Hydrogenation of Inorganic Metal Carbonates: A Review on Its Potential for Carbon Dioxide Utilization and Emission Reduction

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MeCO₃ → MeO₁₋ₙ

CₓHᵧOₓ

MeCO₃ + O₂ → CO₂ + O₂

Roasting

MeCO₃ + H₂ → CₓHᵧOₓ

Hydrogenation
Carbonaceous minerals represent a valuable and abundant resource. Their exploitation is based on decarboxylation at elevated temperature and under oxidizing conditions, which inevitably release carbon dioxide into the atmosphere. Hydrogenation of inorganic metal carbonates opens up a new pathway for processing several metal carbonates. Preliminary experimental studies revealed significant advantages over conventional isolation technologies. Under a reducing hydrogen atmosphere, the temperature of decarboxylation is significantly lower. Carbon dioxide is not directly released into the atmosphere, but may be reduced to carbon monoxide, methane, and higher hydrocarbons, which adds value to the overall process. Apart from metal oxides in different oxidation states, metals in their elemental form may also be obtained if transition-metal carbonates are processed under a hydrogen atmosphere. This review summarizes the most important findings and fields of the application of metal carbonate hydrogenation to elucidate the need for a detailed investigation into optimized process conditions for large-scale applications.

1. Introduction

Carbon dioxide (CO$_2$) is an abundant chemical species. On earth, it is present in all three aggregate states: in gaseous form in the atmosphere (approximately 2.5 x 10$^{18}$ tons), in the dissolved state in the hydrosphere (approximately 10$^{12}$ tons), and in the solid state fixed in carbonate rocks (approximately 10$^{24}$ tons).[1] Hence, more (by a factor of 10$^9$) terrestrial carbon is fixed in carbonate rocks in the earth’s crust than is actually present in the gaseous atmosphere. Carbonate rocks have been known as a valuable and abundant resource for a long time. The history of inorganic metal carbonate chemistry dates back to the early ages of solid-state chemistry. The thermal decomposition, meaning decarboxylation reactions of metal carbonates in an oxidizing atmosphere, also known as calcination, roasting, or burning, depending on the metal species involved, represent processes that were developed first on experience, later on research, and finally on technological optimization in industrial production plants. Cato, for instance, mentioned the burning of limestone (calcite, CaCO$_3$) in kilns in 184 B.C. In the 1700s, Joseph Black gave the first systematic technical explanation of the calcination of limestone, also including the evolution of gaseous carbon dioxide.[2] Lime (CaO) is one of the cheapest and most widely used alkalinizing chemicals and the main constituent of cement production. The production of magnesium oxide (magnesia, MgO) through calcination of magnesite (MgCO$_3$) for refractory manufacture was established over 100 years ago in Austria.[3] The roasting of iron carbonate (siderite, FeCO$_3$) is used for iron and steel production in areas with vast mineral iron carbonate reserves, such as Austria[4] and China.[5] The cement industry, iron production, and manufacture of magnesia sinter make use of large quantities of the respective metal carbonates. Further industrial applications of metal carbonates of, for instance, nickel, cobalt, manganese, and zinc, or more precisely of their respective oxides or the metals in their elemental form, include the production of catalysts (catalytic material and porous support), pigments and glass, the ceramics industries, and the electronics industries.[6,7]

During the decarboxylation of metal carbonates to yield the respective metal oxide (MeO), inevitably one mole of CO$_2$ and/or carbon monoxide (CO) evolve per mole of metal oxide formed. The metal oxide, in turn, gives access to reformation into the corresponding carbonate through CO$_2$ uptake. This characteristic provides the basis for carbon capture and storage (CCS) technologies, referred to as mineral carbonation, in which CO$_2$ is fixed to and stored as carbonate minerals, mainly in the form of calcium and magnesium carbonate.[8]

Whereas the decarboxylation products of main-group elements (e.g., alkaline-earth-metal carbonates) are the corresponding metal oxides and CO$_2$ [Eq. (1)], the decomposition of transition-metal carbonates follows a more complex reaction pathway [Eq. (2)] because redox processes may take place. The redox behavior of the transitions metals allows the reduction of CO$_2$ to CO by means of thermodynamic fundamentals. The solid products can be metal oxides and mixtures of metal oxides that adopt different oxidation states.[9]

$$\text{MeCO}_3 \leftrightarrow \text{MeO} + \text{CO}_2 \quad (1)$$

$$\text{MeCO}_3 \leftrightarrow \text{MeO}_{1-x} + (1-x) \text{CO}_2 + x \text{CO} \quad (2)$$

In carbonaceous metal decarboxylation, the reaction conditions, especially the nature of the gas atmosphere, play a crucial role in the course of the reaction. If carried out in a reducing atmosphere with hydrogen (H$_2$), a fascinating reaction network is observed. Equation (3) shows the reaction for the hydrogenation of alkaline-earth-metal carbonates, whereas Equation (4) gives a potential reaction pathway for the hydrogenation of transition-metal carbonates. Apart from metal oxides and mixtures of metal oxides in different oxidation states, metals in their elemental form can be formed as solid products from transition-metal carbonates. Gaseous products may include methane (CH$_4$) in addition to or in place of CO$_2$ and CO.[10]

Some citations even report the formation of higher hydrocarbons (C$_x$-C$_y$).[11–13] In this context, it is noteworthy that an admixture of iron oxides enables the direct conversion of calcium carbonate into C$_3$-C$_4$ hydrocarbons.[14]
Transition metals are well established catalysts in Fischer–Tropsch (FT) synthesis,\textsuperscript{[14–16]} and the water-gas shift reaction.\textsuperscript{[17–20]} FT synthesis, namely, the catalytic polymerization and hydrogenation of CO, gives access to the synthesis of hydrocarbons (alkanes, alkenes, and oxygenated hydrocarbons) from syngas, CO and H\textsubscript{2}.\textsuperscript{[21]} The reaction for the synthesis of alkanes is shown in Equation (5) as an example. The reverse water-gas shift reaction yields CO from CO\textsubscript{2} through reduction with hydrogen [Eq. (6)]. Consequently, the presence of transition metals in metal carbonate hydrogenation opens up a pathway for the synthesis of hydrocarbons, instead of simply releasing CO\textsubscript{2} into the gas phase.

\begin{align}
\text{MeCO}_3 + 4 \text{H}_2 & \rightarrow \text{MeO} + \text{CH}_4 + 2 \text{H}_2\text{O} \quad (3) \\
\text{MeCO}_3 + (1 + y + 4 z) \text{H}_2 & \rightarrow \text{MeO}_{1+y} + (1-y-z) \text{CO}_2 + y \text{CO} + z \text{CH}_4 + (x + y + 2 z) \text{H}_2\text{O} \quad (4)
\end{align}

\begin{align}
n \text{CO} + (2 n + 1) \text{H}_2 & \rightarrow \text{C}_n \text{H}_{2n+2} + n \text{H}_2\text{O} \quad (5) \\
\text{CO}_2 + \text{H}_2 & \rightarrow \text{CO} + \text{H}_2\text{O} \quad (6)
\end{align}

In addition to different gaseous products that are released from metal carbonates under reducing conditions, changing the gaseous atmosphere from inert to reducing also has an effect on the morphology of the solid products.\textsuperscript{[22]} In most cases, the reducing agent in reductive metal carbonate decarboxylation is hydrogen. Until now, the production of hydrogen on an industrial scale has mainly (>95\%) been based on fossil fuels, for instance, through steam reforming of methane or gasification of coal and hydrocarbons, which, apart from hydrogen, generates CO\textsubscript{2}.\textsuperscript{[23, 24]} Apart from conventional production routes, hydrogen can also be produced renewably and sustainably from various sources (e.g., water electrolysis or water splitting through photocatalysis,\textsuperscript{[25, 26]} solar thermal production,\textsuperscript{[27]} photosynthesis by algae,\textsuperscript{[28]} reforming of biomass,\textsuperscript{[29]}). Hydrogen storage is challenging, however, and requires a completely new distribution system.\textsuperscript{[30]}

Whereas the decomposition of various metal carbonates in a vacuum or under an oxidizing or inert atmosphere has been well investigated and reported (e.g., for FeCO\textsubscript{3} in vacuum,\textsuperscript{[31]} oxygen,\textsuperscript{[31–33]} and nitrogen,\textsuperscript{[34–36]}), information on metal carbonate hydrogenation is scarce. Reduction of carbonates in aqueous solution is also well described in the literature and is not covered herein.\textsuperscript{[37–42]} Metal carbonate hydrogenation is not only challenging from a reaction mechanism point of view, but also features some characteristics that render it promising in terms of carbon capture and utilization (CCU), hydrogen storage, and novel production technologies in metallurgy. The purpose herein is to provide a comprehensive literature review on metal carbonate hydrogenation and to discuss potential applications. After describing their natural occurrence (Section 2), thermodynamics of metal carbonate hydrogenation are specified (Section 3). Experimental studies that have been conducted so far are listed in Section 4. After summing up the main benefits of metal carbonate hydrogenation (Section 5), feasible process options are illustrated and evaluated (Section 6). Finally, Section 7 identifies future needs for detailed research.

2. Natural Occurrence

Inorganic carbonates, characterized by planar $[\text{CO}_3]^{2–}$ complexes with metal ions, form one of the most important mineral groups. Taxonomy is based on cations and/or anions outside of the $[\text{CO}_3]^{2–}$ complexes. Water-free mineral carbonates may feature calcite- (trigonal, scalenohedral), dolomite- (trigonal, rhombohedral), and aragonite-type (orthorhombic) structures. Carbonates with additional anions may contain OH\textsuperscript{−} anions or water.
2.1. Main-group elements

2.1.1. Alkaline metal carbonates

Mineral lithium carbonate (Li$_2$CO$_3$), zabuylite, occurs in the lithosphere as an ore companion, mainly imbedded in halite in rock salt and in saline lakes. Sodium carbonate (Na$_2$CO$_3$, natrite, also known as soda) appears in saline lakes and minerals such as trona Na$_2$(CO$_3$)$_2$(HCO$_3$)$_2$$\cdot$H$_2$O and natron Na$_2$CO$_3$$\cdot$10H$_2$O. It undergoes a rapid change superficially in air to thermonatrite (Na$_2$CO$_3$$\cdot$H$_2$O). Potassium carbonate (K$_2$CO$_3$) is called potash because it was historically produced by treating wood ash with water in a pot. There are no K$_2$CO$_3$-containing ores known that would be worth mining. It is generally produced from electrolytically produced KOH and CO$_2$. Rubidium (Rb$_2$CO$_3$) and cesium (Cs$_2$CO$_3$) carbonates are naturally found together in low concentrations accompanying sodium- and potassium-containing ores. Similar to the other alkaline metals, they also collect in saline lakes. Francium isotopes (Fr$_2$CO$_3$) are radioactive and only found in traces in the lithosphere.\[43, 44\]

2.1.2. Alkaline-earth-metal carbonates

Beryllium carbonate (BeCO$_3$) barely exists in minerals because it is easily decomposed into beryllium oxide and CO$_2$ and therefore, only stable in a CO$_2$ atmosphere. It exists naturally in the mineral nivelyllite NaBe(CO$_3$)$_3$(OH)$_2$$\cdot$2H$_2$O. Magnesium carbonate (MgCO$_3$) is found in the lithosphere as magnesite MgCO$_3$ and dolomite CaMg(CO$_3$)$_2$, such as in the Southern Alps—the Dolomites. Mining of magnesite is one of the main resources for magnesium carbonate. Calcium carbonate (CaCO$_3$) mainly forms calcite CaCO$_3$ and dolomite CaMg(CO$_3$)$_2$. Mining of these minerals is the main source for calcium carbonate. Three different naturally occurring crystal structures of calcium carbonate exist: calcite, aragonite, and vaterite. In calcite, the central Ca$^{2+}$ ion is coordinated by six oxygen atoms, whereas in aragonite nine oxygen atoms coordinate the central Ca$^{2+}$ ion. Strontium carbonate (SrCO$_3$) is found in the naturally occurring mineral strontianite. Barium carbonate (BaCO$_3$) forms in the lithosphere as witherite.\[43, 44\]

2.1.3. Further main-group metals

Lead carbonate (PbCO$_3$) is found as cerussite. Caustic aluminum carbonate is found in the mineral dawsonite NaAl(CO$_3$)(OH)$_2$.\[43, 44\]

2.2. Transition metals

Manganese is present in the lithosphere nearly as frequently as carbon or phosphorus. Manganese carbonate (MnCO$_3$) is found in the mineral rhodochrosite and as an ore companion of iron. Iron carbonate (FeCO$_3$) is found in the lithosphere as siderite and ankerite (Ca(Mg,Fe)$_2$(CO$_3$)$_3$), for example, at the Erzberg in Styria, Austria, and in China. Cobalt occurs in diverse forms in the lithosphere, often as an ore companion. Nevertheless, no major cobalt carbonate (CoCO$_3$)-containing ore is known. Cobalt carbonate can be produced by precipitation of water-soluble cobalt(II) salts with alkaline-earth carbonates. Nickel exists in diverse forms in the lithosphere, but no nickel carbonate ores are known. The industrially most important nickel carbonate is caustic nickel carbonate, $2\text{NiCO}_3\cdot3\text{Ni(OH)}_2\cdot4\text{H}_2\text{O}$, produced by precipitation of aqueous nickel sulfate with sodium carbonate. Caustic nickel carbonate can be dehydrated to give anhydrous nickel carbonate or the hexahydrate NiCO$_3$$\cdot$6H$_2$O. Copper carbonate (CuCO$_3$) occurs naturally as azurite $2\text{CuCO}_3\cdot\text{Cu(OH)}_2$ (blue) and malachite $\text{CuCO}_3\cdot\text{Cu(OH)}_2$ (green). Silver carbonate (Ag$_2$CO$_3$) is not found in minerals, but precipitates from water by using soluble silver species and alkaline-metal carbonates, such as soda. Zinc carbonate (ZnCO$_3$) exists as smithsonite. Cadmium carbonate (CdCO$_3$) is mostly found as an ore companion of smithsonite.\[43, 44\]

3. Thermodynamics of Metal Carbonate Hydrogenation

Thermodynamic analysis of alkaline, alkaline-earth, and transition-metal carbonates between 400 and 1200 K at ambient pressure shows increasing standard free energies of reaction, $\Delta G^0$, for methane formation with increasing temperature. Due to strongly positive $\Delta G^0$ values ($>60$ kJ mol$^{-1}$), methane formation is not possible through hydrogenation of alkaline-metal carbonates (Figure 1a). Among alkaline-earth-metal carbonates, only hydrogenation of MgCO$_3$ features a negative $\Delta G^0$, favoring CH$_4$ formation (Figure 1b). Hydrogenation of the transition-metal carbonates MnCO$_3$, FeCO$_3$, CoCO$_3$, NiCO$_3$, CuCO$_3$, and ZnCO$_3$ to their respective bivalent oxides, CH$_4$, and H$_2$O is favorable (Figure 1c).

Figure 2 compares conventional beneficiation of FeCO$_3$ under oxidizing conditions with hydrogenation of FeCO$_3$. Both routes are thermodynamically favorable in the temperature range examined (400–1200 K), although reduction of hematite (Fe$_2$O$_3$) features significantly higher standard free energies of reaction.

Hydrogenation of the transition-metal carbonates and MgCO$_3$ to yield CH$_4$ exhibit pronounced exothermic behavior ($\Delta H^0 < -50$ kJ mol$^{-1}$).

4. Experimental Studies

Experimental studies on the hydrogenation of metal carbonates are scarce. Although first reports date back to the late 1960s, to the best of our knowledge, there are only 20 scientific publications from six research groups. Interestingly, hardly any cross reference exists between the studies.

Giardini and Salotti from the University of Georgia, USA, were the first to report on reactions between mineral calcite, dolomite, and siderite with pressurized hydrogen and the concomitant formation of hydrocarbons.\[41, 45, 46\] The primary purpose of their study was to address geological issues, such as the formation of hydrocarbons from inorganic sources occurring in the earth’s crust. A patent was filed on this topic.\[47\] The experimental apparatus consisted of a 25 cm$^3$ externally heated “cold seal”-type vessel, in which the carbonate charge was enclosed in a platinum foil, and left unscaled and sus-
pended in the heated part of the vessel. Before usage, the minerals were handpicked for impurities, crushed, and heated in 30% hydrogen. The natural mineral deposit and the composition of the minerals were not stated.

From 1987, Reller and co-workers from the University of Zürich, Switzerland, investigated the thermal reactivity of pure alkaline-earth-metal carbonates, 3d transition-metal carbonates, and metal-doped alkaline-earth-metal carbonates in pure and dilute hydrogen by thermogravimetric (TG) experiments.\[10, 48, 49\]

Two groups from Japan—one from the Tokyo Institute of Technology,\[50\] the other from Kobe University—investigated metal carbonate hydrogenation in the 1990s. Tsuneto et al. used NiCO$_3$ and CoCO$_3$ without additional catalysts and a series of metal carbonates doped with catalytically active metals, and hydrogenated them in a fixed-bed flow reactor at atmospheric pressure.\[50\] Formation of gaseous products was reported in $\mu$mol h$^{-1}$ at a total gas flow of 9.6 cm$^3$ min$^{-1}$ and feed samples of 2 g after 0.5–1 h. To estimate the reaction rate, we calculated the hourly conversion of the respective carbonate to CH$_4$ (CtM in %h$^{-1}$), as depicted from Equation (7). Data listed in the table coincided only partially with the data given in the main text of their paper.\[50\] In case of discrepancies, data listed tabularly were used herein.

$$\text{CtM} = \left(1 - \frac{n_0 \text{ carbonate} - n_{\text{CH}_4}}{n_0 \text{ carbonate}}\right) \cdot 100 \quad (7)$$

Yoshida et al. focused on CH$_4$ formation from metal-catalyzed CaCO$_3$ hydrogenation, in comparison to hydrogenation of pure CaCO$_3$.\[51\] Experiments were carried out by means of the temperature-programmed hydrogenation technique, and for isothermal kinetic runs two apparatuses were applied: a Cahn electrobalance and a closed circulation apparatus.

In 2009 and 2013, Jagadeesan et al. from the Jawaharlal Nehru Centre for Advanced Scientific Research, India, investigated CaCO$_3$ and mixed-metal/CaCO$_3$ hydrogenation promoted with catalytically active metallic nanoparticles in a continuous-flow, packed-bed, stainless-steel reactor and managed to directly convert the inorganic carbonates into C$_1$–C$_3$ hydrocarbons.\[13, 52\]

The effect of reaction temperature, pressure, and gas atmosphere on the reaction kinetics of mineral FeCO$_3$, MgCO$_3$, and CaMg(CO$_3$)$_2$ hydrogenation has recently become subject of detailed investigation by Baldauf-Sommerbauer et al. from Graz University of Technology, Austria.\[12, 53, 54\] Experiments were carried out in a thermobalance and a tubular reactor setup.
A detailed list of the abovementioned studies, starting with the most recent ones, is given in Table 1. The investigations can be divided into two groups: 1) hydrogenation of single-metal carbonates without additional catalysts, applied either as mineral ore or in synthetic form; 2) mixed-metal/metal carbonates, mainly synthetic, in which one of the metals, mostly transition metals, acts as an internal catalyst. In general, synthetic carbonates and mixed-metal/metal carbonates were produced by precipitation and coprecipitation from aqueous solution of NaHCO₃.

4.1. Single-metal carbonates

Hydrogenation of single-metal carbonates includes the alkaline-earth-metal carbonates MgCO₃, CaCO₃, SrCO₃, BaCO₃, and CaMg(CO₃)₂ and the 3d transition-metal carbonates MnCO₃, FeCO₃, CoCO₃, NiCO₃, and ZnCO₃. Decomposition of the respective carbonates in a reducing hydrogen atmosphere occurs at lower temperatures than that of decomposition under inert or oxidizing conditions.

4.1.1. Alkaline-earth metals

MgCO₃, CaCO₃, BaCO₃, and SrCO₃

Reller et al.[48] and Padeste[49] performed TG measurements with finely ground MgCO₃ and CaCO₃ mineral, and synthetic SrCO₃ and BaCO₃ at atmospheric pressure. Equal amounts of CO₂ and CO, together with H₂O, were formed as gaseous products from MgCO₃. In the case of CaCO₃, the main volatile compound was CO (CO/CO₂ ≈ 10:1) from which a change in the degradation mechanism was concluded. The concomitant formation of CO in addition to CO₂ and H₂O was dedicated to the reduction of CO₂ through the reverse water-gas shift reaction [Eq. (6)]. The amount of CO increases with increasing atomic mass of the alkaline-earth-metal cation due to higher decarboxylation temperatures (T(MgCO₃) < 800 K, T(CaCO₃) ≈ 900 K) and the endothermic nature of the reverse water-gas shift reaction, which shifts the equilibrium composition towards the product CO at higher temperatures. The reaction temperature for decarboxylation in hydrogen was lowered by at least 150 K compared with the analogous reaction in a nitrogen atmosphere. In a hydrogen atmosphere, all four alkaline-earth-metal carbonates fully degraded below temperatures of 1200 K into their respective oxides MgO, CaO, SrO, and BaO. They formed as solid conglomerates of microcrystalline domains with diameters of 10–20 nm and showed a pronounced reactivity towards the respective hydroxides and towards recarbonation.[48] If synthetic CaCO₃ crystals were degraded in nitrogen and hydrogen atmospheres, distinct destruction in nitrogen occurred, which suggested that diffusion of H₂ into the carbonate, where it directly reacted with fixed CO₂ and reverse diffusion of formed CO and H₂O proceeded faster than that of CO₂ diffusion.[50,48]

Kinetic studies with CaCO₃ were performed by Yoshida et al. in a closed circulation apparatus at a fixed H₂ pressure of 0.13 × 10⁵ Pa and 748 K.[51] The reaction was of half-order with respect to H₂ with an activation energy of 236 kJ mol⁻¹. Initial reaction rates did not differ for varying CaCO₃ amounts, which was explained by decomposition of CaCO₃ and hydrogenation of released CO₂ to CO. The lowest temperature at which hydrogenation occurred was 700 K. At temperatures of 700–773 K, only CO formed. Above 773 K, CO and CO₂ formed. The formation of the two gaseous products differed over the course of time. Whereas CO pressure steadily increased with time, CO₂ pressure abruptly reached a maximum value of 22.7 Pa and did not change subsequently.

Baldauf-Sommerbauer et al. examined the effect of reaction temperature (748–778 K) and pressure (ambient to 1.2 MPa overpressure) on the reductive calcination of magnesite (5–8 mm) in a fixed-bed tubular reactor with 70% hydrogen and nitrogen.[53] MgCO₃ conversion rose with increasing reaction temperature (e.g., from 45% at 748 K to 96% at 778 K). Under isothermal conditions, the conversion decreased with increasing pressure (e.g., at 763 K from 76% at ambient pressure to 67% at 1.2 MPa overpressure). In contrast to the findings of Reller et al.,[48] CH₄ was found in addition to CO₂, CO, and H₂O as gaseous products [Eq. (8)].

\[
(a + b + c) \text{MgCO}_3 + (b + 4 c) \text{H}_2 \rightarrow (a + b + c) \text{MgO} + a \text{CO}_2 + b \text{CO} + c \text{CH}_4 + (b + 2 c) \text{H}_2\text{O}
\] (8)

Low temperature and elevated pressure facilitated CH₄ formation. Moderate to high temperature and low pressure facilitated CO formation. The CH₄ yield was 38.6% after 20% MgCO₃ conversion at 748 K and 1.2 MPa overpressure. With respect to the reaction mechanism, decreasing CH₄ formation with increasing magnesite conversion indicated a dependency on the amount of MgCO₃. Baldauf-Sommerbauer et al. related the increase of CO concentration with rising MgCO₃ conversion to the amount of MgO. To scrutinize this interpretation, they examined reductively calcined MgO for its catalytic properties for CO₂ conversion with H₂. At ambient pressure and 0.3 MPa overpressure, only CO formed. At 0.8 MPa overpressure, traces of CH₄ occurred in addition to the major product CO. These findings revealed significant reverse water-gas shift activity of reductively calcined MgO, but no CH₄ formation. CH₄ formation during reductive calcination of magnesite seemingly proceeds through a different mechanism.

Giardini and Salotti reported the formation of CH₄ and ethane (C₂H₆) through heating (693–1243 K) of calcite and dolomite under a pressurized hydrogen atmosphere (0.7–80 MPa H₂); however, it was not comprehensible whether the pure minerals were used or if the reaction was catalytically accelerated.[51,45–47] In their main publication,[11] they stated that metallic Ni, Pt, Cu, Ti, Mg, and Fe; commercial mixtures of 0.5% Pd, Pt, Rh on alumina and dried silica gel; activated alumina; hematite, magnetite; chromic oxide; chromium trioxide; and Kieselguhr mixtures were added, but no precise information was given on the type of catalyst for individual experimental data. The catalyst admixture was neither mentioned in the first publication[46] nor in the patent application.[47] Apparently, none of the catalytically active materials had a discernible effect on the rate of reaction. The reaction kinetics were thus expected to fit
### Table 1. Papers on metal carbonate hydrogenation dating back to the 1960s until the present (2018), ranked in chronological order.

| Material component | Additional catalyst | Feed gas comp. | Experimental apparatus | Sample size | Sample mass [g] | Flow rate [cm³·min⁻¹] | T [K] | P [MPa] | Ref. | Year |
|--------------------|---------------------|----------------|------------------------|-------------|-----------------|-----------------------|-------|---------|------|------|
| mineral MgCO₃/CaMg(CO₃)₂ | no | H₂ (90 vol %), N₂ (10 vol %) | tubular reactor (T316 SS, \(d = 2.5\) cm, \(l = 80\) cm) | 5–8 mm | 121 | 500 | 768–808 | amb | 0.3, 0.8 (o.p.) | [54] | 2017 |
| mineral MgCO₃ | no | H₂ (90 vol %), N₂ (10 vol %) | tubular reactor (T316 SS, \(d = 2.5\) cm, \(l = 80\) cm) | 5–8 mm | 115 | 500 | 748, 763, 778 | amb | 0.3, 0.8 (o.p.) | [99] | 2016 |
| mineral FeCO₃ | no | H₂ (70 vol %), N₂ (30 vol %) | thermobalance (HR = 1.8, 3, 5, 10 K·min⁻¹) | 100–200 µm | 0.02 | 100 | < 1023 | amb | [12] | 2016 |
| mineral FeCO₃ | no | H₂ (90 vol %), N₂ (10 vol %) | tubular reactor (T316 SS, \(d = 2.5\) cm, \(l = 80\) cm) | 0.5–1 mm | 60 | 867 | 623, 648 | amb | [96] | 2016 |
| CaCO₃ | Fe | H₂ | continuous-flow, packed-bed reactor (SS) | n.a. | 0.04 | 3 | 573–873 | amb | [13] | 2013 |
| MeCa(CO₃)₂ (Me = Co, Ni, Fe; Me/Ca = 1:1); Me′Me′′Ca(CO₃)₂ (Me′Me′′ = CoNi, NiFe, FeCo; Me′/Me′′/Ca = 1:1:2) | no/yes, NPs of Co/CaO/CoO, Ni/CaO, GoNi/CoO/CoO | H₂ | tubular reactor (SS, \(d = 0.6\) cm, \(l = 30\) cm) | n.a. | 0.05 | 3.5–8 | 823 | amb | [52] | 2009 |
| CaCO₃ | no/yes, Pd, Ir (5 wt %) | H₂ (< 0.027 MPa) | temp-programmed hydrogenation (HR = 3 K·min⁻¹), Cahn electrobalance (3.62 cm²), closed circul. apparatus (275 cm³) | n.a. | | 0.015, 0.1, 570 | 60 | 573–698 | amb | [51] | 1999 |
| NICO₃·Ni(DH)₂-4H₂O, CoCO₃·CuCO₃·Ni(OH)₂, Na₂CO₃·K₂CO₃, Mg(OH)₂·H₂O, BaCO₃, CaCO₃ | no/yes; Ni, Fe, Co, Pd, Pt, Cu (2 wt %) | H₂ (50 vol %), He (50 vol %) | fixed bed flow reactor | n.a. | 2 | 9.6 | 473–673 | amb | [50] | 1992 |
| MnCO₃, FeCO₃, CoCO₃, NICO₃, ZnCO₃, caustic 3d transition-metal carbonates (Cu, Ni, Zn, CuNi, CuCo, CuZn, Ni/Zn) | no, influence of type of energy | H₂ (5 % H₂ in Ar) | TG/MS (HR = 10 K·min⁻¹) | | | \(\approx 15 \times 10^{-3}\) | 30 | < 900 | amb | [22] | 1992 |
| Mg₃(OR)₄(CO₃)₄·4H₂O | no/yes, Ni | H₂ | TG/DTA, TG/MS | n.a. | 8.2 \times 10^{-3} | 30 | < 900 | amb | [56] | 1991 |
| MgCO₃·CaCO₃·SrCO₃·BaCO₃·FeCO₃ | no/yes; Ni, Ru, Rh for CaCO₃ | H₂ (0.1 MPa) | TG/MS (HR = 10 K·min⁻¹) | n.a. | \(\approx 15 \times 10^{-3}\) | 30 | < 1200 | amb | [10, 55] | 1991 |
| CaCO₃ | Fe, Ni, Cu, Co, Ru, Rh, Pd, Ag | H₂ | TG/MS | n.a. | 10–12 \times 10^{-3} | 30 | < 950 | amb | [49, 55] | 1990–1989 |
the uncatalyzed hydrogenation of calcite. Due to high initial hydrogen concentrations relative to calcite, the reaction kinetics simplified to pseudo-first-order kinetics, with an activation energy of 75 kJ mol\(^{-1}\) at 14 MPa.\(^{[46]}\) Hydrogenation of calcite started at 773 K. It was primarily dependent on temperature and secondarily dependent on pressure and time and proceeded in a crystallographically anisotropic manner. As solid products, CaO, Ca(OH)\(_2\), graphite (C), and a black residue, possibly solid hydrocarbons, formed. At higher temperatures, CaO was the principal solid product. CH\(_4\) and H\(_2\)O were ubiquitous gaseous products, whereas C\(_2\)H\(_6\) and CO appeared under certain specific conditions. CO\(_2\) was never detected in remarkable amounts (>0.01%). CO\(_2\) if formed, immediately converted into CH\(_4\), CO, and H\(_2\O\). The maximum CH\(_4\) content (on a dry basis) was 3.2% (and 96.75% H\(_2\)) at 988 K, 61 MPa, and 16 h. The reaction was dependent on the type of surface because powdery CaCO\(_3\) reacted faster than a single rhomb of equal weight.

\textit{Mg\(_2\)(OH)\(_2\)(CO\(_3\))\(_4\) \cdot 4H\(_2\)O}

Hydrogenation of hydromagnesite [Mg\(_2\)(OH)\(_2\)(CO\(_3\))\(_4\) \cdot 4H\(_2\)O] to MgO occurred in two steps and finished at temperatures lower than 750 K. The first step corresponded to loss of water. In the second step, CO\(_2\) released from Mg\(_2\)(OH)\(_2\)(CO\(_3\))\(_4\) and yielded MgO as the final solid product.\(^{[56]}\)

\textit{CaMg(CO\(_3\))\(_2\)}

The effect of reaction temperature (793 K–1108 K) and initial hydrogen pressure (14–34 MPa) on the hydrogenation of dolomite (40–60 mesh) was investigated by Giardini and Salotti.\(^{[46]}\) As for calcite, there was no clear information on the catalyst admixture. We assume that the main findings apply to the hydrogenation of dolomite without additional catalysts. Solid products included CaCO\(_3\), Ca(OH)\(_2\), CaO, noncrystalline Mg(OH)\(_2\), graphite, and a “soot-like” material; gaseous products CH\(_4\), C\(_2\)H\(_6\), CO, and CO\(_2\). H\(_2\O\) was the oxygenated product in all experiments. A two-step reaction mechanism was proposed in which noncrystalline Mg(OH)\(_2\) or MgO formed [Eq. (9)]. At 34 MPa, the reaction started at 793 K.

\[
\text{CaMg(CO}_3\text{)}\text{)}_2 + 4 \text{H}_2 \rightarrow \text{CaCO}_3 + \text{Mg(OH)}_2 + \text{CH}_4 + \text{H}_2\text{O} \quad (9)
\]

Reller et al. found that the decarboxylation temperature of dolomite and the ratio of the gaseous products CO and CO\(_2\) lay between the corresponding values of the two pure carbonates CaCO\(_3\) and MgCO\(_3\).\(^{[48]}\)

Baldauf-Sommerbauer et al. suggested the hydrogenation of mixed magnesite/dolomite (1:1 mol/mol) for the synthesis of CO.\(^{[54]}\) TG measurements showed two decomposition steps. Compared with the reaction in nitrogen, a hydrogen atmosphere leads to a decrease of the decomposition temperature of 60 K for the first step and 100 K for the second step. In the first step, the decomposition of concomitant MgCO\(_3\), FeCO\(_3\), and MnCO\(_3\) to the respective bivalent oxides and CO\(_2\) was observed. Then CaMg(CO\(_3\))\(_2\) decomposed into CaO, MgO, and CO\(_2\). Reductive calcination experiments in a tubular reactor in-
dicated a sequential mechanism of calcination followed by hyd

drogenation of CO$_2$. CH$_4$ was only formed in traces, even at
elevated pressure. It is assumed that CH$_4$ formation was kine

tically hindered. A CO yield of 61–73% was achieved for partial
reductive calcination of the magnesite content below 813 K.
An increase of pressure did not affect the formation of CO, but
caus ed a slight retardation of the reaction.

4.1.2. Transition-metal carbonates

The minerals MnCO$_3$ (rhodochrosite) and FeCO$_3$ (siderite), and
synthesized CoCO$_3$, NiCO$_3$, and ZnCO$_3$ were investigat ed.
Synthesis requires hydrothermal conditions at high pressure.
According to the size of their cations, the 3D transition-metal ca

arbonates crystallize in a trigonal calcite-type structure.$^{[22,57]}

As postulated by Emmenegger$^{[22]}$ from hydrogenation ex

p eriments in pure and dilute hydrogen (5% H$_2$ in Ar), the par

tial hydrogen pressure decisively influences the hydrogenation
reaction. Different solid products—transition-metal oxides and
elemental transition metals arise—depending on the selected
atmosphere, and morphological features may be controlled. In
hydrogen, decarboxylation temperatures drop, in comparison
to the respective reaction under an inert atmosphere. Dilute
hydrogen results in a lower temperature drop. The degra
dation temperature drops with decreasing radius of the transition-
metal cations: Mn$^{2+}$ (0.8 Å) > Fe$^{2+}$ (0.76 Å) > Co$^{2+}$ (0.74 Å) >
Ni$^{2+}$ (0.72 Å) > Mg$^{2+}$ (0.65 Å). The ratio of gaseous products
CO$_2$, CO, CH$_4$, higher hydrocarbons, and H$_2$O varies, de
pend ing on the transition-metal species. According to Reller et al.,
CO$_2$ is released during transition-metal carbonate hydrogenation,
and further catalytically hydrogenated.$^{[10]}$ In the course of de

carboxylation, the catalysts Me or Me/MeO form in situ. Fe, Co,
and Ni act as efficient hydrogenation catalysts.

$\text{MnCO}_3$

In pure and dilute (5% H$_2$ in Ar) hydrogen, the mineral MnCO$_3$

decarboxylated to MnO without changing its oxidation
number at 643 K. As gaseous products, traces of unconverted
CO$_2$, CO, and H$_2$O formed. Consequently, manganese effi
ciently catalyzed the reverse water-gas shift reaction. In dilute hyd
rogen, this reaction was retarded. After a period of induction, re

leased CO$_2$ was further converted into CO and H$_2$O. Compared
with pure hydrogen, the chemical equilibrium barely lay on
the side of the product.$^{[22]}

$\text{FeCO}_3$

Salotti and Giardini first studied the hydrogenation of siderite
(40–60 mesh) at reaction temperatures of 618 to 878 K and ini

tial partial hydrogen pressures of 1.4 to 34 MPa (H$_2$).$^{[46]}$ Because
there was no precise information on the catalyst admixtures
reported, we assumed that the main findings applied to side
r ite only. At temperatures above 728 K, the solid products con

sisted of elemental Fe and wüstite (FeO). At lower tempera
tures (673 K and 14 MPa H$_2$), magnetite (Fe$_3$O$_4$) formed. From
minute and rare flecks, Giardini and Salotti assumed that also

graphite was formed.$^{[11]}$ Wüstite was the primary alteration
product [Eq. (10)]. Further reduction of wüstite to elemental Fe
[Eq. (11)] or oxidation of wüstite to magnetite [Eq. (12)] de

pended on the reaction temperature and the ultimate H$_2$/H$_2$O
ratio. A low reaction temperature and dry hydrogen need to
be provided to effect reduction.

\begin{equation}
\text{FeCO}_3 + 5 \text{H}_2 \rightleftharpoons \text{FeO} + \text{CH}_4 + 2 \text{H}_2\text{O} \tag{10}
\end{equation}

\begin{equation}
\text{H}_2 + \text{FeO} \rightleftharpoons \text{Fe} + \text{H}_2\text{O} \tag{11}
\end{equation}

\begin{equation}
\text{H}_2\text{O} + 3 \text{FeO} \rightleftharpoons \text{Fe}_3\text{O}_4 + \text{H}_2 \tag{12}
\end{equation}

CH$_4$ and H$_2$O were ubiquitous gaseous products, whereas
CO, CO$_2$, and the higher hydrocarbons ethane (C$_2$H$_6$), pro
pane (C$_3$H$_8$), and butane (C$_4$H$_{10}$) were present over a limited tem

perature and pressure range. An inverse relationship existed be
 tween the temperature and the length of the hydrocarbon ch

ain, meaning that a lower initial reaction temperature results in
a more complex hydrocarbon species. At 673 K (14 MPa H$_2$),
the gaseous product on a dry basis contained 4.45 mol% CH$_4$,
0.28 mol% ethane, 0.01 mol% propane, and 0.03 mol% butane.
At 728 K (1.4 MPa H$_2$), the concentration of CH$_4$ slightly
decreased (4.34 mol%), whereas the concentrations of higher
hydrocarbons increased (0.42 mol% ethane, 0.23 mol% pro
pane, 0.05 mol% butane). At 878 K and 14 MPa H$_2$, only CH$_4$
was detected. CO$_2$ only formed at 798 K (34 MPa H$_2$). Giardini
and Salotti explained this by the thermal stability of the hydro
carbons.$^{[11]}$ The reaction temperature for siderite hydrogena
tion is low enough to ensure thermal stability of ethane, pro
pane, and butane. They concluded that higher hydrocarbons
formed directly through a reaction on the mineral surface,
rather than in a subsequent reaction between released gases
and hydrogen.

This conclusion contradicts the findings of Reller et al., who
explained the formation of CO and CH$_4$ by in situ formation of
catalytically active transition-metal species.$^{[10]}$ Emmenegger
compared the hydrogenation of siderite in pure and dilute hy
drogen (5% H$_2$ in Ar).$^{[22]}$ In pure hydrogen, the formation of
mainly elemental Fe together with FeO as solid products was
observed. At elevated temperature above 823 K, decomposi
tion was slow and not yet finished at 973 K. The gaseous pro
ducts CH$_4$, H$_2$O, and CO were formed. Higher hydrocarbons
were not found. CO$_2$ was also released. The reaction pathways
in Equations (13) and (14) were postulated for siderite hydro
genation. Because Fe was not the main product, according to
Equation (14) reduction occurred only partially. The reverse
water-gas shift reaction for the reduction of CO$_2$ to CO was re
ported.

\begin{equation}
\text{FeCO}_3 \rightleftharpoons \text{FeO} + \text{CO}_2 \tag{13}
\end{equation}

\begin{equation}
\text{FeO} + \text{H}_2 \rightleftharpoons \text{Fe} + \text{H}_2\text{O} \tag{14}
\end{equation}

In dilute hydrogen, CH$_4$ did not form. The major amount of
CO$_2$ released from siderite [Eq. (13)] was not converted, but
formed the main product of the product gas. Reduction of in
termediate FeO was incomplete and only minor amounts of Fe
were formed. In addition to the distinct difference in product
composition between conversion in pure and dilute hydrogen atmospheres, solid products also differed in morphology. In pure hydrogen, the solid product contained a high amount of crystalline parts, whereas the product in dilute hydrogen featured a higher amount of fine particles. The conversion temperature significantly reduced in pure hydrogen (603 K), with respect to an inert helium atmosphere (653 K). In dilute hydrogen, decarboxylation started at 623 K.

Baldauf-Sommerbauer et al. suggested the hydrogenation of siderite as a means for sustainable iron production. They performed kinetic computations to study the reaction kinetics of iron formation, and considered the concomitant decompositions of the accessory matrix carbonates of calcium, magnesium, and manganese. The original mineral consisted of three main carbonate components of siderite FeCO₃ with partial Mg and Mn substitution, ankerite (Ca₆Fe₃Mg₃Mn₃)CO₃ and dolomite CaMg(CO₃)₂. Potassium, aluminum, and silicon existed in the form of muscovite KAl₃(AlSi(OH))₂, whereas a major part of the silicon was quartz (SiO₂). A concentrated siderite specimen (size fraction 100–200 μm) was used for kinetic analysis in a thermobalance. During conversion under a hydrogen atmosphere, the FeCO₃ content of mineral siderite was converted into elemental Fe ([79 ± 2] wt%; Eq. (15)]. From calcium, magnesium, and manganese carbonates, the respective oxides formed (Eq. (16)).

\[
\text{FeCO}_3 + H_2 \rightarrow Fe + H_2O + CO_2 \quad (15) \\
(Ca,Mg,Mn)CO_3 \rightarrow x \text{CaO} + y \text{MgO} + z \text{MnO} + CO_2 \quad (16)
\]

The model-free kinetic analysis, according to the Ozawa–Flynn–Wall, Kissinger–Akahira–Sunose, and Friedman approaches, gave a parallel kinetic model. With multivariate nonlinear regression, the kinetic parameters (Eₐ = 151.8 kJ mol⁻¹, log 10(A) = 8.751 s⁻¹) were determined. A two-dimensional Avrami–Erofeev model was applicable for the conversion of FeCO₃ into Fe. Therefore, a temperature-controlled nucleation and diffusional growth mechanism was suggested. For the concomitant formation of CaO, MgO, and MnO, multiparameter autocatalysis models were used without applying multistep kinetics. At 723 K, more than 95% conversion within less than 60 min reaction time was observed. Increasing temperature leads to a faster reaction, but a lower yield of elemental Fe.

CoCO₃ and NiCO₃

Hydrogenation of synthetic CoCO₃ and NiCO₃ was investigated by Emmenegger and Tsuneto et al. Tsuneto et al. hydrogenated commercial transition-metal powders of CoCO₃ and NiCO₃·Ni(OH)₂·4H₂O in a fixed-bed flow reactor at atmospheric pressure and 473 K. In both cases, CH₄ formed after a period of induction, in which only CO₂ evolved through thermal decomposition. In the case of CoCO₃, a maximum methane formation rate of 97 μmol h⁻¹ was achieved after 55 h. With NiCO₃, the methane formation rate reached a maximum value (72 μmol h⁻¹) after 7 h and hydrogen (12 mmol h⁻¹) was consumed completely. At 523 K, CH₄ and CO₂ formed promptly. The formation of metallic Co and Ni, together with the period of induction for methane formation, suggests that Ni and Co act as hydrogenation catalysts for CO₂.

Emmenegger performed TG experiments with synthetic CoCO₃ and NiCO₃ in helium and pure and dilute hydrogen (5% H₂ in Ar). The temperature at which carbonate degradation started dropped from 603 K in helium to 543 K in pure hydrogen for CoCO₃. For NiCO₃, a similar temperature dependency of conversion, with 623 K in helium, 548 K in dilute hydrogen, and 513 K in pure hydrogen, was observed. Under a hydrogen atmosphere (pure and dilute), elemental Co and Ni formed as solid products. Similar behavior between CoCO₃ and NiCO₃ was also visible, in terms of the gaseous product stream. The main gaseous products CH₄ and H₂O formed. The byproducts CO₂ and barely any CO were detected. The formation of gaseous products proceeded simultaneously. CO₂ fully converted after a certain period of induction, which indicated that cobalt and nickel catalyzed the hydrogenation of CO₂ to CH₄. Conversion differed with respect to the rate of reaction in dilute hydrogen: at the beginning, the conversion of NiCO₃ was slower than that of CoCO₃. In both cases, the catalytic activity for CO₂ hydrogenation dropped drastically and the main gaseous products were CO₂ and H₂O [Eqs. (13) and (14) for CoCO₃ and NiCO₃] and only minor amounts of CO. These reactions seemed to occur simultaneously because CO₂ and H₂O formed concurrently. From CoCO₃ conversion, barely any CH₄ formed, but still significant amounts of CH₄ arose from NiCO₃. Consequently, Ni was confirmed to be a more efficient catalyst in a dilute hydrogen atmosphere than Co.

ZnCO₃

Contrary to other 3d transition-metal carbonates, Emmenegger found that decomposition temperatures of ZnCO₃ increased from 583 K in pure hydrogen to 628 K in dilute hydrogen (5% H₂ in Ar). Due to a lower hydrogen concentration, the equilibrium composition of the reverse water-gas shift reaction preferably consists of H₂ and CO₂. Zinc did not show any catalytic activity for the reduction of evolved CO₂. The composition of the gaseous product mixture (CO₂, CO, and H₂O) resembled that expected for the water-gas equilibrium.

**Caustic 3d transition-metal carbonates**

Emmenegger investigated the hydrogenation of caustic 3d transition-metal carbonates of the type Meₓ+y(OH)(CO₃)ₓ[Zn(OH)]_{y-2}H₂O (Me = Cu, Ni, Zn), combinations thereof (Cu/Ni, Cu/Co, Cu/Zn, Ni/Zn), and mixed caustic transition-metal/Mg carbonates (MeMg(CO₃)₂ with Me = Fe, Co, Ni, Cu, Zn; Me₂Mg(CO₃)₃ with Me₂ = CuZn, Ni/Zn, Cu/Ni). Decomposition temperatures were lower than those of the respective neutral carbonates. Loss of crystal water and condensation of OH⁻ with caustic carbonates was observed. Higher water concentration shifts the equilibrium composition of potential CO₂ hydrogenation to the reactant side. Consequently, all caustic metal carbonates show low catalytic hydrogenation activity compared...
with that of the respective neutral carbonates. Mixed transition-metal/Mg carbonate systems show pronounced catalytic activity, which highlights the effect of the noncatalytic support material MgO. MgO forms fine particles that give access to high dispersion of the transition metals or alloys.\textsuperscript{[22]}

### 4.2. Main-group metal carbonates combined with transition metals

An admixture of transition metals to main-group metal carbonates opens up a new pathway in metal carbonate hydrogenation: because many transition metals catalyze hydrogenation reactions, CO\(_2\) evolved from the carbonate is converted into CO, CH\(_4\), or higher hydrocarbons C\(_x\)H\(_y\) and C\(_x\)H\(_{y+1}\)O\(_x\). The catalytically active transition-metal species is formed in situ during the decomposition reaction. A wide range of transition metals (Fe, Ni, Co, Cu from the 3d group; Ru, Rh, Pd, Ir from the 4d group) was used for doping of various main-group metal carbonates, such as Li\(_2\)CO\(_3\), Na\(_2\)CO\(_3\), K\(_2\)CO\(_3\), CaCO\(_3\), MgCO\(_3\), SrCO\(_3\), and BaCO\(_3\). Mixed alkaline-earth-metal/transition-metal carbonates of the type Me\(_2\)Ca(CO\(_3\))\(_2\) and Me\(_2\)Me\(_2\)(CO\(_3\))\(_2\) were also investigated.

In general, two promising effects take place. First, the decarboxylation temperature of the alkaline and alkaline-earth-metal carbonates drops. Second, different gaseous compounds evolve during decomposition due to the catalytic activity of the transition-metal species. The product composition depends on the transition metal in the carbonate.

#### 4.2.1. Alkaline-carbonate systems

Tsuneto et al. hydrogenated nickel-doped (2 wt\%) Li\(_2\)CO\(_3\), Na\(_2\)CO\(_3\), and K\(_2\)CO\(_3\) at 400 K and atmospheric pressure.\textsuperscript{[49]} Nickel powder was mechanically mixed with the carbonate sample. CO\(_2\) was not detected after 1 h from Li\(_2\)CO\(_3\) and Na\(_2\)CO\(_3\) decomposition, according to thermodynamics. Traces of CO\(_2\) were detected from K\(_2\)CO\(_3\) (<2 \(\mu\)mol h\(^{-1}\)) at a total gas flow rate of 9.6 cm\(^3\) min\(^{-1}\)). With all three carbonates, minor amounts of CH\(_4\) were formed (Li\(_2\)CO\(_3\): 1.3 \(\mu\)mol h\(^{-1}\), \(\text{CtM} = 0.005\%\), Na\(_2\)CO\(_3\): 2.5 \(\mu\)mol h\(^{-1}\), \(\text{CtM} = 0.013\%\), K\(_2\)CO\(_3\): 1.8 \(\mu\)mol h\(^{-1}\), \(\text{CtM} = 0.012\%\)).

#### 4.2.2. Alkaline-earth-metal carbonates

Hydrogenation of calcite and dolomite minerals at elevated temperatures (calcite: 693–1143 K, dolomite: 793–1108 K) and elevated pressure (calcite: 1.4–55 MPa H\(_2\), dolomite: 14–34 MPa H\(_2\)) was investigated by Giardini and Salotti.\textsuperscript{[31]} In their report, it is ambiguous to which experimental runs metallic Ni, Pt, Cu, Ti, Mg, and Fe, or commercial mixtures of 0.5% Pd, Pt, and Rh on alumina and dried silica gel, activated alumina, hematite, magnetite, chromic oxide, chromium trioxide, Kieselguhr mixtures, hydrous and anhydrous oxides, and pyrolytic carbon were added as potential catalysts. None of the catalytically active materials had a discernible effect on the rate of reaction. The metals Pt, Fe, and Ni catalytically promoted pyrolytic dissociation of formed CH\(_4\) (Eq. (17)). For calcite, they reported the formation of CaO [Eq. (18)]; Ca(OH)\(_2\) [Eq. (19)]; graphite; and, at temperatures above 973 K, carbon soot-like material, which was seemingly amorphous carbon formed through thermal dissociation of CH\(_4\) [Eq. (17)]. Gaseous products were CH\(_4\), C\(_2\)H\(_6\), CO, CO\(_2\), and H\(_2\). Below the dehydration temperature, Ca(OH)\(_2\) was the stable solid product.

\[
\begin{align*}
CH_4 & \leftrightarrow C + 2H_2 \\
CaCO_3 + 4H_2 & \leftrightarrow CaO + CH_4 + 2H_2O \\
CaCO_3 + 4H_2 & \leftrightarrow Ca(OH)_2 + CH_4 + H_2O 
\end{align*}
\]

They assumed that CH\(_4\) and its higher homologues, if thermally stable under the reaction conditions, formed directly through methanation of calcite, rather than through reactions between H\(_2\), CO\(_2\), and CO. CO\(_2\) and CO were only detected at low pressure (1.4 MPa) and high reaction temperature (973 K). Reller et al. investigated the effects of CO, Ni, and Cu doping (10\%) on the hydrogenation of MgCO\(_3\) and CaCO\(_3\).\textsuperscript{[46]} Mixed alkaline-earth-metal/transition-metal carbonates, Mg–Me and Ca–Me carbonates, were prepared by coprecipitation with sodium carbonate from the respective nitrate solutions. In a second study, the effect of coprecipitated Ni, Ru, and Rh was reported.\textsuperscript{[40]} The decarboxylation temperatures dropped in the range of 200 K to, at most, 400 K in the case of Ni, compared with the decarboxylation of the pure carbonates in a nonreducing atmosphere. Mixtures of CO and CO\(_2\) were released if Cu was used as a coprecipitate. In the case of Co, predominantly CH\(_4\) formed together with minor amounts of CO. The formation of CO\(_2\) was negligible. With Ni on MgCO\(_3\) and CaCO\(_3\), more than 90\% of the gaseous product was CH\(_4\). The formation of C\(_2\)H\(_6\) species from CaCO\(_3\) in H\(_2\) was not detected at atmospheric pressure (\(p = 0.1\) MPa). The solid products consisted of a mixture of microcrystalline alkaline-earth-metal oxides and elemental transition metals. Reller et al. confirmed that the formed solid products acted as effective catalysts for the partial reduction of CO\(_2\) to CO or direct conversion of CO\(_2\) into CH\(_4\). For Ni–Ca carbonate systems, the activity of the system was explained by the high dispersion of the catalytically active transition metal in the CaCO\(_3\) matrix.\textsuperscript{[46]} Consequently, the combination of transition-metal carbonates with alkaline-earth-metal carbonates improves the catalytic activity of the in situ formed transition-metal species if an appropriate dispersion or active surface area is generated during decarboxylation; an effect that cannot be accomplished with pure transition-metal carbonates only.

Padeste et al. published a detailed study comparing the influence of the 3d transition metals Fe, Ni, Co, and Cu and the 4d transition metals Ru, Rh, Pd, and Ag on the thermal decomposition of CaCO\(_3\) in hydrogen.\textsuperscript{[49]} The mixed-metal carbonates were produced by coprecipitation. Whereas 3d metal carbonates, except for FeCO\(_3\), normally precipitate as caustic carbonates (hydroxocarbonates) from aqueous solutions, ions of the 4d metals Rh, Ru, and Pd precipitate as oxides or oxide hydrates and Ag predominantly forms the simple carbonate Ag\(_2\)CO\(_3\). Samples from NiCO\(_3\)/CaCO\(_3\) and CoCO\(_3\)/CaCO\(_3\) showed that two-phase systems formed, even at transition-metal car-

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\textsuperscript{[22]}
bonate concentrations of 5%, rather than replacing large amounts of Ca\(^{2+}\) by transition metals with similar ionic radii. TG measurements showed that thermal decomposition in hydrogen proceeded in two steps: First, decomposition and reduction of the transition-metal carbonate below temperatures of 600–700 K with \(\text{H}_2\text{O}\) evolution. Second, CaCO\(_3\) decomposition at temperatures above 600–700 K. \(\text{H}_2\text{O}\) evolution might result from loss of coprecipitated water, decomposition of hydroxides to oxides [Eq. (20)], reduction of \(\text{CO}_2\) [Eqs. (21) and (22)], and reduction of the metal oxide formed [Eq. (23)].

\[
\begin{align*}
2\text{OH}^- & \rightarrow \text{O}^{2-} + \text{H}_2\text{O} \\
\text{CO}_3^- + \text{H}_2 & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{CO}_3^- + 4 \text{H}_2 & \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \\
\text{MeO}^- + \text{H}_2 & \rightarrow \text{Me} + \text{H}_2\text{O}
\end{align*}
\]

The reaction in Equation (23) was observed for all transition-metal carbonates. CO formation [Eq. (21)] did not occur in this temperature range and \(\text{CH}_4\) formation [Eq. (22)] was only observed for Ni and Co. During the CaCO\(_3\) decomposition step, \(\text{CO}_2\) [Eq. (24)], CO [Eq. (25)], and \(\text{CH}_4\) [Eq. (26)] formed as volatile carbon products.

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \\
\text{CaCO}_3 + \text{H}_2 & \rightarrow \text{CaO} + \text{CO} + \text{H}_2\text{O} \\
\text{CaCO}_3 + 4 \text{H}_2 & \rightarrow \text{CaO} + \text{CH}_4 + 2 \text{H}_2\text{O}
\end{align*}
\]

Most \(\text{CO}_2\) reduces to CO and \(\text{CH}_4\). A correlation between the decomposition temperature and the distribution of the volatile products based on the thermodynamics of the different reactions was described: carbonates that evolve predominantly \(\text{CH}_4\) at the lowest temperature, whereas carbonates that release CO as the main gaseous compound have the highest decomposition temperature, which resembles the behavior of pure CaCO\(_3\). Whereas Fe, Cu, and Ag showed little influence \(T_{\text{decomposition}} = 730–880 \text{ K, } \text{CH}_4 > 1 \%, \text{CO} > 90 \%\) on the thermal decomposition of CaCO\(_3\) in hydrogen, Co and Pd had a medium effect \(T_{\text{decomposition}} = 680–850 \text{ K, } 20 \% < \text{CH}_4 < 70 \%, \text{and Ni, Ru, and Rh had a pronounced effect } T_{\text{decomposition}} = 620–780 \text{ K, } \text{CH}_4 > 95 \%\).

Hydrogenation of 4MgCO\(_3\)·Mg(OH)\(_2\)·5H\(_2\)O (at 573 K), CaCO\(_3\) (at 473, 573 and 673 K), and BaCO\(_3\) (at 673 K) in the presence of Ni powder in a fixed-bed reactor was compared by Tsucheto et al.\(^{[49]}\) MgCO\(_3\) was readily hydrogenated to form a considerable amount of \(\text{CH}_4\) (1600 \(\mu\text{mol h}^{-1}\)) with an hourly conversion to \(\text{CH}_4\) of 38.9% and minor amounts of \(\text{CO}_2\) (290 \(\mu\text{mol h}^{-1}\)). Contrary to MgCO\(_3\), no \(\text{CO}_2\) was released from CaCO\(_3\) and BaCO\(_3\), under the conditions investigated. \(\text{CH}_4\) formed in minor amounts from BaCO\(_3\) (1.8 \(\mu\text{mol h}^{-1}\), \(\text{CtM: 0.018} \%\)) and higher amounts from CaCO\(_3\) (95 \(\mu\text{mol h}^{-1}\), \(\text{CtM: 0.475} \%\)) at 673 K. The effect of reaction temperature was also investigated for Ni-doped CaCO\(_3\). Although \(\text{CH}_4\) formation was not suppressed at temperatures as low as 473 K, the rate of \(\text{CH}_4\) formation decreased with decreasing temperature (473 K: 3.7 \(\mu\text{mol h}^{-1}\), \(\text{CtM: 0.019} \%\); 573 K: 8.5 \(\mu\text{mol h}^{-1}\), \(\text{CtM: 0.053} \%\); 673 K: 95 \(\mu\text{mol h}^{-1}\), \(\text{CtM: 0.475} \%\)). To connote, a remarkable shift of 400–500 K towards lower hydrogenation temperatures occurred in comparison to undoped CaCO\(_3\) (1172 K). Similar to the work of Padeste et al.,\(^{[48]}\) Tsucheto et al.\(^{[49]}\) investigated the effect of the transition metals Fe, Ni, Pd, Pt, and Cu on CaCO\(_3\) hydrogenation at 673 K. The order of the catalytic activity was Ni > Co > Pt > Fe > Cu > Pd. This sequence confirms the results of Padeste et al.,\(^{[49]}\) apart from Pd, which was attributed medium influence in the former study. Long-term hydrogenation was investigated for Ni-doped CaCO\(_3\) at 673 K. The \(\text{CH}_4\) formation rate was constant for 7 days. Within 15 days, a total of 95% of CaCO\(_3\) was converted. As solid products, CaO and Ca(OH)\(_2\) formed according to Equations (26) and (27).

\[
\begin{align*}
\text{CaCO}_3 + 4 \text{H}_2 & \rightarrow \text{Ca(OH)}_2 + \text{CH}_4 + \text{H}_2\text{O}
\end{align*}
\]

Because the rate of \(\text{CH}_4\) formation was greater than that of \(\text{CO}_2\) evolution, Tsucheto et al. concluded that direct CaCO\(_3\) hydrogenation occurred on the CaCO\(_3\) surface by hydrogen spill-over from a Ni surface, rather than thermal decomposition of CaCO\(_3\) followed by hydrogenation of released \(\text{CO}_2\).\(^{[50]}\)

Yoshida et al. studied methane formation through the hydrogenation of CaCO\(_3\) catalyzed by Pd and Ir (5 wt %) over a temperature range of 573–698 K.\(^{[51]}\) Temperature-programmed hydrogenation data revealed high-temperature tails and lower temperatures for the start of decomposition. These findings were explained by an increase of available reactive hydrogen at low temperature, probably due to adsorbed H atoms. An admixture of transition metals that are able to dissociate H atoms lower the starting temperature of metal oxide reduction.\(^{[52]}\) Due to the low equilibrium decomposition pressure of CaCO\(_3\) at 573 K (0.0015 Pa), it was assumed that, with transition-metal catalysts, hydrogenation occurred through direct interaction of CaCO\(_3\) and H atoms to form \(\text{CH}_4\). It is possible that reaction intermediates formed in the CaCO\(_3\) surface layer, but this assumption has not been validated. Activation energies derived from experiments in an electrobalance were 105 and 111 kJ mol\(^{-1}\) for the Ir- and Pd-catalyzed reactions, respectively. The reaction rate increased steadily with increasing \(\text{H}_2\) pressure and remained constant at sufficiently high pressures. Yoshida et al. dedicated this tendency to a transition in reaction kinetics from slightly higher than first order at low pressures to zero order at high pressures. From reaction kinetics, it was suggested that the rate of dissociative adsorption of \(\text{H}_2\) on the metal surface was fast relative to the overall reaction rate.\(^{[51]}\)

Jagadeesan et al. extensively studied hydrocarbon formation from various mixed inorganic carbonates and made remarkable conclusions about hydrocarbon selectivity for \(\text{C}_1-\text{C}_8\) chain lengths.\(^{[13,52]}\) In the first study, Jagadeesan et al. examined methane formation from mixed alkaline-earth-metal/transition-metal carbonates at 823 K.\(^{[52]}\) The operating pressure was not stated and the assumption could thus be made that the work was carried out at atmospheric pressure. In a second paper by Jagadeesan et al., however, it was stated that the earlier study was performed at 0.3–0.5 MPa.\(^{[31]}\) The mixed carbonates were prepared by precipitation from aqueous solutions of NaHCO\(_3\),
and had a composition of MeCa(CO)\(_3\)\(_2\), in which Me was Co, Ni, or Fe in a Me/Ca ratio of 1:1, and Me\(_x\)Me\(_y\)Ca(CO)\(_3\)\(_2\), in which Me\(_x\)Me\(_y\) was CoNi, NiFe, or FeCo in a ratio Me\(_x\)/Me\(_y\)/Ca of 1:1:2. Solid decomposition products consisted of nanoparticles of metal dispersed on metal oxide. Hydrogenation of CoCa(CO)\(_3\)\(_2\) gave CO and CH\(_4\) as major gaseous products. As the reaction proceeded, transition-metal nanoparticles formed on the carbonate surface, which catalyzed the subsequent conversion of CO\(_2\) to CH\(_4\). An increasing amount of H\(_2\) facilitated the formation of transition-metal nanoparticles through the reduction of metal ions. The carbones completely decomposed. For CoCa(CO)\(_3\)\(_2\) at 823 K, the optimal H\(_2\) flow rate for maximum conversion and CH\(_4\) selectivity was 8 cm\(^3\) min\(^{-1}\) for 5 h. These conditions applied to all mixed carbones. Again, the type of transition metal had a leading role on product gas composition. With Co, complete carbonate conversion occurred with a selectivity to CH\(_4\) of 80% (20% CO\(_2\)). All other transition metals and transition-metal combinations yielded 100% CH\(_4\) selectivity at reduced conversion. CO, H\(_2\), O\(_2\), and coke were not found. 

Carbonate conversion dropped in the order of NiCa (81%) > CoNi (77%) > FeCo (76%) > NiFe (16%) > Fe (4%). Fe exhibited poor conversion. However, in the presence of Fe (Fe, NiFe, FeCo), traces of higher hydrocarbons up to C\(_4\) formed. The introduction of Pt or K into FeCa(CO)\(_3\)\(_2\) did not increase the formation of higher hydrocarbons. Because reduced transition-metal particles appeared to be essential for high CH\(_4\) selectivity, catalyst nanoparticles were prepared separately by heating freshly prepared transition-metal carbones in H\(_2\). They contained nanoparticles of transition metals, bivalent metal oxide, and CaO and were highly efficient in catalyzing the conversion of CO\(_2\) to CH\(_4\). With CoCa(CO)\(_3\)\(_2\), if mixed in a 50:50 weight ratio with metal–metal oxide nanoparticles, the amount of CH\(_4\) formed during the first 2 h was four times higher. Studies on the effect of transition-metal–metal oxide nanoparticles on hydrogenation of mixed carbones indicated a change in reaction kinetics. In the presence of Co/CaO/CoO catalysts, H\(_2\) efficiency improved to yield 100% CH\(_4\) selectivity for CoCa(CO)\(_3\)\(_2\), in contrast to 80% in the absence of the catalyst. The effect of Co on the methanation of carbones was higher than that of Ni and Fe, and combinations thereof. The catalyst nanoparticles were also capable of decomposing the natural minerals calcite and dolomite. Complete conversion of MgCO\(_3\) and CaCO\(_3\) with 100% CH\(_4\) selectivity was achieved with Co/CaO/ CoO. The type of catalyst significantly influenced the ability to convert CaCO\(_3\) into CH\(_4\), Ni, and Co, for instance, worked well individually, but were less active upon combination. Fe was not very active itself, but effectively catalyzed CaCO\(_3\) decomposition in combination with Ni and even more effectively with Co. CaCO\(_3\) conversion decreased in the order of Co (100%) > Ni (80%) > Fe (18%) for single transition metals and FeCo (89%) > NiFe (40%) > CoNi (34%) for combinations thereof.

In a second study, Jagadeesan et al. directly focused on the formation of C\(_3\)-C\(_8\) hydrocarbons from CaCO\(_3\) through iron oxides.\(^{[13]}\) The starting carbonate, denominated FeCaCO\(_3\), consisted of CaCO\(_3\) and Fe oxides with Fe/Ca molar ratios, x, of 0–5. The carbonate contained Fe in the form of Ca\(_{1-x}\)Fe\(_x\)CO\(_3\) in the calcite structure (for x < 2). Excess Fe was present as FeO\(_2\) and increased with increasing x. The effect of reaction temperature (573–873 K) was investigated at ambient pressure and a H\(_2\) flow rate of 3 cm\(^3\) min\(^{-1}\) in a continuous-flow packed-bed reactor. The reaction time was 2 h, after which time no further decomposition of the carbonate occurred. In any case, carbonate conversion was not complete. At 673 K, the carbonate conversion and yield of carbohydrates (23% at x = 5) were highest. Further gaseous products were CO\(_2\) and CO. Iron metal (α-Fe, iron oxides (Fe\(_x\)O\(_y\), γ-Fe\(_x\)O\(_y\), α-FeOOH, CaFe\(_2\)O\(_4\)), and carbide (d-Fe\(_C\), γ-Fe\(_C\)) particles formed as solid residues supported on Ca-rich oxides. The level of conversion and yield of hydrocarbons, suggesting higher hydrocarbon selectivity, increased with increasing molar ratios of Fe/Ca. At x = 5, the yield of the gaseous products CH\(_2\), CH\(_3\), CH\(_4\), C\(_2\)H\(_6\), C\(_2\)H\(_4\), and CO and CO\(_2\) was 5, 7, 4, 4, 6, and 21%, respectively. In the absence of Fe, mainly CO\(_2\) formed with traces of CO. Consequently, Fe not only improved carbonate decomposition, but also the subsequent hydrogenation of released CO\(_2\) to higher hydrocarbons. For all molar ratios, the relative C\(_2\)H\(_4\) yield was highest among all hydrocarbons. The yield of C\(_2\)H\(_4\) increased with increasing amounts of Fe, which suggested that higher concentrations of Fe favored C–C coupling, rather than dehydrogenation. The total hydrocarbon yield from Fe-catalyzed CaCO\(_3\) hydrogenation was comparable to that in the FT synthesis. A reaction mechanism based on carbonate decomposition to CO\(_2\), which underwent further reduction to CO and hydrocarbons, was stated. According to Jagadeesan et al., the formation of CO was crucial because CO and H\(_2\) were adsorbed on the catalyst surface and gave rise to hydrocarbon formation. They speculated that particle size played an important role in the selectivity of the reaction. From FT synthesis, it is known that smaller particles show lower H\(_2\) chemisorption potential, which favors the formation of olefins instead of C–C coupling.\(^{[63]}\)

5. Main Benefits

The main benefits of metal carbonate hydrogenation may be summed up as outlined in the following sections.

5.1 CO\(_2\) emission reduction

CO\(_2\) is the primary greenhouse gas emitted through human activities. In 2015, the global CO\(_2\) concentration in the atmosphere reached an average value of (399.4 ± 0.1) ppm.\(^{[64]}\) At present, the industrial sector is responsible for approximately one-third of the total anthropogenic CO\(_2\) equivalent (CO\(_2\)e) emissions.\(^{[65]}\) Decarboxylation of metal carbones under reducing conditions may contribute to a substantial decrease of CO\(_2\) emissions, especially in high-emission industrial sectors, such as the iron and steel industry, in which carbonaceous ores are used.\(^{[12]}\) As opposed to conventional decarboxylation processes, CO\(_2\), is not released into the atmosphere, but reduced to CO, CH\(_4\), and higher hydrocarbons. The formation of reduced carbon species in the gas atmosphere adds value to the overall process compared with state of the art decarboxylation under oxidizing conditions.
5.2. Renewable production of chemicals and fuels

At present, the three major carbon feedstocks are still petroleum, coal, and biomass. Because most of earth’s carbon (> 99.9%) exists as carbonates, carbonateous minerals may provide a potential carbon source for hydrocarbon synthesis in the future. The conversion of carbonateous inorganic rocks (e.g., calcite, magnesite, dolomite) to organic compounds may help to fulfill future energy requirements and provide a renewable and nearly inexhaustible resource for the production of chemicals.\(^{[85]}\)

Because methane naturally occurs in biogas, power generation is still its main purpose. The conversion of biogas to electricity is standard technology. Apart from the production of synthesis gas (syngas) and its utilization, further uses of methane include catalytic and noncatalytic oxidative coupling (OCM) to \(\text{C}_2\) hydrocarbons, direct oxidation to methanol or formaldehyde, oxidative methylolation of hydrocarbons by methane, and oxidative carboxylation of methane by CO to acetic acid.\(^{[86]}\) The generation of \(\text{H}_2\) from \(\text{CH}_4\) is industrially accomplished through steam methane reforming, but the conversion can also be achieved by pyrolysis.\(^{[87–89]}\)

From syngas, which is the feed material for a FT process, a synthetic crude oil (syrup) is obtained. The syrup consists of a multiphase mixture of hydrocarbons, oxygenates, and water. Refining of the syrup yields products that are traditionally produced from conventional crude oil, such as transportation fuels and chemicals.\(^{[21,71]}\)

5.3. Hydrogen storage

Hydrogenation of metal carbonates can also be seen as a means of chemical hydrogen storage in the form of \(\text{CH}_4\)\(^{[72]}\) or fuels produced from syngas.\(^{[73,74]}\) This is similar to the power-to-methane (PtM) concept that converts electrical into chemical energy by using captured CO\(_2\) and \(\text{H}_2\) from water electrolysis.\(^{[75,76]}\) The main advantage of these alternative hydrogen-storage technologies is the availability of storage and distribution systems prepared for natural gas and liquid hydrocarbon fuels. In regions where a natural gas infrastructure exists, both concepts provide a promising option to absorb and exploit surplus renewable energy.

5.4. Catalyst preparation

Tailor-made solid products, regarding composition and morphology, may be achieved through adjusting the process conditions, especially the gas atmosphere. Morphology plays a crucial role if the solid products represent catalytically active materials, both catalytically active material and support material.\(^{[89]}\) A hydrogen atmosphere opens up a new pathway for transition-metal carbonate transformation into finely dispersed, active catalysts for in situ or ex situ use.\(^{[10]}\) Although initial morphological studies seem promising, the catalytic activity of reductively calcined material has not yet been tested. To the best of our knowledge, only reductively calcined MgO was studied for its catalytic properties for \(\text{CO}_2\) conversion with \(\text{H}_2\), revealing reverse water-gas shift activity.\(^{[55]}\) Long-term stability was not considered.

5.5. Chemical solar energy storage

Experiments with energetic light, for instance Vis or UV radiation, indicate that irradiation affects the course of metal carbonate decarboxylation.\(^{[10]}\) The mechanistic course could depend on the wavelength of the radiation source, giving access to new pathways for the application of solar energy in solar furnaces. In principle, solar energy can be stored and transformed by means of cyclic inorganic processes. Primary electron spectroscopy for chemical analysis (ESCA) experiments revealed the difference between thermal hydrogenation and hydrogenation induced by irradiation.\(^{[22]}\) The results confirmed an effect of the type of energy (UV/Vis radiation) on the mechanism and kinetics of decomposition, but precise conclusion was feasible and no further reports were made.\(^{[77]}\)

6. Potential Fields of Application

Two fields of application were identified and analyzed regarding potential, limitations, and domains requiring further research. Both elucidate the need for further studies in industrialsized reactors, allowing appropriate process conditions to be stated for industrial application.

6.1. CCU based on mineral carbonation

Mineral carbonation is a novel, widely investigated concept for \(\text{CO}_2\) capture and storage based on weathering of limestone in nature.\(^{[9,78–83]}\) In mineral carbonation, high concentrations of captured \(\text{CO}_2\) from an industrial or power-sector source react with metal oxide [\(\text{MeO}\), mainly CaO or MgO; Eq. (28)] or metal hydroxide bearing materials to form the corresponding insoluble carbonate.

\[
\text{MeO} + \text{CO}_2 \rightarrow \text{MeCO}_3 + \text{heat} \tag{28}
\]

Due to the lower energy state of inorganic carbonates relative to \(\text{CO}_2\), the reaction is exothermic. Therefore, in theory, the process does not require any energy input, but produces heat. Unfortunately, extensive preparation of the solid reactants (including mining, transportation, grinding, and activation, if necessary); the use, recycling, and loss of additives and catalysts; and disposal of carbonates and byproducts render the overall process energy intensive and require external high-grade energy sources.\(^{[104]}\) Due to its thermodynamics, carbonate formation is favored at low temperatures. High temperatures favor the reverse reaction, namely, decarbonation, which is generally referred to as calcination.

Appropriate carbonateous feedstock sources include abundant silicate rocks that involve laborious mining and alkaline industrial residues that are readily available, but only on a small scale (e.g., slag from steel production or fly ash).\(^{[86]}\) Pure calcium and magnesium oxides and hydroxides provide the ideal source material because they are more readily carbonat-
ed than that of the corresponding silicates. However, due to their high reactivity, they are scarce in nature.\cite{76, 84}

There are several single (direct) or multistep (indirect) dry or wet process routes. In aqueous environment, carbonation is faster, but, due to higher dilution and lower reaction temperatures, the heat of reaction is difficult to retrieve. The dry process is a simpler approach that brings gaseous CO$_2$ into contact with particulate metal oxide bearing materials. Easy recovery of the heat of reaction is beneficial for this method, but the bottleneck is the slow rate of reaction at suitable temperature levels. It is only feasible at elevated pressures for refined, rare materials, such as the oxides and hydroxides of calcium and magnesium.\cite{36, 84}

The generated carbonates (CaCO$_3$, MgCO$_3$), if not disposed of, are used for mine reclamation or in construction.

It is expected that alkaline-earth-metal carbonates will give access to reversible thermal decarbonation/recarbonation cycles if decarbonation is carried out under a reducing hydrocarbon atmosphere.\cite{55} In H$_2$, CO$_2$ is not released into the flue gas, but further reduced to CO.\cite{86} Reductively calcined MgO, CaO, SrO, and BaO were found to be constituted of solid conglomerates of microcrystalline domains featuring pronounced reactivity towards recarbonation; a fact that renders them promising as potential CO$_2$-trapping systems.\cite{48} Repeated carbonation/recarbonation cycles omit excessive measures for reactant preparation, makeup of additives and catalysts, and product disposal. Consequently, the net energy input required is potentially lower. Once prepared, refined, small particles of metal oxides can be repeatedly used; this poses a pronounced advantage for the reaction of dry CO$_2$ gas with solid oxides not only as far as labor input is concerned, but also for the rate of reaction. It is well known that small particle sizes facilitate high reaction rates.\cite{78} In conventional mineral carbonation of CO$_2$, most of the energy required is needed for grinding of the feedstock to particles of 100 μm. During carbonation, the formation of silica and carbonate layers on the mineral surface hinders the reaction and limits conversion. Carbonate layers are barely prevented, but silica layers do not form because pure metal oxides are applied. Conventional CO$_2$ mineralization is criticized for its tremendous environmental impact associated with large-scale mining directly leading to land clearing and product disposal; an issue that does not need any consideration if the metal oxides are repeatedly used.

Through transition-metal doping of the solid reactant, a composite system may be generated, in which CO$_2$ is trapped on metal oxides (carbonation/recarbonation step) and subsequently transformed into higher organic species through hydrogenation of the metal carbonate (decarboxylation step; Figure 3).\cite{55}

The technology for mineral carbonization is still immature. The concept of a closed CO$_2$ circuit based on decarbonation through hydrogenation followed by recarbonation is a promising concept. Nevertheless, it is merely based on primary laboratory-scale experiments and further research is required for a feasible economic analysis.

For a new 600 MW, coal-fueled power plant with an annual CO$_2$ emission of 4 Mt/year$^{-1}$, a total energy requirement of 580 kWh for CO$_2$ capture and carbonation has been estimated.\cite{9} Because most of the energy is needed for grinding of the feedstock material (280 kWh) and this step is omitted for repeated decarbonation/recarbonation cycles, power plant efficiencies may increase from 23.6 to 33% and CO$_2$ avoidance rates from 72.5 to 82% for the concept of a closed CO$_2$ circuit.\cite{9} In the literature, reported cost estimations of various carbonation routes differ significantly. At present, direct aqueous technologies seem to be the most realistic ones with costs ranging from €60 to 100 t$^{-1}$ CO$_2$ fixed.\cite{87} Additional CO$_2$ emissions associated with the energy required for the carbonation process will boost the costs to €80 to 130 t$^{-1}$ CO$_2$ fixed. Further taking into account the costs for capturing CO$_2$ from a power plant yields total costs of €150 t$^{-1}$ CO$_2$ avoided for a full CCS system with mineral carbonation.\cite{9}

At this point, composite systems derived from transition-metal doping that may not only trap CO$_2$, but also transform it into higher organic species are not considered. Further energy, and consequently, cost savings are expected due to increasing reaction rates of carbonation based on the use of refined metal oxide reactants with small particle sizes. Metal doping also allows for lower reaction temperatures for the carbonation step and decreasing activation energies. Furthermore, dry carbonation will allow for easy accessibility of the heat of reaction of carbonation. Currently, cost estimation is not feasible because the type of catalyst, hydrocarbon species generated, and hydrocarbon selectivity still need to be established. Initial studies highlight its potential and elucidate the need for further research into process conditions and the long-term stability of the system, which are crucial factors for its economic viability.

6.2. Direct reduction of mineral iron carbonate

Austria and China have major siderite reserves for iron and steel production. Siderite beneficiation is challenging because of the low iron content of the ore compared with magnetite and hematite ores. The industrial practice is to blend siderite with other high-grade ores in the sinter plant. During the sintering process, siderite is converted into hematite through roasting in air. The sinter product is fed to the blast furnace (BF), in which it is preferably reduced with coke via CO, pro-
ducing at least 1.5 mol CO₂ per mole of iron due to the stoichiometry of reaction. Consequently, at least 2.5 mol CO₂ are emitted during the production of 1 mol iron from iron carbonate.

Direct hydrogen reduction of the mineral iron carbonate represents a novel process concept for sustainable pig iron production. It is a high-potential approach for significant energy savings and CO₂ emission reduction, especially if coupled with catalytic CO₂ hydrogenation (e.g., methanation) to further convert inevitably released CO₂ (Figure 4).[12] Due to the debate about a sustainable energy supply, research into methanation has increased tremendously in recent years and is readily available.[88–95]

6.2.1. Proof of concept

TG studies revealed that mineral iron carbonate was directly reduced to elemental iron under a hydrogen atmosphere. Iron carbonate reduction was represented by a distinct mass loss below 723 K, which was followed by a small relative mass loss spanning over a broad temperature range (723–923 K) allocated to the concomitant decomposition of manganese, magnesium, and calcium carbonate to the respective oxides.[12]

In the ideal case of complete carbonate conversion, elemental iron is formed together with CO₂, CO, CH₄, and potentially even higher hydrocarbons (CₓHₓ). Baldauf-Sommerbauer et al. investigated the effect of temperature (Figure 5) and pressure on the composition of the product gas that consisted of CO₂, CO, and CH₄.[96] Elevated pressure and low temperature increased the yield of CH₄. CO formation was preferred at low pressure and higher temperatures.

CO₂ emission savings of at least 60% are possible because, at most, 1 mol CO₂ is released per mole of elemental iron. If hematite is reduced with hydrogen, 1.5 mol hydrogen is required per mole of elemental iron. Consequently, up to 33% less reducing agent is needed if direct siderite reduction is applied, due to circumventing the hematite route. Direct siderite reduction can be run at relatively low temperatures (673–773 K) compared with other metallurgical iron carbonate beneficiation processes, such as the Midrex® process for direct iron oxide reduction with natural gas (1053–1073 K) or the classical BF process (1773 K).[97]

6.2.2. Case studies

A comparison of four different case studies with the state-of-the art BF process highlights the potential of the concept of direct hydrogen reduction of the mineral iron carbonate.

As feed material, the mineral siderite with a characteristic composition of a concentrated siderite sample from the Styrian Erzberg in Austria (Table 2) was chosen. Iron was assumed to occur in the form of FeCO₃ (79 wt %) and CaFe(CO₃)₂ (5 wt %). Minor components were MgCO₃, MnCO₃, SiO₂, and Al₂O₃.

The classical BF process serves as benchmark. It consists of a sintering step under oxidizing conditions (Eqs. (29)–(33), 1373 K) in which FeCO₃ is transformed into Fe₂O₃ for reduction in the BF [Eq. (34), 1773 K].

![Figure 4. Process concept for direct iron production from the mineral siderite followed by off-gas valorization by catalytic CO₂ hydrogenation, for example, methanation.](image)

![Figure 5. Dry product gas composition for the direct hydrogen reduction of the mineral siderite at 623 and 648 K; 60 g siderite, size fraction: 0.5–1 mm, H₂/N₂ = 9:1, 867 cm³·min⁻¹, ambient pressure.](image)
FeCO₃ → FeO + CO₂  
2 FeO + 0.5 O₂ → Fe₂O₃  
MgCO₃ → MgO + CO₂  
MnCO₃ → MnO + CO₂  
CaFe(CO₃)₂ → CaO + FeO + 2 CO₂  
Fe₂O₃ + 3 C → 2 Fe + 3 CO  

During direct hydrogen reduction to elemental iron, several reactions are conceivable for FeCO₃ [Eqs. (35)–(37)] and CaFe(CO₃)₂ [Eqs. (38) and (39)], depending on the product gas. The reaction temperature was set to 773 K.

FeCO₃ + 2 H₂ → Fe + CO + 2 H₂O  
FeCO₃ + 5 H₂ → Fe + CH₄ + 3 H₂O  
FeCO₃ + H₂ → Fe + CO₂ + H₂O  
CaFe(CO₃)₂ + 2 H₂ → CaCO₃ + Fe + CO + 2 H₂O  
CaFe(CO₃)₂ + 5 H₂ → CaFeO + Fe + CH₄ + 3 H₂O

To calculate CO₂ emissions, direct emissions of CO₂ and CO are summed due to CO oxidation to CO₂ [Eq. (40)]. Oxidation of CO contributes to CO₂ emission, but reduces the total energy demand. A reduction in energy demand because of CH₄ was also considered. Hydrogen supply was assumed to be accomplished by water electrolysis (4.8 kWh Nm⁻³⁻¹).²⁴,²⁵

CO + 0.5 O₂ → CO₂  

Four case studies, Red1, Red2, Red3, and Red4, represent the extreme cases (Red1 and Red2) and mixed cases (Red3 and Red4). In Red1, full carbon conversion to CO was assumed [Eqs. (35) and (38)]. CH₄ formation was postulated for Red2 [Eqs. (36) and (39)]. For Red3, 50% CO and 50% CH₄ were assumed. Red4 reproduces the experimental product composition depicted in Figure 5 (49% CO₂, 27% CH₄, 24% CO).

Total CO₂ emissions and the total energy demand for all four cases are compared with the benchmark BF process in Table 3. The results quantify the capability of CO₂ emission reduction. The classical BF process releases 2212 kg CO₂ t⁻¹ pig iron. 100% CO formation (Red1) saves 64% of the CO₂ emitted in the benchmark process. No CO₂ is released if full conversion to CH₄ is hypothesized (Red2). This scenario exhibits the highest energy demand of 5267 kWh (111% compared to the BF process) and is not aspiring to from an economic point of view. Scenarios with CO and CH₄ (Red3 and Red4) show excellent CO₂ emission reduction (82 and 74%) and decreased energy demand (11 and 28%, although a hydrogen supply from water electrolysis was chosen), which underlines the high potential of the proposed concept.

Direct iron carbonate reduction is a high-potential candidate to open up a new route for environmentally benign pig iron production. The findings are based on TG experiments with siderite²¹ and tests in a tubular reactor setup;²⁶ thus direct conclusions for application in large-scale reactors and optimized process conditions (e.g., particle size, temperature) cannot be drawn yet. Iron separation from the unconverted siderite matrix and gangue through magnetic separation was suggested in the literature, but still needs verification. Nevertheless, the presented case studies highlight the potential of reductive calcination of siderite and the need for ongoing research in this field.

### Table 2. Mean composition of the mineral siderite from the Styrian Erzberg in Austria.

| Component     | Mass fraction |
|---------------|--------------|
| FeCO₃         | 0.79         |
| CaFeCO₃       | 0.05         |
| MgCO₃         | 0.07         |
| MnCO₃         | 0.05         |
| SiO₂          | 0.03         |
| Al₂O₃         | 0.01         |

### Table 3. Total CO₂ emission and total energy demand for the case studies Red1 (100% CO formation), Red2 (100% CH₄ formation), Red3 (50% CO and 50% CH₄), and Red4 (49% CO₂, 27% CH₄, 24% CO) compared with the benchmark BF process.

| Case study | CO₂ emission [kg CO₂ t⁻¹ Fe] | Energy demand [GJ t⁻¹ Fe] | [kWh] |
|------------|------------------------------|---------------------------|-------|
| BF         | 2212                         | 17.1                      | 4755  |
| Red1       | 788.5                        | 11.4                      | 3156  |
| Red2       | 0                            | 19.0                      | 5267  |
| Red3       | 394.3                        | 15.2                      | 4211  |
| Red4       | 569.9                        | 12.2                      | 3401  |

7. Summary and Outlook

Various aspects render metal carbonate hydrogenation a powerful means for direct and indirect CO₂ emission reduction, CO₂ utilization, and metal carbonate exploitation.

Under a hydrogen atmosphere, the decarboxylation temperature is significantly lower than that of the respective reaction under inert conditions. Doping with transition metals further lowers the temperature level. The combination of decarboxylation and CO₂ reduction with the renewable energy carrier hydrogen transforms the conventional endothermic process into an overall exothermic process, which allows for significant energy savings.

In reductive metal carbonate decarboxylation, CO₂ is not (or only partially) released, but reduced to CO, CH₄, and higher hydrocarbons. The composition of the gaseous reaction product strongly depends on the gas atmosphere (pure or dilute hydrogen); the presence of transition-metal species acting as in situ catalysts; and the reaction temperature, pressure, and residence time. Apart from metal oxides in various oxidation states, elemental metals are obtained as solid reaction products from transition-metal carbonates. Tailormade products, in terms of composition and morphology, would give access to novel production routes for catalysts.
Until now, preliminary studies focusing on feasibility and chemism have mainly been made with metal carbonates in small-scale apparatus, lacking transferability to industrial scale. Additionally, disagreement exists concerning the reaction mechanisms. Whereas some researchers propose the direct reaction of hydrogen with fixed CO in the carbonate, others assume that hydrogen reacts with released CO₂. Degradation studies in hydrogen and nitrogen revealed differences in morphology that indicate the direct reaction of H₂ with CO₂; however, several aspects require closer examination, especially when it comes to optimized process conditions for industrial applications. Once clarified, metal carbonate hydrogenation could provide a quantum leap in high-emission industrial sectors, such as the iron and steel industry, if a renewable hydrogen supply is accomplished. Further potential fields of applications include the renewable production of chemicals and catalyst preparation.

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Conflict of interest

The authors declare no conflict of interest.

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