Carbon Dioxide Splitting:

A Summary of the Peer-Reviewed Scientific Literature

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Increasing concentrations of carbon dioxide (CO_2) in the atmosphere have stimulated significant global research and development efforts regarding the reduction in CO_2 emissions from all point and non-point sources. In addition to technologies that do not use carbon feedstocks or which capture and "permanently" store CO_2 (*i.e.*, sequestration), there is considerable worldwide interest among the academic, industrial, and government communities regarding methods for dissociating waste stream carbon dioxide molecules into their constituent carbon and oxygen ("CO_2 splitting") atoms as a final "end-of-pipe" treatment option. The splitting of carbon dioxide has also been actively discussed and researched in the space exploration and extraterrestrial colonization programs for several decades.[1] This document summarizes the peer-reviewed open source scientific literature regarding carbon dioxide splitting.

The catalyzed or uncatalyzed splitting of carbon dioxide involves the following overall reaction:

$$CO_2 \rightarrow C + O_2 \qquad (\mathbf{1})$$
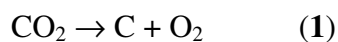
Two mechanistic pathways are possible, with both likely involving the initial splitting of CO_2 to carbon monoxide and oxygen:

$$CO_2 \rightarrow CO + \tfrac{1}{2}O_2 \qquad (\mathbf{2})$$
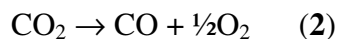
The equilibrium of reaction (**2**) lies strongly to the left, and in the absence of active removal of one (or both) products, equilibrium production of CO and O_2 varies from <1% at <2000 K up to

about 60% at temperatures between 3000 K and 3500 K.[2]

The completion of the splitting process may then occur either via the Boudouard reaction (**3**) or direct splitting of carbon monoxide to carbon and oxygen (**4**):

$$2CO \rightarrow 2C + CO_2 \qquad (\textbf{3})$$

$$CO \rightarrow C + \tfrac{1}{2}O_2 \qquad (\textbf{4})$$
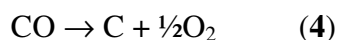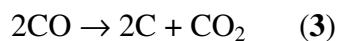
In the Boudouard reaction, the formal oxidation state of oxygen is unchanged, and remains at -2 in both the CO reactant and the CO_2 product. The carbon in the CO reactant undergoes an intermolecular redox disproportionation, changing from a formal oxidation state of +2 in the CO starting material to 0 in the solid carbon product and +4 in the CO_2 product.

This is a reasonable thermal redox transition, as carbon is readily obtainable in formal oxidation states ranging from -4 (as in methane, CH_4) to +4 (as in CO_2). In contrast, oxygen generally only varies between oxidation states ranging from 0 (as in diatomic oxygen, O_2) to -2 (as in CO_2), with reactive intermediate states such as +1 (as in hydrogen peroxide, H_2O_2) and $+\tfrac{1}{2}$ (as in KO_2) also known. The formal oxidation state of oxygen is not changed in the Boudouard reaction, and remains at -2 in the CO starting material and in CO_2 product.

There is evidence in the literature, based on work in the analogous water splitting field for hydrogen production (where the O-H bonds in water [459 kJ/mol] are much weaker than either the C=O bonds in CO_2 [783 kJ/mol] or C≡O bond [1076 kJ/mol] in CO), that reaction (**4**) could

only likely be achieved via extremely high temperatures (>2500°C) or via high-energy inputs (*e.g.*, plasma discharges). For this reason, any thermal splitting of CO_2 will likely proceed by way of reactions (**2**) and (**3**).

The most pertinent studies for thermal CO_2 splitting involve the application of zirconia membrane reactor systems by Nigara and Cales [3] and Itoh *et al.* [4] to enhance the direct thermal decomposition of CO_2 at high temperatures. Both works do not consider the complete splitting of CO_2 to C and O_2, but rather examine the dissociation of CO_2 to CO and O_2. As both sets of authors note, the thermal dissociation of CO_2 to CO and O_2 depends on both temperature and the initial concentration of CO_2, with higher conversions at increasing temperatures and CO_2 concentrations. However, equilibrium conversions according to reaction (**2**) remain very low (<1%) even at elevated temperatures.

Nigara and Cales used a calcium oxide zirconia membrane and CO_2 thermal dissociation reactor with CO sweep gas at the permeate side to achieve <u>input</u> conversion efficiencies of CO_2 to CO of up to 22% at between 1400°C and 1800°C. However, the <u>overall</u> conversion efficiency of CO_2 was much lower (close to the thermodynamic equilibrium conversion of 1.2%), because O_2 permeating the membrane subsequently reacted with the CO sweep gas to reform CO_2.

Itoh *et al.* employed a CO_2 thermal dissociation reactor with an oxygen permeable yttria-stabilized zirconia membrane and argon as the sweep gas to selectively remove the oxygen gas product from this reaction, thereby removing the chemical equilibrium limitation and achieving higher conversions. Reactions were carried out at atmospheric pressure and in the temperature

range of about 1300°C to 1500°C, and mathematical models of the reactor were constructed using basic physical and chemical descriptors of the system. A number of sensitivity analyses were conducted to examine the effects of thermal CO_2 dissociation conversion as functions of reactor length, CO_2 feed rate, oxygen partial pressure, and membrane thickness. Despite the removal of oxygen via the zirconia membrane during reactor operation, optimized overall dissociation conversions of only up to 0.5% were attained. Neither Nigara and Cales nor Itoh *et al.* observed any carbon formation from the complete splitting of CO_2 to C and O_2.

More recently, Fan *et al.* [5] examined the thermal splitting of CO_2 in a mixed-conducting oxide ($SrFeCo_{0.5}O_x$) membrane reactor and found that a 10% conversion of CO_2 to CO could be obtained when using methane as the sweep gas on the permeate side. No evidence of CO splitting to carbon and oxygen gas was obtained.

Work by a group at Nanjing University of Technology in China coupled the thermal decomposition of CO_2 to CO with the partial oxidation of methane to syngas ($CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$) in a dense mixed-conducting membrane reactor.[6] In this system, CO_2 splitting to CO and oxygen gas took place on one side of the membrane, and the reaction of methane and oxygen occurred on the other side of the membrane. Between 900°C and 1000°C, CO_2 splitting to CO achieved about 11% and 15% conversions, respectively. Increasing CO_2 feed rate to the reactor decreased the conversion efficiency, which raises some concerns regarding industrial scale-up for such a process. In addition, the oxygen partial pressure gradient across the membrane may lead to phase separation, which is an operating and maintenance concern for any membrane-based CO_2 splitting systems.

Two studies from a group at the University of Tokyo that may provide evidence of CO_2 splitting potential involved the synthesis of various carbon nanomaterials via plasma discharges in supercritical carbon dioxide.

In their first study, Ito *et al.* [7] generated pulsed discharges with a nickel cathode-nickel anode type electrode and generated carbon nanostructured materials with supercritical CO_2 as the sole raw material. Aggregates of nanopolyhedra and nanotubes were obtained, and high-magnification transmission electron microscopy work revealed nanopolyhedra with 10-30 nm diameters comprising concentric graphitic shells. While the authors did not confirm formal CO_2 splitting by way of a mass balance and evidence of O_2 gas formation, the experimental absence of reactor component degradation and the use of only CO_2 as the starting material argues in favor of proof-of-principle for relatively controlled splitting of CO_2 into nanomaterials.

In a follow-up study,[8] Tomai *et al.* continued their work on generating carbon nanomaterials by the apparent formal splitting of CO_2. Using a dielectric barrier discharge (DBD) microplasma in supercritical carbon dioxide, no carbon materials could be formed in atmospheric-pressure CO_2 environments, but various carbon materials, such as amorphous carbon, graphite and nanostructured carbon materials were created in supercritical CO_2. In the vicinity of the CO_2 critical point, the quantity of carbon nanostructured materials, such as carbon nanotubes and carbon nanohorns, was larger than under other supercritical CO_2 conditions. By varying the power frequency of the plasma discharge, the form of the synthesized carbon materials could be changed. Optimum carbon nanomaterial syntheses were obtained at near room temperature

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(*ca.*30°C). Raising the temperature to between 50°C and 80°C and increasing the pressure up to 8 to 12MPa led to the formation of graphite and amorphous carbon rather than nanomaterials.

Other work has shown that CO_2 can be thermally dissociated to carbon monoxide behind reflected shock waves at temperatures between 3200°C and 4600°C and pressures of 45 kPa to 100 kPa.[9] No evidence of carbon formation was observed in this temperature-pressure range under equilibrium conditions.

As noted above, the thermal splitting of CO_2 is likely to proceed via reactions (**2**) and (**3**). Reaction (**3**), also known as the Boudouard reaction, has been the subject of intensive study over the past century. Although the Boudouard reaction is thermodynamically spontaneous, carbon deposition in the absence of a catalyst is minimal owing to the high uncatalyzed activation barrier.[10] Ferromagnetic metals are the most active catalysts for the Boudouard reaction, with a descending order of activity as Fe>Co>Ni.[11] The reaction on an iron catalyst is widely used for the production of graphitized carbon black as a solid-state synthesis on the surface of a solid-state catalyst.[12] The gas-phase Boudouard reaction has been dismissed as requiring extremely high gas temperatures available in only shock tube experiments and/or collisions of two highly vibrationally excited CO molecules, which is the main reason why the Boudouard disproportionation reaction is not commonly observed in the gas phase.[13]

A wide literature exists on the catalyzed Boudouard reaction for producing solid carbon, including reviews on the controlled deposition of carbon nanomaterials and associated economic analyses for full commercial production.[14]

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In addition to the catalyzed and uncatalyzed splitting of CO_2 into its elemental components of carbon and oxygen, CO_2 may also react chemically with other non-CO_2 compounds (notably metals) to produce carbonaceous materials. The literature in this field is relevant to CO_2 splitting, as it helps understand the potential controlled reactivity in guiding CO_2 splitting towards desired products.

In what appears to be the first complete chemical reduction of CO_2 to carbon, Tamaura and Tabata used cation-excess magnetite (Fe_3O_4) and achieved conversion efficiencies near 100% at 290°C.[15] During the reaction, the oxygen in CO_2 is transferred in the form of O^{2-} to the cation-excess magnetite and no gas (*i.e.*, O_2) is evolved. No CO_2 was decomposed with magnetite below 250°C, and only a small amount of CO_2 was decomposed at 290°C with metals such as Mg, Al, and Cu. Similar work by Kodama *et al.* decomposed both CO_2 and CO into graphite carbon with active wustite (FeO) at 300°C.[16] The same mechanism as Tamaura and Tabata was proposed, namely the oxide transfer to the reduced metal.

Additional work on chemical CO_2 degradation with wustite showed that at 500°C, the CO_2 decomposition likely occurs in two steps.[17] The first step involves CO_2 reacting with wustite to form magnetite and CO, and that the magnetite then acted as a catalyst for the disproportionation of CO into graphite and CO_2 via the Boudouard reaction. No oxygen gas was produced.

Several studies have also used zero-valent metals to synthesize various nanomaterials from the decomposition of CO_2 and CO. Liu *et al.* synthesized carbon nanoflasks by reacting CO with

magnesium metal at 900°C for 3 hours (and at high pressure) via the following overall reaction:

$CO_{(g)} + Mg_{(s)} \rightarrow MgO_{(s)} + C_{(s)}$.[18] About 100% conversion of CO to solid carbon was attained, and

about 15% of all carbonaceous material was present as nanoflasks. Similar work by Motiei *et al.*

reacted CO_2 with magnesium metal in a closed cell for 3 hours at 1000°C to form MgO and

carbon nanomaterials such as nanotubes and nested fullerenes.[19] The yields of carbonaceous

materials were reported at about 16%, of which the carbon nanotubes made up about 10%.

Lithium has also been used as the reductant to form carbon nanotubes from CO_2 at 440°C,

550°C, and 700°C.[20] The authors found that, under their conditions, when metallic potassium or

sodium replaced lithium, no nanotubes were formed, but instead, all carbon produced was in the

graphite form. Lower concentrations of CO_2 in the reactor (*i.e.*, lower CO_2 pressure) shifted the

products away from nanotubes and towards graphite. Higher temperatures (up to 700°C) led to

lower nanotube yields versus 550°C, but a higher nanotube crystallinity and length was

observed. To examine the mechanism of the reaction, control experiments were also performed

in copper versus stainless steel reactors, and with/without lithium. The type of reactor material

(copper versus steel) did not influence nanomaterial formation, and the absence of the lithium

reductant led to no reaction of CO_2 at 550°C over 10 hours (showing that the CO_2 reaction could

not proceed by purely thermal routes).

More recent work by Chen's group at the University of Science and Technology of China

continued their studies on the formation of carbon nanomaterials via the metallic reduction of

CO_2.[21] All the carbon nanotubes grown in the temperature range from 650°C to 750°C using

sodium as the reductant exhibited bamboo-like structure. Increasing temperature led to longer

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and thinner nanotubes. In contrast, nanotubes grown via the reaction of supercritical CO_2 with metallic lithium do not display bamboo-shaped structures, but a majority of the lithium-produced structures (*ca.* 70%) have a double-helix structure. During the syntheses, the outer graphitic layers may react with CO_2 (presumably by the Boudouard reaction) at temperatures <600°C, leading to erosion of the graphite and formation of porous nanotubes. At temperatures >600°C, no surface erosion was observed.

Chen's group has also moved into forming diamonds via the reduction of CO_2 with metals. In their first work, metallic sodium was used to reduce CO_2, and at 440°C and 800 atm, the total yield of diamond and graphite was about 16.2%, with the maximum transformation ratio for CO_2 to diamond at 9%.[22] At temperatures <400°C and lower pressures, only graphite is formed. Follow-up work with metallic lithium and potassium demonstrated that these metals could also produce diamonds from CO_2 in yields up to 10%.[23] Octahedral and hexahedral diamond particles in the size range from 4 to 450 μm were formed at temperatures of 400°C to 600°C. Larger diamonds could be produced by using metallic potassium as reductant.

Solid phases of carbon dioxide and/or carbon monoxide have also been suggested as a means of enhancing the feasibility of the overall splitting process. This is because a general trend observed in molecular solids at high pressure is the destabilization of the intramolecular bonds due to the strengthening of the intermolecular interactions at short distances. This process can result in the formation of non-molecular solid phases of polymeric, extended covalent, metallic, or ionic character.[24,25] However, at ambient temperatures (*ca.* 300 K) and pressure (*ca.* 1 atm), both CO_2 and CO exist as molecular gases.

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Historical studies on CO_2 have shown the existence of two molecular solid phases of CO_2: a cubic phase I and an orthorhombic phase III.[26,27] Both phases I and III are stabilized by quadrupolar interactions between the linear molecules.[28] Other polymorphs have been synthesized, including a bent molecular-phase IV,[29] a polymeric phase V,[30],[31] and a dimeric paired phase II (Figure 1).[32] These phases differ greatly in molecular configuration, intermolecular interaction, and chemical bonding.
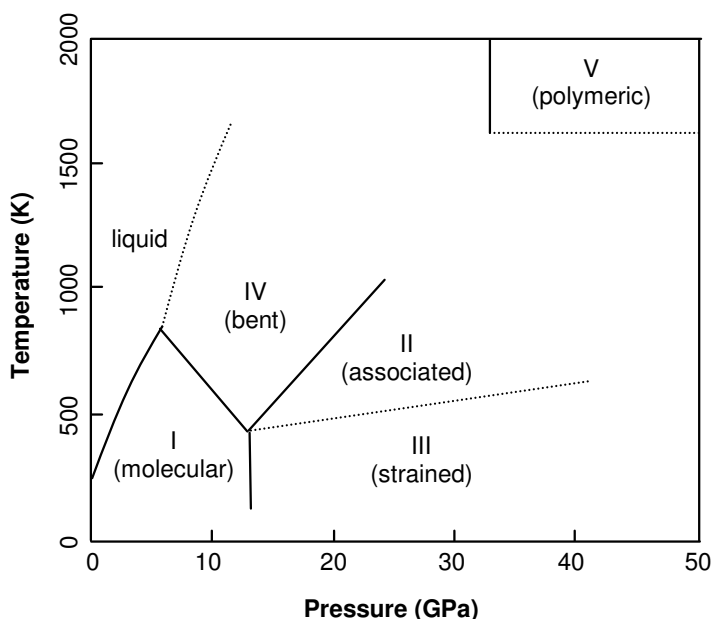
Figure 1. High temperature-high pressure phase diagram of carbon dioxide. Adapted from ref. [32].

At ambient temperature, CO_2 crystallizes into phase I at 0.5 GPa, having a linear solid form with weak quadrupolar intermolecular interactions and a low bulk modulus. Above 12 GPa, phase I transforms into an orthorhombic phase III that remains stable to 80 GPa. These phases are metastable, and thus, above 12 GPa at room temperature, CO_2 can exist in any of four different

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phases (II, III, IV, and V) depending on the sample history.[32] Recently, a new molecular phase VII has been identified at the intersection of phases I, IV, and the fluid phase.[33]

Less work has been done on the phase diagram of carbon monoxide, with published data only available for a modest range of pressures and temperatures. At room temperature, CO is a fluid up to 2.5 GPa, above which it freezes into a disordered hexagonal β-CO phase. Above 5.2 GPa at near 300 K, β-CO rearranges into the disordered cubic δ-phase. The δ-phase can react photochemically and/or thermally to form a suboxide material having the general formula C_3O_2 and an oxalic anhydride with the general formula C_2O_3, both being colored species with a vinyl ester and carbonyl units.[34,35,36,37]

The established literature shows that solid/associated phases of CO_2 and CO can only be accessed at pressures in the GPa range, which would require large energy inputs to solidify the materials. Thus, utilizing these "non-traditional" phases of CO_2 and/or CO does not appear to be a viable strategy for splitting carbon dioxide.

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