages when feeding only 20 bar CO at 250 °C for 9 hours. Fig. 4(b) shows the conversion of CO for the blank experiment and the cases with Mg(OH)₂ and Mg₂SiO₄. In the absence of the alkaline resource, CO conversion of 72.4% is noted (Fig. 4(b)). Gas analyses did not indicate any CH₄ formation demonstrating that the Pt/Al₂O₃ catalyst is effective in converting CO and steam to CO₂ and H₂. The observed higher selectivity towards H₂ using low-temperature Pt/Al₂O₃ catalyst is consistent with previous literature on WGSR.²⁷ Compared with the blank experiment without any alkaline source, WGSR reactions in the presence of a slurry bearing Mg(OH)₂ or Mg₂SiO₄ enhanced CO conversion and H₂ yield and lowered the concentration of gaseous CO₂ due to *in situ* CO₂ capture. In contrast to the blank experiment without the alkaline source, CO conversions in the presence of Mg(OH)₂ and Mg₂SiO₄ at 250 °C are 81% and 79.7%, respectively, as seen in Fig. 4(b). The molar compositions of H₂ and CO₂ in the gas phase are 50.8% and 30.3% for H₂ and CO₂ for the blank experiment. In contrast, H₂ concentrations increase by 18% and 9.5%, and CO₂ concentrations decrease by 15.9% and 6.1% in the presence of Mg(OH)₂ and Mg₂SiO₄ compared to the blank experiment (Fig. 4(a)).

The relative composition of H₂ in the gas phase is 8.6% higher when Mg(OH)₂ is used for CO₂ capture as opposed to Mg₂SiO₄. CO₂ concentrations are nearly 10% lower when Mg(OH)₂ is used as opposed to Mg₂SiO₄. Higher H₂ concentrations and lower CO₂ concentrations in the presence of Mg(OH)₂ *versus* Mg₂SiO₄ are attributed to the faster dissolution kinetics of Mg(OH)₂ relative to Mg₂SiO₄.⁶⁷ The enhanced release of Mg²⁺ ions favors CO₂ capture and the forward WGSR reaction which results in enhanced H₂ conversions and CO consumption (Fig. 4(a) and (b)).

3.4 Enhancement in H₂ conversion with *in situ* CO₂ capture as a function of time using Mg(OH)₂ and Mg₂SiO₄ materials

One of the key uncertainties in enhancing H₂ conversions with *in situ* CO₂ capture is the influence of the reactivity of the alkaline resources in hydrothermal environments. In this context, even though it is known that Mg(OH)₂ is



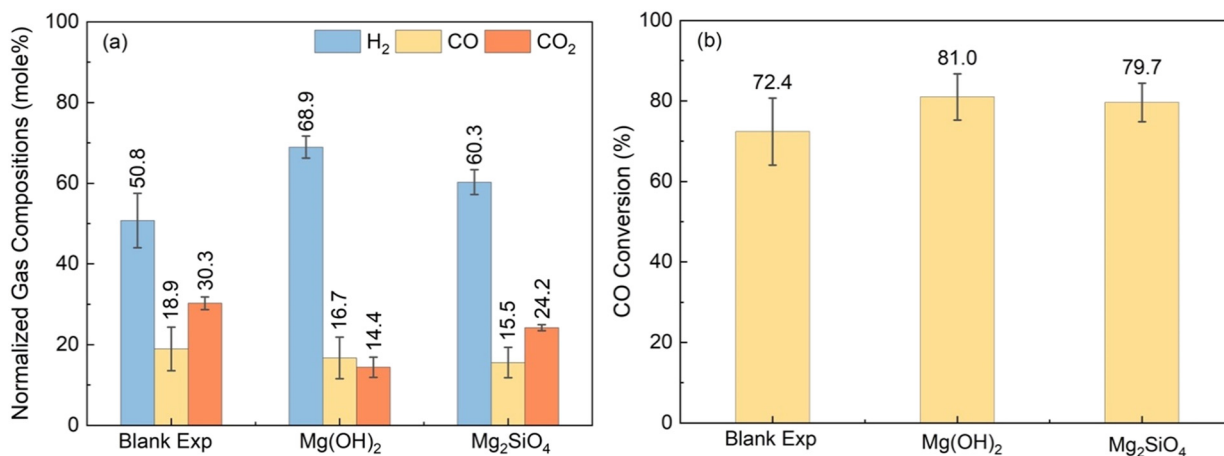


Fig. 4 Contrasting the influence of Mg(OH)₂ and Mg₂SiO₄ on the water gas shift reaction (WGS) as determined from H₂, CO, and CO₂ compositions in (a) and CO conversions in (b). Experiments are conducted at 250 °C, 20 atm for 9 h. The blank experiment is conducted over 3 g of Pt/Al₂O₃ catalyst without alkaline source. The Mg(OH)₂ and Mg₂SiO₄ cases are conducted over 3 g of Pt/Al₂O₃ catalyst with a sorbent-to-liquid weight ratio of 3 : 10, leading to mole percentages of 8.48% for Mg(OH)₂ and 3.70% for Mg₂SiO₄, respectively.

more soluble and has faster kinetics of dissolution compared to Mg₂SiO₄, the kinetics associated with accelerating WGS are not well understood. Several factors could be competing in this integrated and enhanced WGS approach.

First, the gas phase conversion of CO and steam to H₂ and CO₂ can be limiting. Second, the solubility of CO₂ and reactivity of Ca- and Mg-bearing silicates and hydroxide to capture CO₂ can be slow. Based on the changes in the compositions of the gas phase over time, the factors limiting the conversion of CO and H₂O to H₂ with *in situ* CO₂ capture can be determined. To this end, experiments are conducted with Mg(OH)₂ and Mg₂SiO₄ at 250 °C, 20 atm as a function of reaction time. The normalized gas phase compositions for reactions conducted at 3, 6, 9, and 12 hours are shown in Fig. 5(a) and (b) in the presence of Mg(OH)₂ and Mg₂SiO₄, respectively.

In the first three hours of the reaction with Mg(OH)₂ as the alkaline source, H₂ composition is 53.4% while that of CO and CO₂ are 18.7 and 27.9%, respectively. An increase in H₂ composition to 68.9% and a decrease in CO and CO₂ compositions to 16.7% and 14.4%, respectively are noted in the 9-hour cases. These results indicate that Mg(OH)₂ is effectively enhancing CO conversions and H₂ yields with inherent CO₂ capture. Therefore, the WGS is not the limiting factor in H₂ conversion in the first nine hours of the reaction. However, increasing the reaction time from 9 hours to 12 hours, lowered H₂ compositions from 68.9% to 60.9%. CO and CO₂ compositions increased from 16.7 to 23.4% and 14.4 to 15.8%, respectively, when the reaction time is increased from 9 hours to 12 hours. These results suggest that CO₂ capture is the likely limiting factor as the reaction time increases from 9 to 12 hours. This observation can be attributed to the fact that at increased reaction times, the

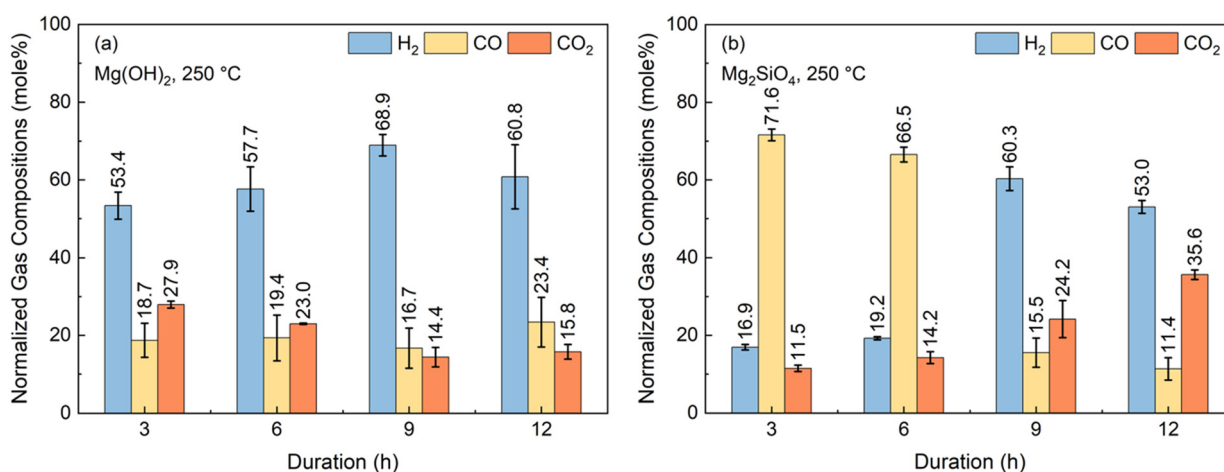


Fig. 5 Determination of time dependence on the concentrations of H₂, CO, and CO₂ when the WGS is coupled with *in situ* CO₂ capture and mineralization using (a) Mg(OH)₂ and (b) Mg₂SiO₄. The Mg(OH)₂ and Mg₂SiO₄ cases are conducted at 250 °C and 20 atm over 3 g of Pt/Al₂O₃ catalyst with a sorbent-to-liquid weight ratio of 3 : 10, leading to mole percentages of 8.48% for Mg(OH)₂ and 3.70% for Mg₂SiO₄, respectively.



availability of Mg^{2+} ions for CO_2 capture is likely decreasing over time. Slower dissolution rates of $Mg(OH)_2$ over time due to mass transfer arising from the formation of Mg-carbonates⁶⁸ or due to the saturation of the solution with Mg^{2+} ions are attributed to the decrease in H_2 and increase CO_2 compositions at 12 hours.

In contrast, Mg_2SiO_4 for *in situ* CO_2 capture yielded significantly different results compared to the use of $Mg(OH)_2$ (Fig. 5(b)). H_2 compositions are 16.9% and 19.2% respectively, at 3 hours and 6 hours of reaction time, while CO compositions are 71.6% and 66.5% in the presence of Mg_2SiO_4 . These results indicate that the WGS is the limiting step in the first 6 hours of reaction in the presence of Mg_2SiO_4 . This is likely due to the slower dissolution behavior of Mg_2SiO_4 to release Mg^{2+} ions compared to that of $Mg(OH)_2$. As a result, *in situ* CO_2 capture and subsequent enhancement in H_2 yields is limited in the presence of Mg_2SiO_4 in the first six hours of the reaction. At 9 hours of reaction time, H_2 composition is 60.3%. CO composition of 66.5% at 6 hours decrease to 15.5% at 9 hours of reaction time (Fig. 5(b)). These results indicate that while the kinetics of WGS are slower in the first 6 hours of the reaction in the presence of Mg_2SiO_4 compared to in the presence of $Mg(OH)_2$, comparable compositions are achieved when the reaction time is 9 hours.

As in the case of Mg_2SiO_4 , a decrease in H_2 compositions and increase in CO_2 compositions is observed when the reaction time is 12 hours. H_2 compositions decrease from 60.3% to 53.0% while CO_2 compositions increase from 24.2% to 35.6% at 12 hours of reaction. The relative decrease in H_2 compositions and increase in CO_2 compositions at 12 hours is attributed to the mass transfer limitations associated with the dissolution of Mg-silicate and Mg-hydroxide. Therefore, these studies indicate that WGS can be the initial slow step in the presence of Mg_2SiO_4 as opposed to $Mg(OH)_2$ during

the first 6 hours of reaction. Non-monotonic changes in the concentrations of H_2 , CO , and CO_2 observed as the reaction time increases from 9 hours to 12 hours are likely due to limitations from the slow dissolution of $Mg(OH)_2$ and Mg_2SiO_4 to release Mg^{2+} ions for CO_2 capture.

3.5 Influence of Mg- and Ca-bearing hydroxides and silicates on enhanced H_2 conversion with *in situ* CO_2 capture

Contrasting the influence of Mg- and Ca-bearing silicates and hydroxides on enhanced H_2 conversion coupled with *in situ* CO_2 capture can unlock new opportunities for the utilization of a wide range of alkaline feedstocks. Ca-bearing hydroxides and silicates are abundant in fly ash and slags.⁶⁹ Mg-bearing hydroxides and silicates are abundant in ultramafic and mafic mine tailings.⁷⁰ To this end, experiments are conducted at 300 °C in the presence of 8 bar of CO and 12 bar of N_2 in the gas phase and $Mg(OH)_2$, $Ca(OH)_2$, Mg_2SiO_4 , or $CaSiO_3$ to capture CO_2 in a slurry phase over a reaction time of 12 hours, as noted in section 3.1. Pt/Al_2O_3 catalyst is used as a low-temperature WGS catalyst. N_2 gas is used as a reference due to its inert nature and constant quantity before and after the reaction which enables the determination of the moles of gas products formed. The influence of $Mg(OH)_2$, $Ca(OH)_2$, Mg_2SiO_4 , or $CaSiO_3$ on compositions of H_2 , CO , and CO_2 are shown in Fig. 6.

The influence of WGS alone in the absence of Ca- and Mg-bearing hydroxide and silicate determined at the same experimental conditions as the others showed that H_2 , CO , and CO_2 account for 41.85%, 33.76%, and 24.39%, respectively (Fig. 6(a)). Relative to this blank experiment, the highest enhancement in H_2 conversion and CO_2 suppression was observed in the presence of $Ca(OH)_2$. In this best case scenario with $Ca(OH)_2$, H_2 yield is 72.67% which is 30.82% higher compared to the blank experiment. CO_2 yields are

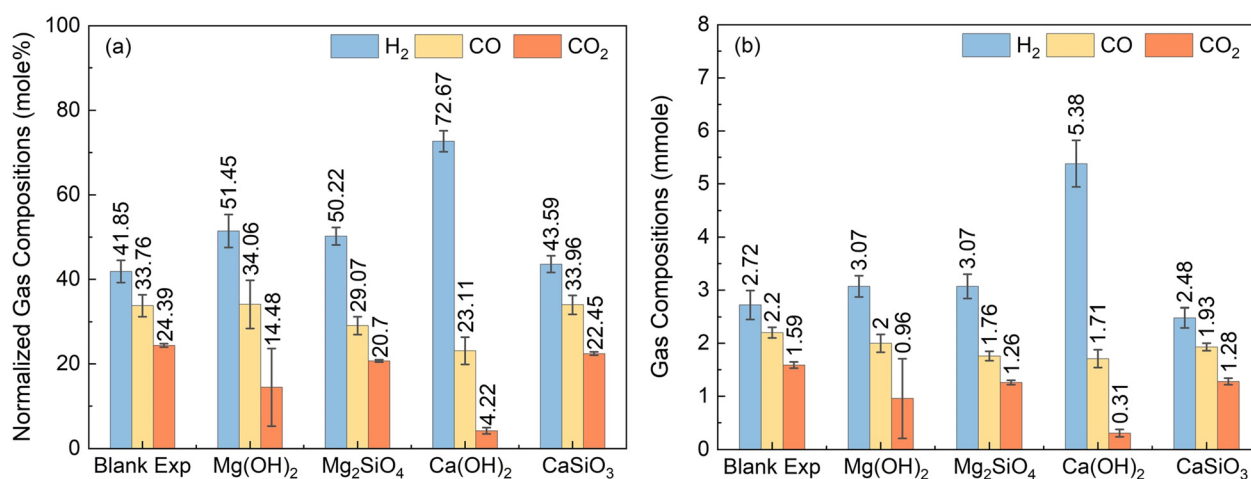


Fig. 6 Contrasting the influence of alkaline resources such as $Mg(OH)_2$, Mg_2SiO_4 , $Ca(OH)_2$, and $CaSiO_3$ on enhancing H_2 yield with *in situ* CO_2 capture and mineralization where (a) represents normalized gas mole percentages and (b) represents exact gas moles. Experiments are conducted at 300 °C, 20 atm for 12 h. The blank experiment is conducted over 3 g of Pt/Al_2O_3 catalyst without any alkaline source. The test experiments are conducted over 3 g of Pt/Al_2O_3 catalyst with a sorbent-to-liquid weight ratio of 3:10, leading to mole percentages of 8.48% for $Mg(OH)_2$, 3.70% for Mg_2SiO_4 , 6.80% for $Ca(OH)_2$, and 4.45% for $CaSiO_3$, respectively.



suppressed by 20.17% to 4.22% relative to the blank experiment indicating that $\text{Ca}(\text{OH})_2$ in the slurry is highly effective in capturing CO_2 emissions. Significant enhancement in WGSR is also evident from the changes in CO compositions which are lowered by 10.65% compared to the blank experiment. In comparison to $\text{Ca}(\text{OH})_2$, the H_2 yields are ~50–51% in the presence of $\text{Mg}(\text{OH})_2$ and Mg_2SiO_4 which are lower. Interestingly, CO compositions are 5% lower when Mg_2SiO_4 is used compared to $\text{Mg}(\text{OH})_2$, indicating WGSR is enhanced in the presence of Mg_2SiO_4 . However, the higher solubility of $\text{Mg}(\text{OH})_2$ compared to Mg_2SiO_4 enhances CO_2 capture lowering CO_2 compositions by 6.22% when $\text{Mg}(\text{OH})_2$ is used related to Mg_2SiO_4 .⁶⁷

The reactivity of CaSiO_3 in enhancing H_2 yield and suppressing CO_2 emissions is lower compared to the other alkaline sources. Compared to the blank experiment, the composition of H_2 is 1.74% higher, CO is similar, and CO_2 is ~2% lower. While these results indicate that CaSiO_3 enhances H_2 conversion and enables CO_2 capture, substantial changes relative to the blank experiment are not observed. The composition data in mmols are reported in Fig. 6(b) for use in subsequent modeling efforts. The results reported in Fig. 6 indicate that the effectiveness of the alkaline sources in enhancing H_2 yields while capturing CO_2 emissions follows this order: $\text{CaSiO}_3 < \text{Mg}_2\text{SiO}_4 < \text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2$. As hypothesized, the reactivity of Ca- and Mg-bearing hydroxides in enhancing H_2 yield and suppressing CO_2 emissions is higher compared to that of the corresponding silicates. The higher solubility and faster dissolution rates of Ca- and Mg-bearing hydroxides compared to the corresponding silicates facilitates enhanced CO_2 capture and H_2 conversion.⁶⁷

3.6 Mechanistic insights underlying enhancement in H_2 conversion coupled with *in situ* CO_2 capture and mineralization

The key reasons for the differences in the reactivity of Ca- and Mg-bearing silicates vs. hydroxides are the slower kinetics of dissolution of silicates and the formation of a

silica passivation layer which is known to limit mass transfer.^{71,72} Fig. 7 represents the multiphase chemical reaction mechanisms associated with carbon mineralization by harnessing hydroxides versus silicates. While the CO_2 hydration reactions to produce bicarbonate and carbonate species remain unchanged, the leaching of the metal into the solution results in the formation of a silica-rich layer in the case of silicates unlike in hydroxides. It is interesting to note that despite the slower kinetics of Mg-silicate dissolution and the formation of a silica layer that can limit mass transfer, comparable gas phase compositions of H_2 , CO, and CO_2 are noted with $\text{Mg}(\text{OH})_2$ and Mg_2SiO_4 (Fig. 6). However, the kinetics associated with enhancing H_2 conversion with *in situ* CO_2 capture and mineralization can differ significantly as noted in Fig. 5. The slow kinetics of WGSR observed up to 6 hours in the presence of Mg_2SiO_4 are attributed to limited availability of Mg^{2+} ions to capture CO_2 and facilitate the forward reaction. However, beyond 6 hours of reaction time, the observed enhancement in H_2 yields and corresponding decrease in CO_2 emissions is attributed to the availability of sufficient Mg^{2+} ions to capture CO_2 and aid the forward WGSR to produce H_2 .

Prior studies have shown that temperatures above 100 °C and high partial pressures of CO_2 aid the carbon mineralization of olivine.^{39,73} The solubility of CO_2 , and dissolution of Mg_2SiO_4 to release Mg^{2+} ions for capturing CO_2 and producing carbonates at the experimental conditions used in this study are analogous to those reported in prior studies. Therefore, despite the slow initial kinetics of Mg_2SiO_4 , the release of Mg^{2+} ions over time results in comparable H_2 , CO, and CO_2 compositions as when $\text{Mg}(\text{OH})_2$ is used. It is also interesting to note that Mg_2SiO_4 is more effective in enhancing WGSR compared to CaSiO_3 . Prior studies reported that CaSiO_3 is reactive at temperatures as low as 110 °C for carbon mineralization, unlike Mg_2SiO_4 .⁷⁴ Possible reasons for the lower-than-expected reactivity of CaSiO_3 are the formation of a silica passivation layer that is thicker and limits mass transfer at the experimental conditions reported in this study. To uncover if CO_2 uptake by the alkaline slurry results in the formation of solid carbonates, detailed structural and morphological analyses are investigated and reported in the following section.

3.7 Structural and morphological analyses of the alkaline sources

To determine if the captured CO_2 only dissolves in the aqueous phase or reacts to produce solid carbonates, the changes in the structural and morphological features of the alkaline resources are determined. The crystalline features in unreacted and reacted Ca- and Mg-bearing silicates and hydroxides using X-ray diffraction (XRD) measurements (Fig. 8). As shown in Fig. 8(a), the unreacted $\text{Mg}(\text{OH})_2$ exhibits the typical diffractogram of hexagonal $\text{Mg}(\text{OH})_2$ brucite structure with characteristic XRD peaks at 33.2°, 38.1°, 50.6°, 58.7°, 68.3°, and 72.1° (see peaks in black).

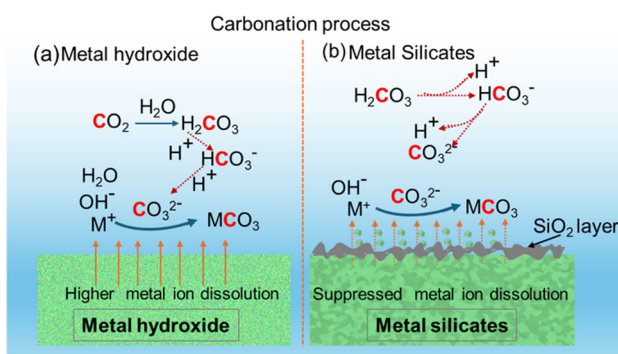


Fig. 7 Schematic diagram of surface reactions, dissolution, and mineralization process over (a) metal hydroxides and (b) metal silicates sorbents.



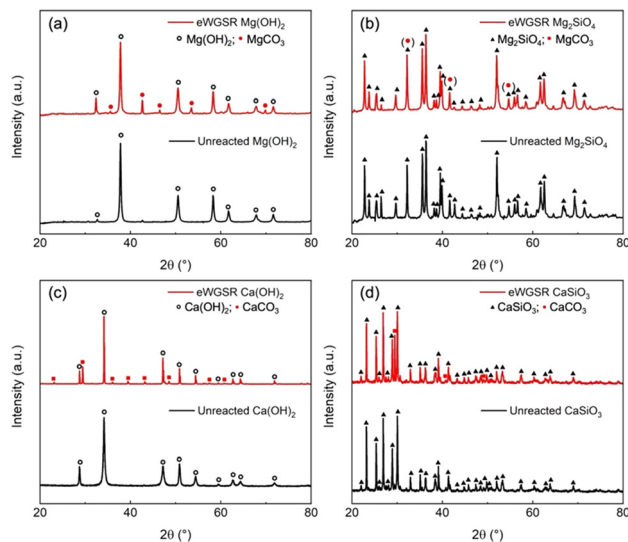


Fig. 8 Determination of the crystalline phases before and after reaction starting with (a) Mg(OH)₂, (b) Mg₂SiO₄, (c) Ca(OH)₂, and (d) CaSiO₃ using X-ray diffraction (XRD) analyses.

These peaks are well in accordance with the reported literature (PDF 44-1482).⁷⁵ The diffractogram of the reacted solid (peak in red) revealed the existence of magnesite (MgCO₃) peaks along with suppression of Mg(OH)₂ intensities. This co-existence indicates the dissolution of Mg(OH)₂ and the capture and conversion of CO₂ to produce MgCO₃.⁷³ To investigate if MgCO₃ is formed starting from Mg₂SiO₄ precursors, XRD data of the unreacted and reacted materials are collected and shown in Fig. 8(b). The X-ray diffraction pattern corresponding to the monoclinic structure of unreacted Mg₂SiO₄ is shown in Fig. 8(b).

The reacted Mg₂SiO₄ product exhibits a very similar scattering pattern as the unreacted material, which can result from overlapping between (104) peak of the generated magnesite and (130) peak of the residual Mg₂SiO₄.^{76,77} To further distinguish the different phases and prove the formation of carbonate, additional characterization is required. Interestingly, the absence of the nesquehonite (MgCO₃·3H₂O) or hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O) phases in our case is due to the higher stability of anhydrous magnesite (MgCO₃) at elevated temperatures and pressures.³⁹ Additionally, the formation of Mg-carbonate can be influenced by numerous other factors, including the reaction time, ionic strength or the addition of reagents including salts.³⁹ Thus, in this study, the formation of anhydrous magnesite (MgCO₃) can be attributed to the application of high temperatures of 250–300 °C with elevated CO₂ partial pressures in the range of 10–20 atm for reaction durations of 9–12 hours.

The structural arrangement characterization of the Ca cases shows a similar trend with Mg cases, in which the anhydrous calcite (CaCO₃) is the unique carbonate product due to the favorable reaction conditions. Fig. 8(c) illustrates the XRD peaks of unreacted Ca(OH)₂ at 28.7°, 34.1°, 47.2°,

50.6°, 54.3°, 62.3°, and 64.3° corresponds to the (100), (101), (102) (110), (111), (201) and (112) planes, respectively. Several studies have reported similar patterns of Ca(OH)₂.^{78,79} After the enhanced WGSR, the reacted product shows the presence of both Ca(OH)₂ and CaCO₃ phases (JCPDS 84-1276 and 85-1108, respectively). The occurrence of peaks at 23.1°, 29.5°, 31.6°, 36.1°, 39.5°, 43.3°, 47.2°, 47.6°, 48.6°, 57.5°, 61.1°, and 64.5° corresponds to (012), (104), (006), (110), (114), (202), (024), (018), (116), (112) (119), and (300) planes, respectively. These XRD patterns corresponded to the rhombohedral crystal structure of CaCO₃.⁸⁰ Furthermore, Fig. 8(d) shows the diffraction peaks of unreacted sorbents can be indexed as the CaSiO₃.⁸¹ For the reacted CaSiO₃, the XRD peaks resemble the co-occurrence of CaSiO₃ and CaCO₃ phases, which is a low-temperature polymorph of calcium carbonate (JCPDS 00-005-0586).⁸²

Furthermore, the morphologies of the reacted Mg(OH)₂, Ca(OH)₂, Mg₂SiO₄, and CaSiO₃ materials are determined using FE-SEM to identify carbonate-bearing phases. Fig. 9(b) shows the cube-like structure of MgCO₃ with the appearance of residual Mg(OH)₂ after carbon mineralization, confirming the carbonate formation after the enhanced WGSR. Similarly,

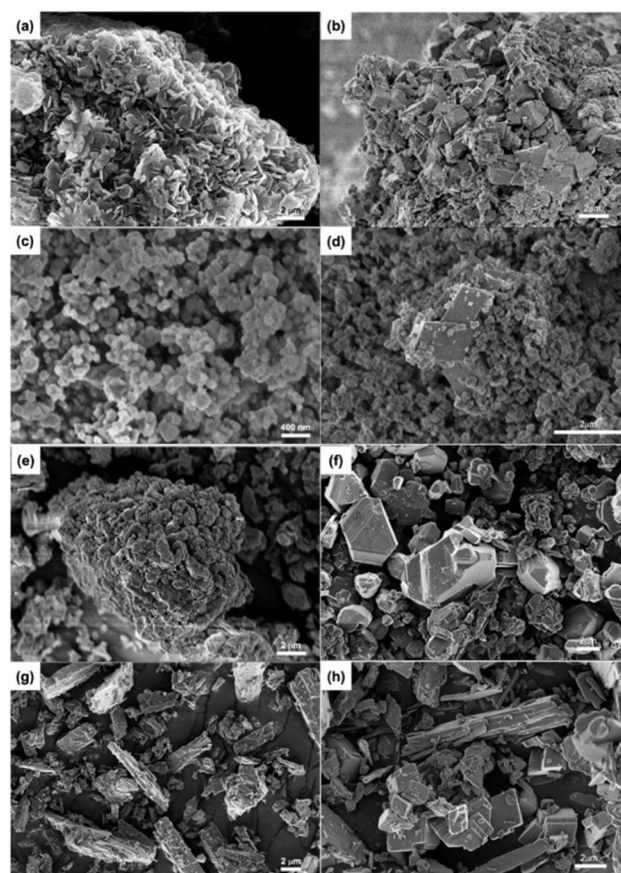


Fig. 9 Morphology of (a) unreacted Mg(OH)₂; (b) reacted Mg(OH)₂; (c) unreacted Mg₂SiO₄; (d) reacted Mg₂SiO₄; (e) unreacted Ca(OH)₂; (f) reacted Ca(OH)₂; (g) unreacted CaSiO₃; (h) reacted CaSiO₃ determined by scanning electron microscope measurements.



Table 2 The surface area, pore volume, and mean pore diameter of the unreacted and reacted alkaline sources as determined using BET analyses and the BJH method

	Unreacted alkaline sources			Reacted alkaline sources		
	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Mean pore diameter (nm)	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Mean pore diameter (nm)
Mg(OH) ₂	9.78	0.047	4.01	6.48	0.05	3.93
Mg ₂ SiO ₄	17.41	0.050	2.81	14.93	0.08	3.93
Ca(OH) ₂	24.29	0.107	3.72	4.81	0.01	1.50
CaSiO ₃	5.00	0.020	2.66	6.20	0.02	3.94

the cube-shaped MgCO₃ particles emerged in the case of reacted Mg₂SiO₄ materials (Fig. 9(d)).

Interestingly, the granular particles covered on cubic MgCO₃ particles can be attributed to the residual Mg₂SiO₄ and associated SiO₂ layer resulting from silicate dissolution. Similar phenomena are also observed in the reacted Ca(OH)₂ and CaSiO₃ materials (Fig. 9(f) and (h)). Additionally, the large hexagonal particles indicate the significant dissolution and recrystallization of initial Ca(OH)₂ sorbents (Fig. 9(f)), and the elongated particles correspond to the residual CaSiO₃ materials (Fig. 9(g) and (h)). Interestingly, the XRD analysis does not show the clear existence of crystalline phases rich in silica, indicating the potential presence of an amorphous silica-rich layer or glassy SiO₂ coating that may cause the suppression in metal dissolution in CaSiO₃, Mg₂SiO₄, responsible for the low extents of carbon mineralization.

As a further clarification of the sorbents' morphological evolution, the surface area and the pore distribution determined by BET analysis are listed in Table 2. The decreased surface area in Mg(OH)₂, Mg₂SiO₄, and Ca(OH)₂ cases indicates the formation of larger carbonate particles like MgCO₃ and CaCO₃ (Fig. 9(a)–(f)). Notably, the significant surface area reduction in the Ca(OH)₂ case aligns with its more effective CO₂ mineralization and the corresponding greater carbonate formation. In contrast, due to the larger particle size and limited pore volume in the unreacted CaSiO₃ compared with the generated CaCO₃, the small increase in the surface area and pore volume after reaction are attributed to the dominance of dissolution over carbon mineralization (Fig. 9(g) and (h)). Furthermore, the pore size distributions determined using the BJH model are illustrated in Fig. S4.† The unreacted hydroxide sorbents exhibit relatively narrow pore distributions, centered at approximately 4.01 nm for Mg(OH)₂ and 3.72 nm for Ca(OH)₂. Post-reaction, significant pore structure rearrangements are observed, leading to reductions in both pore volume and diameter, particularly for Ca(OH)₂. Additionally, the formation of MgCO₃ results in more well-ordered pore and particle size distributions compared to the Mg₂SiO₄ precursor. Conversely, significant changes in the pore size distribution of CaSiO₃ before and after reaction are not observed due to the relatively low extent of carbon mineralization.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) analysis is also performed on unreacted sorbents

and reacted products to confirm carbonate formation after the enhanced WGS. As shown in Fig. 10(a) and (c), unreacted hydroxide sorbents exhibited only one peak between 3600–3700 cm⁻¹, indicating the purity of starting materials (Mg(OH)₂, Ca(OH)₂).⁸³ On the other hand, the occurrence of new peaks around 1400–1500 cm⁻¹, 850–890 cm⁻¹, and 700–750 cm⁻¹ corresponds to C–O asymmetric stretching vibrations, the C–O bending vibration, and the in-plane bending vibration of O–C–O, respectively, in the carbonated products formed after the enhanced WGS.^{84,85} Furthermore, peaks shown in ATR-FTIR of unreacted Mg₂SiO₄ sorbents around 600–650 cm⁻¹ are consistent with SiO₄ bending and stretching modes, respectively, while the peak around 1000 cm⁻¹ represents asymmetric stretching modes of Si–O–Si.^{86,87} As shown in Fig. 10(b), despite its very low intensity, the peak at 1100 cm⁻¹ could be interpreted as a symmetric C–O stretching vibration band indicating the carbon mineralization of Mg₂SiO₄.⁸⁴ Moreover, in the case of CaSiO₃ materials, the presence of peaks approximately 600–700 cm⁻¹, 900 cm⁻¹ corresponds to the symmetrical stretching of O–Si–O bonds and Si–O–Ca bonds, while the peaks between 1000–1100 cm⁻¹ correspond to a symmetrical stretching of Si–O–Si bonds, respectively.⁸⁸ As shown in Fig. 10(d), the typical peaks from silicate remained constant

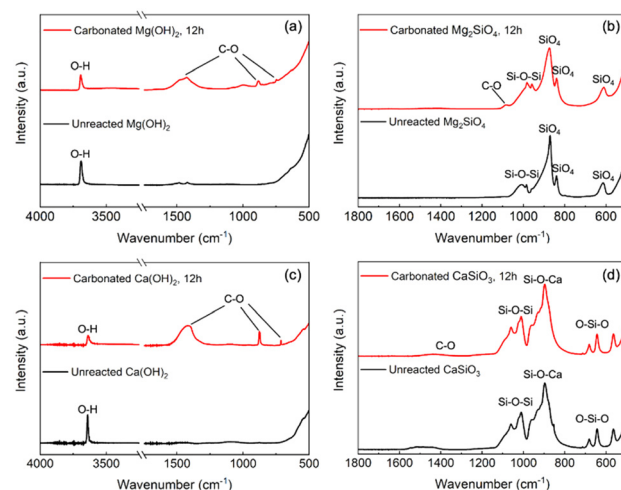


Fig. 10 Identification of different functional groups using attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy measurements in unreacted and reacted (a) Mg(OH)₂; (b) Mg₂SiO₄; (c) Ca(OH)₂; (d) CaSiO₃ materials.



after the enhanced WGSR with a little shoulder around 1400 cm^{-1} , indicating the asymmetric stretching mode of C–O, proving the carbon mineralization of CaSiO_3 material.⁸⁵

Further, to investigate the effect of eWGSR on the metal hydroxides and metal silicates, XPS analyses are conducted. The XPS spectra were calibrated based on the carbon C–C peak (284.8 eV).⁸⁹ Fig. S5(a1) and (a2)† shows the O 1s deconvolution result for unreacted and reacted $\text{Mg}(\text{OH})_2$ materials. The high-resolution XPS spectrum of unreacted $\text{Mg}(\text{OH})_2$ exhibit a peak at binding energy of 531.7 eV which suggests the existence of hydroxyl (OH) species. Furthermore, the reacted $\text{Mg}(\text{OH})_2$ materials showed slight changes in O 1s spectrum (Fig. S5(a2)†). Binding energy (BE) peaks are observed at 531.8 eV and 533.34 eV which correspond to hydroxyl (OH) and carbonate (CO_3^{2-}) species, respectively.^{90,91} Similar trends are observed within the unreacted and reacted $\text{Ca}(\text{OH})_2$ materials. The hydroxyl (OH) peak at 531.9 eV exclusively appears in the unreacted $\text{Ca}(\text{OH})_2$ while the hydroxyl peak at 531.8 eV and carbonate peak at 532.9 co-exists in the reacted $\text{Ca}(\text{OH})_2$ material (Fig. S5(b1) and (b2)†). To further determine the influence of enhanced WGSR on metal silicates (CaSiO_3 and Mg_2SiO_4), the valance state of the oxygen in the unreacted and reacted silicates are studied using XPS analyses. Fig. S6† shows the carbon (C1s) spectra from unreacted and reacted Mg_2SiO_4 , CaSiO_3 materials consisting of two main components arising from C–C (~ 284.4 eV) and O=C (carboxyl, ~ 288.6 eV).^{92,93} Compared to unreacted counterparts, the reacted materials exhibit higher intensity signal of C 1s indicating the presence of carbonate (CO_3^{2-}) species. The C 1s peak values observed between 289.5 eV and 289.7 eV are well-matched with the carbonate (CO_3^{2-}) species in the reported literature.^{94,95}

Insights into the changes in the structure of silicon are obtained from XPS analyses. Fig. S7(a1)† shows that O 1s peak at 531.35 eV corresponds to the SiO_4 tetrahedra in the unreacted Mg_2SiO_4 .⁹⁶ Additionally, the O1s peak tail at a higher binding energy region around 533.6 eV could result from minor amorphous SiO_2 content.⁹⁷ On the other hand, the reacted Mg_2SiO_4 materials ((Fig. S7(a2)†) show deconvoluted peaks at 531.1, 532.3, and 533.5 eV which corresponds to the residual Mg_2SiO_4 , the generated carbonate and the amorphous SiO_2 resulting from silicate dissolution.^{98–101} On the contrary, Fig. S7(b1)† shows that unreacted CaSiO_3 exhibits a SiO_2 peak at 533.5 eV other than the typical SiO_3 peak at 532 eV, indicating the presence of an amorphous phase in the unreacted sorbent.^{97,102} After the enhanced WGSR, the O1s peaks of the reacted CaSiO_3 shift towards a high binding energy range. More specifically, the existence of deconvoluted O1s peaks at 531.4 eV, 532.9 eV, and 533.3 eV correspond to the residual SiO_3 , generated carbonate and SiO_2 , which confirms carbonate formation and the dissolution of calcium silicate material.

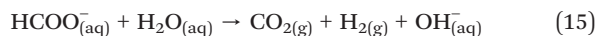
Further, Fig. S7(c1) and (d1)† depicts the existence of Si2p broad peak at the binding energy of 102.7 eV and 103.2 eV for unreacted Mg_2SiO_4 and CaSiO_3 , respectively.¹⁰³ It's worth noting that the SiO_2 peaks around 104 eV appear in both the

silicates, corresponding to the results from O1s peak.¹⁰⁴ However, after carbon mineralization, Si 2p deconvoluted spectra shows the diminished SiO_4 or SiO_3 peaks with intensified SiO_2 peaks for both silicates, indicating the dissolution of silicate and the generation of Si-rich passivation layer.^{105,106} Additionally, the relatively high amorphous SiO_2 component in the unreacted CaSiO_3 compared to Mg_2SiO_4 likely suppresses the dissolution of CaSiO_3 , thus resulting in lowering H_2 yields compared to Mg_2SiO_4 materials.

To quantitatively evaluate the carbonate phases, the carbon/metal ratios are calculated before and after the enhanced WGSR based on the atom% from XPS (Fig. S8†). The detected carbon phase in the unreacted carbonate-free sorbents can be attributed to the adventitious carbon on samples' surface due to the carbon contamination during air exposure.¹⁰⁷ However, neglecting the impact from adventitious carbon, the carbon/metal atomic ratio after the enhanced WGSR increased to 0.58 with $\text{Mg}(\text{OH})_2$, 0.78 with $\text{Ca}(\text{OH})_2$, 0.06 with Mg_2SiO_4 , and 0.1 with CaSiO_3 , respectively. In terms of the carbonate fraction, the increased carbon/metal ratio of Mg_2SiO_4 requires doubling to compare with other sources due to its doubled stoichiometric coefficient of metal ion, which results in a 0.12 increase in Mg_2SiO_4 carbon/metal atomic ratio after the enhanced WGSR. In this case, the varying trend in carbon/metal atomic ratio increases perfectly aligns with the enhanced WGSR: $\text{Ca}(\text{OH})_2 > \text{Mg}(\text{OH})_2 > \text{Mg}_2\text{SiO}_4 > \text{CaSiO}_3$, indicating the strong positive correlation between the enhanced H_2 yields and carbonate formation.

3.8 Insights on the mechanisms of the enhanced WGSR and *in situ* CO_2 capture and carbon mineralization

Given the multiphase reaction described in Fig. 1, the key reaction mechanisms involved in the enhanced WGSR can be delineated as CO oxidation and CO_2 capture. To be more specific, the CO oxidation proceeds *via* two potential approaches simultaneously: (i) the gaseous-phase WGSR with the assistance of noble-metal ($\text{Pt}/\text{Al}_2\text{O}_3$) catalyst (eqn (1)) and (ii) the aqueous-phase CO reaction to form formate followed by subsequent formate decomposition (eqn (14) and (15)).¹⁰⁸

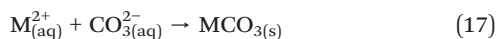
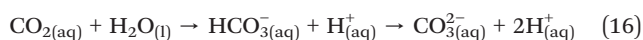


The first mechanism results in maximum H_2 production, while the second mechanism consumes part of the CO supply yet may not produce H_2 eventually due to the limitation of formate decomposition. It is well-reported that the reaction between CO and hydroxide species leads to a competition between CO and CO_2 dissolution in the second mechanism. According to previous studies, higher CO partial pressure in the system may result in a larger amount of expelled CO_2 from the solution and restrict the subsequent carbon



mineralization step.¹⁰⁹ In this situation, the alkalinity of the slurry becomes an essential factor of the aqueous-phase CO oxidation: more sufficient hydroxide ion supply alleviates the competition between CO and CO₂ and promotes both H₂ production and CO₂ capture, which explains the enhancement in performance of hydroxide in this study when compared to their silicate counterparts (Fig. 6). Additionally, to evaluate the impact of the non-decomposed formate, the separated aqueous phase after reactions are characterized by liquid-state nuclear magnetic resonance (NMR), as shown in Table S3.† Although the blank experiment without alkaline sorbent exhibits a relatively high residual formate level in the aqueous phase, only trace amounts of formate (<200 ppm) were detected in the aqueous phase when alkaline resources were applied. The observation indicates the presence of alkaline sorbents effectively catalyzes the decomposition of the generated formate, leading to the near-complete oxidization of dissolved CO into CO₂.

On the other hand, the generated CO₂ from both CO oxidation mechanisms further hydrated to form bicarbonate and carbonate species and released protons into the aqueous phase (eqn (16)).¹¹⁰ Simultaneously, the dissolution of the alkaline resources released the metal cations (M²⁺), which could be enhanced by the increasing proton level. Consequently, the metal cations combine with carbonate species (CO₃²⁻, HCO₃⁻) precipitated out when the solubility limit is reached (eqn (17)). In our case, the carbonate products tend to be in anhydrous form due to their favored chemical stability at the operating temperature (250–300 °C) in this multiphase reaction environment,¹¹¹ which is also confirmed by the characterization of the solid products.



4. Conclusions

In this study, the feasibility of the enhanced WGSR integrated with *in situ* thermodynamically downhill CO₂ capture and mineralization is investigated in the presence of Mg- and Ca-hydroxides and silicates to co-produce H₂ and carbonate-bearing materials. Calibrated tuning of the multiphase chemical interactions is unlocked by deriving the thermodynamical models of the multiphase reactions, where the theoretical prediction of the CO conversion is mutually corroborated with the experimental results. For example, 30.82% more H₂ yields with 20.17% less CO₂ emission achieved with Ca(OH)₂ compared with independent WGS reaction without *in situ* CO₂ capture and mineralization. Thus, these studies proved the hypothesis that the *in situ* capture and mineralization of gaseous CO₂ depletes CO₂ gas compositions and favors the forward reaction to produce H₂. The higher solubility and dissolution rates of Ca- and Mg-

hydroxides favors enhanced H₂ yields. Comparable compositions of H₂ are achieved with Mg(OH)₂ and Mg₂SiO₄ when reacted for 12 hours at 300C despite initial slower kinetics of CO conversion with Mg₂SiO₄ in the first 6 hours of the reaction.

Among the studied alkaline resources for enhanced WGSR, Ca(OH)₂ exhibited unbeatable CO₂ capture over the other sorbents (CO₂ compositions: Ca(OH)₂ (4.22%) < Mg(OH)₂ (14.48%) < Mg₂SiO₄ (20.7%) < CaSiO₃ (22.45%) < blank experiment (24.39%) respectively), when feeding a mixture of CO and N₂ at 300 °C and 20 bar. Additionally, the temporal evolution in H₂ yields and CO₂ capture revealed that the kinetic limitation of the overall reaction was dependent on the sorbent dissolution behavior, especially for the silicate sorbents. The amorphous Si-rich layer generated from silicate dissolution and mineralization passivated the alkaline resources and restricted the rate of enhanced WGSR, particularly in the case of CaSiO₃. The dissolution of Mg- and Ca-bearing hydroxides and silicates, formation of the silica passivation layer, and anhydrous metal carbonate products in the reacted alkaline resources are confirmed from structural and morphological analyses. Detailed characterization and analyses confirmed that anhydrous carbonates (MgCO₃, CaCO₃) are the dominant carbonate-bearing products without any associated hydrated carbonate formations. Quantitative analyses of the reacted products showed that the carbonate content corresponded directly to the trend in H₂ yields. Evidence of comparable H₂ yields with Mg₂SiO₄ and Mg(OH)₂ indicates the feasibility of directly using silicates for enhanced WGSR as opposed to extracting Mg(OH)₂ from Mg₂SiO₄ resources, thus enabling more material and energy efficient pathways for producing H₂ with inherent CO₂ capture and storage in the form on durable Mg- and Ca-bearing carbonates. This approach can also unlock new opportunities in harnessing renewable biomethane for co-producing H₂ with inherent CO₂ capture and mineralization to produce carbonates for use in construction materials by harnessing energy from renewable sources, thus enabling carbon-negative pathways for a sustainable energy and resource future.

Data availability

The data supporting this article have been included in the main manuscript and as part of the ESI.†

Author contributions

Greeshma Gadikota – supervision, conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, software, validation, visualization, writing – original draft, writing – review & editing. Xun Gao – conceptualization, data curation, formal analysis, investigation, methodology, resources, software, validation, visualization, writing – original draft, writing – review & editing; Divya Prasad – investigation,



validation, visualization, writing – review & editing; Mahadeo A. Mahadik – investigation, validation, visualization, writing – review & editing.

Conflicts of interest

Greeshma Gadikota is the co-founder of Carbon To Stone which is commercializing technologies for industrial decarbonization and carbon management. The other authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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