Synergy between dielectric barrier discharge plasma and calcium oxide for reverse water gas shift

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HIGHLIGHTS

- Synergy between plasma and calcium oxide for Reverse Water Gas Shift is found at low temperatures.
- Kinetic description allows quantification of synergy.
- Changes in plasma properties and plasma-chemistry are minimized by reactor optimization.
- Synergy caused by new plasma-catalytic pathway with plasma activated species.

GRAPHICAL ABSTRACT

ABSTRACT

This study reports on synergy between Dielectric Barrier Discharge plasma and calcium oxide as a catalyst for the Reverse Water Gas Shift (RWGS). Any effect of the presence of the catalyst on the contribution of plasma chemistry, i.e. chemical conversion in the plasma, is minimized by using a fixed bed of α-Al₂O₃ particles as a blank experiment and adding a small amount of calcium oxide, with similar dielectric constant, particle size and shape. This approach results in constant plasma power and ensures also that the residence time and specific energy input remain unchanged. Furthermore, synergy is determined based on reaction rates at fixed conditions, i.e. concentrations and temperature, based on kinetic equations derived from integral experiments, describing both thermal operation and plasma operation and both in absence and presence of calcium oxide. This approach has not been applied so far to study plasma-catalysis synergy. The experimental results in thermal and plasma operation are well described with kinetic equations based on power rate laws. Synergy is observed at the lower operational temperatures (640 °C) with a rate-enhancement factor of 1.7, steadily decreasing with increasing temperature until disappearing at 750 °C. The concentrations of CO₂, H₂ and H₂O have no significant influence. Synergy is attributed to a new reaction pathway involving interaction of plasma activated intermediates with the CaO surface, with a relatively low apparent activation barrier of 40 kJ mol⁻¹. Much higher activation barriers are observed for both thermal-catalytic RWGS on CaO (140 kJ mol⁻¹) as well as for plasma operation with Al₂O₃ only (90 kJ mol⁻¹). We suggest that reaction of surface CaCO₃ with plasma generated H radicals is the rate determining step, in contrast to plasma chemistry where CO₂ cannot be activated with H radicals.

1. Introduction

Plasma catalysis is receiving more and more attention in the last few years, since the specific interactions between plasma and catalyst surface may lead to synergistic effects [1–3]. In the last decade research has been focused on conversion of CO₂ [4–8], conversion of hydrocarbons via dry reforming and coupling [9–11] as well as activation of N₂ [12,13]. Ammonia synthesis is an example of an exothermic reaction, where plasma catalysis holds promise because of activation of N₂ at low temperature. Methane coupling and CO₂ dissociation are examples of endothermic reactions, which are more challenging, especially when aiming at conversion beyond...
thermodynamic equilibrium.

Dielectric Barrier Discharge (DBD) plasma reactors are frequently used for studying plasma-catalytic conversion [14–16]. The high AC voltages applied at relatively low frequency (50 to 10^5 Hz) produces a non-equilibrium plasma with very high electron temperatures (1–10 eV equal to 10^4–10^5 K), rather high vibrational temperatures (10^3 K), and rather low rotational and translational temperatures, i.e. the temperature of the gas. Therefore, any temperature increase induced by the plasma is typically smaller than 100 K [14,16]. The concept that energy would be directed directly to bond breaking, without the need to heat up the gas mixture completely, is very attractive as heat exchangers to recover the heat would become redundant. The presence of a dielectric between the two electrodes prevents the formation of hot plasma in sparks, forming instead several microfilaments, resulting in a more uniform plasma. The low gas temperature allows application of a catalyst directly in the plasma without fast sintering and deactivation. Moreover, relatively low temperatures are required for catalysis in the first place, enabling adsorption of molecules, possibly vibrationally excited. Starting and stopping plasma reactors can be achieved much faster than usual thermal reactors, which is an advantage when fast capacity changes are required, e.g. in connection with intermittent energy supply and storage. Furthermore, DBD plasma can be generated at atmospheric pressure, which is interesting from the application point of view.

Promising results were presented for several reactions, including CO2 decomposition and hydrogenation [4,6,17–27] and dry reforming of CH4 [9,10,28–35], in terms of high conversion and selectivity. However, the main issue of DBD reactors remains the low energy efficiency achieved, i.e. the ratio between chemical energy stored in the produced molecules and electrical energy applied, which rarely surpasses 10%. This is caused by both energetically very expensive dissociative excitation by electron impact, consuming a significant part of the energy supplied, as well as dissipation of vibrational excitation to translation and rotation modes, i.e. heating up [36–39]. Microwave plasma reactors, using GHz frequencies, are at one hand more suitable because of less dissociative excitation, but at the other hand operate at much higher temperatures [40–42], limiting the opportunities for plasma catalysis.

Interaction between plasma and catalyst proceeds in many ways [1,2]. The plasma will produce new chemical species including activated species, such as radicals and ions, which may adsorb on the catalyst surface, opening new reaction pathways and influencing the products distribution. Plasma can also induce photocatalytic effects by generating UV irradiation, impingement of charged particles and thermal fluctuations. The surface and subsurface of a catalyst can be modified by plasma via poisoning, implantation, sputtering, and etching. The presence of a catalyst influences the plasma by changing the electrical field distribution, but also modifying the free volume and the residence time in the plasma zone. A DBD plasma in an empty reactor is by nature filamentary, while a packed bed DBD plasma is enhanced at the contact points between particles [43–45]. For all these reasons the effects of plasma and catalyst on a specific reaction are strongly correlated and could result in synergy, i.e. when the reaction rate in presence of both catalyst and plasma is higher than the sum of the rates in presence of plasma-only and catalyst-only at identical conditions [1].

Plasma-catalytic CO2 hydrogenation has been studied for methanation [18,22,26,46–48], production of methanol [25,49] and Reverse Water Gas Shift [22,27]. The catalysts used in these studies have been selected based on their favorable performance in thermal catalysis, e.g. Ni on various supports for methanation [17,21,25,46], Cu for methanol production [24] and Au for RWGS [26]. These studies focused on the assessment of synergy and many claim synergistic effects based on the observation that conversion during thermal operation is low, whereas combination of plasma and catalyst increased the conversion significantly [18,22,26,46–49]. The effect of temperature increase induced by the plasma is explicitly considered in only one study [25]. Moreover, conversion in plasma-only and in plasma with catalyst is compared in some studies without addressing the effect of the presence of the fixed bed catalyst on the plasma properties [18,25,47–49]. The presence of the catalyst as a dielectric material will induce changes in the electrical field distribution, electron energy distribution and number of streamers or surface discharges [19,24,43–45]. Finally, changes in residence time or in Specific Energy Input (SEI, energy input per molecule feed) between empty and packed bed reactors were often not considered [18,25,47–49]. The approach used in this study focuses on minimizing any differences in the plasma, residence time and SEI by keeping the properties of the packed bed almost completely constant. Any thermal effects of the plasma will be estimated and corrected for, based on our previous work [50].

CaCO3 decomposition is the key-step in the Calcium Looping Cycle, a promising option for CO2 separation [51]. In this process, CO2 is absorbed by calcium oxide forming CaCO3, which can be either land-filled or recycled via decomposition, regenerating the sorbent calcium oxide. However, the decomposition reaction requires high temperatures in order to achieve high CO2 concentrations in the outlet, i.e. at least 950 °C to obtain pure CO2 at atmospheric pressure [52]. Such temperatures result in sintering, decreasing the CO2 capture capacity [53–55]. An approach would be to induce decomposition at lower temperatures by using a non-thermal plasma. Our previous work showed that a DBD argon plasma has no effect on the decomposition, except for a modest increase in temperature [50]; the plasma only induces dissociation of part of the CO2 in a consecutive reaction. On the other hand, the presence of hydrogen without plasma decreases the decomposition temperature [56], which has been confirmed by our experiments. Furthermore, the presence of hydrogen causes a shift in the product distribution to CO2, CO and H2O instead of CO2 only. CO may be produced via RWGS (R3) or directly via CaCO3 hydrogenation (R2), as presented in the following scheme.

The introduction of plasma further decreases the decomposition temperature forming the same set of products, i.e. CO2, CO and H2O [57]. The interpretation of these results requires a description of RWGS (R3 in scheme 1) both thermally and in presence of plasma. The goal of this work is to provide a kinetic description of RWGS in presence of calcium oxide and plasma in a temperature window relevant for CaCO3 decomposition, allowing determination of any synergy between plasma and calcium oxide as catalyst based on reaction rates. The synergetic effect will be discussed in terms of interactions of activated species with calcium oxide, by minimizing any influence of the catalyst on the properties of the plasma and consequently the chemical reactions proceeding in the plasma.

2. Materials and methods

2.1. Calcium-oxide, calcium-carbonate and alumina preparation

Calcium oxide was synthesized by calcination of CaCO3 (99%, Sigma Aldrich) in 20% air in N2 at atmospheric pressure in order to remove any organic contaminants, heating the sample until 900 °C (heating rate 15 °C min−1) and keeping the temperature at 900 °C for 3 h. The calcined product was pelletized (pressure 160 bar), crushed

\[
\begin{align*}
\text{CaCO}_3(s) + H_2(g) & \xrightarrow{R_1} \text{CaO}(s) + CO_2(g) + H_2(g) \\
\text{CaO}(s) + CO(g) & \xrightarrow{R_2} \text{CaO}(s) + CO_2(g) + H_2O(g) \\
\text{CaCO}_3(s) & \xrightarrow{R_3} \text{CaO}(s) + CO_2(g) + H_2O(g)
\end{align*}
\]

Scheme 1. Proposition of CaCO3 decomposition in presence of H2.
and sieved in the particles size range of 250–300 µm. Part of the calcium oxide particles thus prepared, was converted to CaCO3 by calcination in 20% CO2 in N2 at 630 °C for 5 h (heating rate 15 °C min⁻¹) and consecutively sintering in pure CO2 at 900 °C for 24 h (heating rate 15 °C min⁻¹). The material was sieved again in order to ensure the particle size range of 250–300 µm. α-alumina (99%, Alfa-Aesar) was treated, pelletized, crushed and sieved following the same procedure.

2.2. Characterization

The specific surface area, pore volume and pore size distribution of the samples were measured both in CaO form as well as in CaCO3 form, after carbonation. The samples were first degassed at 300 °C in vacuum for 3 h. The surface area was calculated based on the BET isotherm for N2 adsorption at −196 °C in a Micrometrics Tristar 3000 analyzer. The pore size distribution was measured by Hg porosimetry in a Quantachrome PoreMaster 33 analyzer. The elemental composition was determined with X-Ray Fluorescence analysis (XRF, Bruker S8 Tiger).

2.3. Reactor setup

Fig. 1 shows a schematic representation of the equipment used to measure plasma enhanced RWGS. The fixed bed reactor is fed with a mix of Ar, H2, CO2 and H2O. Argon is saturated with water and diluted with a pure argon stream in order to vary the water concentration. The temperature of the oven is controlled with a Euro-Therm controller with an accuracy of ±0.5 °C between room temperature and 1000 °C, as reported previously [50]. The isothermal zone is 8 cm long at 900 °C, defined as the part of the reactor with less than ± 1 °C temperature variation. A Quadrupole Mass Spectrometer (MS) measures the composition of the gas mixture leaving the reactor. The MS signal for CO2 (44 m/e) and CO (28 m/e) are calibrated between 0.16% and 5% CO2 and at 5% CO, resulting in a linear relationship as shown in the Fig. A1 of the Appendix A. The reactor is a 4 mm inner- and 6 mm outer-diameter quartz tube. The inner electrode is a stainless-steel rod of 1 mm diameter placed co-axially in the center of the reactor section by the help of a spacer, which is removed when the rod and the packed bed are positioned. The outer electrode is a 1 cm long stainless-steel tube with 6 mm inner diameter, enclosing a plasma zone of 0.035 cm³ in volume. The plasma zone was filled completely with either 100 mg α-Al2O3 or with 10 mg CaCO3 and 95 mg α-Al2O3 for the blank and catalytic experiments respectively, in order to minimize any change in the plasma. Note that the blank experiment includes also any possible contribution of the reactor wall and the surface of the electrode. An AC voltage of up to 5 kV peak to peak is applied to the inner electrode with a constant frequency of 23.5 kHz using a PMV 500–4000 power supply, while the outer electrode is connected to the ground via a probe capacitor of capacity 4 nF. The power of the plasma is calculated using the Lissajous method by measuring the voltage on the inner electrode with a Tektronix P6015A high voltage probe and on the outer electrode with a TT–HV 250 voltage probe as described in literature [58]. An example of Lissajous plot is shown in Fig. A2 of the Appendix A.

2.4. Steady state RWGS experiments in CaO and Al2O3

Either 10 mg CaCO3 with 95 mg Al2O3 or 100 mg α-Al2O3 are placed in the reactor. In most experiments, the CaCO3 is decomposed in-situ by heating in Ar to 680 °C, resulting in a mixture of 6 mg CaO and 95 mg α-Al2O3. This sample is termed “CaO + Al2O3”, as opposed to “CaCO3 + Al2O3” when no in-situ decomposition is applied. The reactor containing alumina only is termed “Al2O3”.

RWGS experiments were initiated by switching the gas composition from pure Ar to CO2, H2 and H2O in Ar, at the selected temperature and constant flowrate of 90 ml min⁻¹. The temperature and concentration of CO2, H2 and H2O are varied between 630 and 820 °C, 0.1 and 0.4%, 2 and 10%, 0 and 0.25% respectively. The reactor reached steady state in typically 10 min after changing conditions. The plasma power is kept constant at either 0 W (plasma-off) or 1 ± 0.1 W (plasma-on) during the experiment. The CO2 conversion is calculated based on the CO2 and CO concentrations in the exit of the reactor according Eq. (1); considering exclusively concentrations measured at the exit at the same time minimizes experimental error caused by drift in the sensitivity of the MS. No correction in the volumetric flow is required since RWGS is the only reaction taking place.

\[ X_{\text{CO2}} = \frac{C_{\text{CO2, out}}}{C_{\text{CO2, in}} + C_{\text{CO2, out}}} \] (1)

Reproducibility was tested by repeating experiments with both different samples and different reactor tubes.

3. Results

CaO and Al2O3 surface areas after short exposure to ambient condition are 5 m²·g⁻¹ and 16 m²·g⁻¹ respectively. XRF data show that the CaO is 99.12% pure with minor contamination of SiO2 and Al2O3, while alumina is 99.9% pure with minor contamination of CaO.
3.1 RWGS over CaO and Al₂O₃

Fig. 2 shows the CO₂ conversion during RWGS over “Al₂O₃”, as well as “CaO + Al₂O₃”, as function of temperature as well as the concentration of CO₂, H₂, and H₂O. The conversions are calculated based on the composition of the outlet stream at the different conditions as shown in Figs. A3 and A4 of the Appendix A. No other products except CO and H₂O have been observed by MS and the mass balance closes within 5%. The sample “CaO + Al₂O₃” showed mild deactivation of 30% during the first 3 h of operation at 820 °C and no further deactivation was observed, as shown in Fig. A5 in Appendix A. The data shown in Fig. 2 are collected after stabilization for 3 h.

The results show that calcium oxide is active for RWGS, while Al₂O₃ is surprisingly also active, although significantly less. Note that no conversion was observed in an empty reactor. Fig. 2 shows that CO₂ conversion increases with temperature and hydrogen concentration, while it decreases with CO₂ and H₂O concentration for both samples. Most of the results are obtained far from thermodynamic equilibrium, as can be seen in Fig. 2.

Fig. 3 shows the CO₂ conversion during RWGS on “CaCO₃ + Al₂O₃” sample. The conversion levels are calculated based on data shown in Fig. A6 in Appendix A, showing that the temperature was increased stepwise. Apparently, CaCO₃ is not active for RWGS because it shows the same conversion as “Al₂O₃” sample. The sharp increase in conversion between 760 and 780 °C is caused by rapid decomposition of CaCO₃ to CaO, as at the same time the sum of CO₂ and CO concentrations in the product increase to much higher values than the CO₂ concentration in the feed, as shown in Fig. A6 in the window between 253 and 260 min. Afterwards, the mass balance closes again within 5%, indicating that the sample is mostly converted to CaO, resulting in a much higher activity. The increase in the sum of CO₂ and CO
concentrations in Fig. A6 corresponds to 91 μmol of desorbed CO₂, indicating that the sample is at least 90% converted to CaO. Thus, calcium oxide is not converted to calcium carbonate during the experiments shown in Fig. 2, since the conversion is always significantly higher than the conversion over Al₂O₃. Furthermore, the experiments in Fig. A3 never showed an offset of the mass balance, which would indicate the formation of CaCO₃. Clearly, the CO₂ inlet concentration lower than 0.5% is too low to cause formation of carbonate even at 630 °C, in agreement with the fact that the equilibrium CO₂ partial pressure for CaCO₃ decomposition is 0.7% at atmospheric pressure [52].

3.2. Effect of plasma on RWGS over CaO and Al₂O₃

Fig. 4 shows the CO₂ conversion obtained during RWGS experiments on “Al₂O₃” and “CaO + Al₂O₃” in presence of plasma. The conversion values are obtained based on the outlet concentrations shown in Figs. A7 and A8 in the Appendix A.

The plasma power is kept fixed at 1 W and the Lissajous plots measured on the two samples show no significant differences, as illustrated in Fig. A2 of the Appendix A. Apparently, the plasma remains similar when adding 6 mg of CaO to 100 mg of Al₂O₃ with similar particle-size and -shape as well as dielectric constant, resulting in similar capacity of the plasma reactor, electrical field distribution and power dissipation.

The results shown in Fig. 4 are corrected for a temperature increase of 10 °C. The estimation, shown in Fig. A9 and explained in Appendix A, is based on the kinetics of CaCO₃ decomposition in argon plasma measured using the same “CaCO₃ + Al₂O₃” sample and reported in our previous work [50].

For both samples, the conversion increases as function of temperature and decreases with CO₂ and H₂O feed concentration. Remarkably, the CO₂ conversion increases with H₂ concentration only when CaO is present, while it shows no significant changes with Al₂O₃ only. Note that the conversion approaches equilibrium for many experimental conditions in the presence of CaO. The conversion in presence of plasma is substantially higher respect to the experiments performed in absence of plasma at the same conditions as shown in Fig. 2 and it further increases in presence of CaO.

In addition to CO and H₂O, also trace amounts of CH₄ were detected, but due to the very low concentration no significant trend is observed, thus methane production is not discussed further. It was ensured that no carbon deposition occurred, based on the observation that no CO₂ is formed during oxidation of the sample in 10% air in argon plasma at 630 °C and plasma power of 3 W after the experiments. The reason for the mild deactivation observed in Fig. A5 remains unknown but change of activity during initial operation is frequently observed in catalysis.

4. Discussion

4.1. Kinetic description

The results in Figs. 2 and 4 show that CaO, as well as Al₂O₃ to lesser
extent, is active for RWGS. The fact that equilibrium is never approached implies that conversion is determined by kinetics. CO₂ conversion increase with increasing temperature, indicating that RWGS on “\(\text{Al}_2\text{O}_3\)” and “CaO + Al₂O₃” is an activated process both in thermal and in plasma operation. CO₂ conversion decrease with increasing CO₂ and H₂O concentrations in all cases, both in thermal and in plasma operation. The apparent negative order in CO₂ is suggesting competitive adsorption of CO₂ and H₂ in combination with a high surface coverage with CO₂. Also, the poisoning effect of H₂O points to competitive adsorption in case of catalytic operation, as experiments are performed far from thermodynamic equilibrium. The results in Figs. 2 and 4 also show that the conversion increases with the hydrogen concentration in thermal operation as well as on “CaO + Al₂O₃” in plasma operation. In contrast, the conversion doesn’t change significantly with hydrogen concentration on “Al₂O₃” in plasma operation.

In order to judge whether there is synergy between plasma and the CaO catalyst, the reaction rate obtained on “CaO” in thermal operation and on “Al₂O₃” in plasma operation must be compared to the rate obtained on “CaO + Al₂O₃” in plasma operation. The results in Figs. 2 and 3 show significant conversion and therefore do not allow direct calculation of reaction rates at one specific temperature, as would be possible in a differential experiment, i.e. conversion is less than typically 10%. In an integral experiment, concentration profiles develop along the axis of the reactor and the local reaction rates vary. Consequently, a valid mathematical description is needed of the kinetics of the reaction catalyzed by alumina and CaO, with and without the presence of the plasma, in order to compare respective reaction rates at identical conditions.

A mechanism-inspired rate equation is used to model the reaction rate for the four cases, i.e. “CaO” and “Al₂O₃” in thermal operation, “CaO + Al₂O₃”, “CaO” and “Al₂O₃” in plasma operation. The rate on “CaO” is calculated by subtracting the contribution of “Al₂O₃” both in thermal and in plasma operations, since alumina appeared not inert. Nevertheless, the equation serves solely as mathematical description of the system and is not related to a microkinetic model. Eq. (2) is used for this purpose, allowing for an accurate description of the kinetics considering the following assumptions, based on the observations discussed above:

- reactant CO₂ and the product H₂O adsorb competitively on both Al₂O₃ and CaO, while CO is assumed to desorb quickly;
- The orders in CO₂ and H₂, i.e. a and b respectively, as well as the adsorption equilibrium constant of the water (\(K_{\text{H}_2\text{O}}\)) are assumed constant with varying reaction conditions;
- The reaction occurs on Al₂O₃ and CaO independently.

The equation also includes a term describing the reversed reaction (WGS) when the conversion approaches the thermodynamic equilibrium, according to the equilibrium constant \(K_{\text{eq,ir}}\) [52], which is particularly the case for “CaO + Al₂O₃” in plasma operation, as shown in Fig. 4.

\[
R_{\text{s,ir}} = \frac{k_0 \exp\left(\frac{E_{\text{a,ir}}}{RT}\right) k_0 \exp\left(\frac{E_{\text{a,ir}}}{RT}\right) [\text{H}_2]^{1 - \frac{K_{\text{eq,ir}}}{K_{\text{H}_2\text{O}}}}} {1 + [\text{H}_2\text{O}]K_{\text{H}_2\text{O}}} \]  

(2)

The same equation is used for the four cases, obviously resulting in different fitting parameters.

The packed bed zone was modeled in 10,000 segments, in which the concentration of the gases was calculated using Eq. (2) iteratively. Values for the fitting parameters were selected by optimizing the fit to the experimental observations. A MATLAB script was developed for that purpose, presented in Appendix A.

The values of the fitted parameters \(k_0\), \(E_{\text{a,ir}}\), \(E_{\text{a,ir}}\), and \(K_{\text{H}_2\text{O}}\) are presented in Table 1. The error margins are determined by a sensitivity analysis of each parameter. The CO₂ conversions obtained by these models show good agreement with the experimental data within the error margins, as shown in Figs. 2–4. The thermal reaction pathways on CaO and Al₂O₃ have a similar apparent activation barrier, but the pre-exponential factor \(k_0\) is 7 times higher on “CaO” respect to “Al₂O₃” only. The apparent reaction order in CO₂ is slightly lower on CaO respect to alumina (0.65 and 0.85 respectively), while the apparent orders for H₂ are similar and close to 1. In presence of plasma the apparent activation energy decreases from 120 to 95 kJ mol⁻¹ with Al₂O₃ only and, more pronouncedly, from 140 to 75 kJ mol⁻¹ when CaO is present. The order in CO₂ and the adsorption constant of H₂O do not change significantly when plasma is applied, while the orders in H₂ diminish strongly, in agreement with the experimental observation in Fig. 4 that the reactions are much less sensitive to the hydrogen concentration in the presence of plasma.

In principle, this model is just a mathematical description of the kinetics; nevertheless, we note that the fitting results in realistic values for activation barriers and reaction orders. More importantly, the model results in a good fit for both thermal as well as plasma experiments.

4.2. Synergy

The reaction rates in the three cases of “CaO” in thermal operation, “Al₂O₃” in plasma operation and “CaO + Al₂O₃” in plasma operation, are compared at fixed concentrations and temperature to assess synergy between CaO and plasma, which is the case if the enhancement factor, defined according Eq. (3), is larger than 1.

\[
\text{Enhancement} = \frac{R_{\text{CaO and Al}_2\text{O}_3 \text{plasma}}}{R_{\text{CaO thermal}} + R_{\text{Al}_2\text{O}_3 \text{plasma}}} \]  

(3)

Both rates in presence of CaO and plasma (\(R_{\text{CaO and Al}_2\text{O}_3 \text{plasma}}\)) as well as the rate in absence of CaO (\(R_{\text{Al}_2\text{O}_3 \text{plasma}}\)) are measured directly and model equations are available (Table 1). The rate equation for the thermal activity of CaO is also available in Table 1, calculated by subtracting the rate over alumina (\(R_{\text{Al}_2\text{O}_3 \text{thermal}}\)) from the rate measured over CaO and alumina (\(R_{\text{CaO and Al}_2\text{O}_3 \text{thermal}}\)), as described above.

Fig. 5 shows the reaction rates as function of temperature on “CaO” without plasma, “Al₂O₃” plasma and “CaO + Al₂O₃” plasma calculated at 0.2% CO₂, 10% H₂ and 0.1% H₂O, which is a condition experimentally studied. Fig. 5 also shows that the enhancement factor decreases as function of temperature, showing synergy for temperatures up to 700 °C and no synergy at 750 °C.

Fig. 6 show the calculated RWGS rates according the model as function of CO₂, H₂ and H₂O concentrations at 640 °C. Fig. 6 suggests constant enhancement factor with varying concentration, as any trend is clearly smaller than the error margin. In all cases, synergy is observed at 640 °C, in contrast to the similar figure at 750 °C (Fig. 7) showing synergy is absent for all concentrations considered.

4.3. General discussion: catalytic, plasma and plasma-catalytic effects

4.3.1. Catalytic effect

The catalytic activity per gram of CaO at 630 °C is typically an order of magnitude lower than the activity of conventional Cu-based catalysts at the same conditions [62]. Clearly, CaO is not a preferred catalytic material, nevertheless it has significant activity, in line with the facts that MgO is also active for RWGS [60] and that CaO is active for WGS, as reported in a study on sorption enhanced WGS [63].

CaO and MgO [59] are much more active for RWGS than Al₂O₃ in thermal operation. Basic oxides adsorb CO₂ strongly [60,61] and are more active, suggesting that the reaction proceeds via surface carbonates. The reaction order in CO₂ observed on CaO (0.65) suggests that the CaO surface is partly covered with carbonates. Apparently, surface carbonate species on CaO are active, whereas the surface of bulk CaCO₃ is not active at all for RWGS (Fig. 3). Furthermore, the order in hydrogen is close to 1 on both CaO and Al₂O₃, indicating that activation of H₂ on the oxides surface is likely the rate determining step (r.d.s.). Alternatively, the coverage with hydrogen, presumably H atoms, is
Table 1
Values of fitting parameters describing the RWGS rate equation for the five cases. The last column, CaO 1 W represents the rate on CaO in plasma operation, obtained by subtraction of “Al2O3 1 W” from “CaO + Al2O3 1 W”; see text for further explanation.

<table>
<thead>
<tr>
<th></th>
<th>Al2O3 0 W</th>
<th>CaO 0 W</th>
<th>Al2O3 1 W</th>
<th>CaO + Al2O3 1 W</th>
<th>CaO 1 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>ln k_0 (s^-1 bar^-1)</td>
<td>19.1 ± 1.2</td>
<td>21.0 ± 1.3</td>
<td>14.0 ± 1.0</td>
<td>13.0 ± 1.5</td>
<td>10.8 ± 2.1</td>
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<tr>
<td>E_a (kJ mol^-1)</td>
<td>120 ± 5</td>
<td>140 ± 10</td>
<td>95 ± 5</td>
<td>75 ± 10</td>
<td>40 ± 20</td>
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<td>a (order for CO2)</td>
<td>0.85 ± 0.05</td>
<td>0.65 ± 0.05</td>
<td>0.6 ± 0.05</td>
<td>0.75 ± 0.05</td>
<td>0.9 ± 0.1</td>
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<tr>
<td>b (order for H2)</td>
<td>0.95 ± 0.05</td>
<td>0.85 ± 0.05</td>
<td>-0.05 ± 0.05</td>
<td>0.25 ± 0.05</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>ln k_RWGS</td>
<td>8.5 ± 0.2</td>
<td>6.7 ± 0.3</td>
<td>6.5 ± 0.1</td>
<td>6.6 ± 0.2</td>
<td>6.5 ± 0.2</td>
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Fig. 5. RWGS reaction rates as function of temperature on “CaO” in thermal operation (◆), “Al2O3” in plasma operation (▲), sum of “CaO” in thermal and “Al2O3” in plasma operation (▼) and “CaO + Al2O3” in plasma operation (●); enhancement factor (□); the concentrations are 10% H2, 0.2% CO2 and 0.1% H2O in Ar, flow rate is 90 ml min^-1.

4.3.2. Plasma effect

Introduction of plasma on both Al2O3 and CaO enhances the RWGS reaction, at least partly due to plasma chemistry in the free space in the packed bed. Fig. 8 presents a reaction scheme for plasma chemistry of CO2 hydrogenation in DBD plasma, based on micro-kinetics at ambient conditions [64]. CO2 dissociates to CO and O, similar to CO2 dissociation as a consecutive reaction during CaCO3 decomposition in an Ar plasma. The presence of H2 opens up a new reaction pathway for O-radicals to form water instead of O2 or recombination with CO. The consecutive products in Fig. 8, i.e. methane, ethane, methanol, formaldehyde, are not observed in our experiments since these reactions are thermodynamically less favored at high temperatures, above 600 °C. Nevertheless, the contribution of plasma-chemistry in our experiments can be discussed based on the reaction scheme Fig. 8, regarding activation of H2 and CO2.

Introduction of plasma on Al2O3 also induces the order in hydrogen to decrease from 1 to 0, indicating that hydrogen activation is not the r.d.s. in the presence of plasma, suggesting that hydrogen is activated in the plasma rather than on the Al2O3 surface. Fig. 8 also shows that RWGS is plasma initiated exclusively via CO2 dissociation via electron impact dissociation or vibrational excitation whereas H radicals cannot activate CO2. Instead, addition of hydrogen causes consecutive conversion of O-radicals to H2O instead of O2. Moreover, OH and CHO radicals generated in the presence of hydrogen rapidly react with CO and O respectively, forming back CO2 and retarding the overall RWGS reaction. Although the conditions of the micro-kinetic study of Fig. 8 are different from our experiments, the reaction pathways in Fig. 8 agree with the observed zero order in hydrogen, suggesting that gas-phase plasma-chemistry is dominant over surface reactions on RWGS over alumina. Otherwise, the apparent order in H2 would be higher than 0 and closer to the order 0.85 as observed on alumina (Table 1). However, further clarification is not subject of this work as a blank experiment with plasma only, i.e. without alumina in an empty plasma reactor, is not included. This was even not attempted because the plasma is influenced by the presence of a packed bed and consequently the residence time, SEI and plasma properties cannot be kept constant, as discussed in the introduction. In fact, the plasma experiment with alumina is the blank experiment, which contains also the contribution of the reactor wall and the surface of the electrode, enabling a valid discussion on plasma-catalytic effects on CaO.

4.3.3. Synergy between CaO and plasma

Synergy between plasma and catalysis will be discussed quantitatively based on comparison of reaction rates at fixed conditions, using the kinetic description discussed above. Furthermore, complicating factors are addressed to the best of our ability, i.e. (i) any thermal effect of plasma, (ii) effect of the catalyst on the residence time in the reactor and (iii) the effect of the catalyst acting as a dielectric material on the plasma properties.

The term synergy is used with different meanings in papers on plasma catalytic CO2 hydrogenation. In many cases, synergy is discussed based on changes in conversion when introducing the catalyst in the plasma [18,22,26,47–49], causing synergy if the combination of plasma and catalyst opens a new catalytic pathway, parallel to the plasma-chemistry pathway with plasma only and the catalytic pathway on the catalyst only. In some cases, synergy is claimed based on increasing selectivity to a specific product by introducing the catalyst in the plasma, e.g. formation of methane or methanol with Ni or Cu catalyst respectively. CO2 conversion is not increased [25] or even decreased [46], indicating that the interaction of plasma and catalyst enhances consecutive reactions with CO as primary product. The results presented here involve one single reaction (RWGS) and quantification of synergy requires the kinetic description as discussed above. The facts that conversions are significant, and the results cannot be considered differential implies that synergy must be discussed based on reaction rates instead of conversions. Any further comparison with these studies is not useful, since RWGS is a different reaction using different catalysts and reaction conditions.

First, we will discuss possible artifacts as well as necessary assumptions considering the three complications described above.

- (i) Any effect of temperature changes induced by plasma is not only small but also have been corrected for as described in the result section. This has not been addressed explicitly in the work on plasma-catalytic CO2 hydrogenation, except by Eliasson et al., estimating the temperature increase in the plasma by modeling heat transfer [25]. Other studies estimated the temperature by measuring either outside the reactor [22,27,46,49] or inside the reactor downstream of the plasma zone [18,26,47].
- (ii) The residence time in all experiments was kept constant, as the total volume of the packed bed was constant. Note that the residence times in the packed bed and the plasma zone are identical. The same approach was used by others, comparing plasma catalytic- and plasma only- activities at constant residence time by including
measurements with unloaded support [22,26,27,46]. These studies used supported metal catalysts, introducing other complications as discussed below. In two studies [22,46], the plasma zone was only partially filled, complicating the interpretation significantly because the plasma properties in the empty part of the reactor and inside the packed bed differ significantly.

(iii) Changes in plasma properties can also be excluded based on three arguments. First, the Lissajous plots on “Al2O3” and “CaO + Al2O3” in plasma operation are very similar, as shown in Fig. A2, suggesting the same electron energy distribution as well as constant power [43,58]. Second, alumina and calcium-oxide have similar dielectric constants, i.e. 9.2 and 11.8 respectively [65], and the size and shape of alumina and calcium-oxide particles are similar as well. Therefore, the number of contact points between particles in the bed, enhancing discharges in the plasma [19,44,45], is constant. It is well known that both dielectric constants and different particles size and shape changes the plasma properties significantly [6,24], but with the precautions discussed above it is reasonable to assume that the plasma properties remain similar. Third, the catalyst contains oxides only and no metal particles, which are reported to intensify the plasma locally [44,66].

Thus, the observed synergy is not caused by changing the plasma but can be attributed to a new catalytic pathway involving activated species in the plasma and the CaO surface. Apparently, the new pathway has a lower activation barrier, as the observed apparent activation energy decreases from 140 to 40 kJ mol\(^{-1}\) when plasma is introduced. The plasma-catalytic pathway is dominant at 640 °C, while at 750 °C the thermal catalytic pathway dominates, because of the high activation barrier, so that no synergy is observed as shown in Fig. 5. Note that the decrease in the enhancement factor with increasing temperature shown in Fig. 5 is not caused by approaching thermodynamic equilibrium, since all rates in Fig. 5 are calculated at fixed concentrations far away from thermodynamic equilibrium [52].

The apparent order for hydrogen of 0.8 on CaO in plasma operation suggests that hydrogen activation in the plasma is involved in the plasma-catalytic pathway. Presumably hydrogen radicals react with surface carbonates on calcium oxide, in contrast to carbonates on alumina since order in hydrogen is zero. Remarkably, activation of CO\(_2\) via hydrogen radicals is not significant in the case of plasma chemistry as discussed above.

These results will be used in a subsequent publication describing decomposition of CaCO\(_3\) in a H\(_2\) containing plasma. We believe that the proposed method allows separation of, at one hand, the influence of surface catalytic reactions on the conversion, versus the influence of the fixed bed as a dielectric material on plasma chemistry in a DBD-plasma catalytic reactor. This may contribute to improved insight in plasma catalysis. Further progress could be anticipated via developing in-situ or preferably operando characterization techniques to study adsorbed species. Attempt with FT-IR failed so far mainly because of the high temperature of operation, but this would certainly the way forward to improve understanding, in combination with reliable kinetic information.

5. Conclusions

Synergy between plasma and calcium oxide for RWGS has been quantified, by minimizing any effect of the presence of the catalyst.
fixed bed as a dielectric material on the contribution of plasma chemistry, i.e. chemical conversion in the plasma, keeping also the specific energy input and the residence time constant. Moreover, synergy is determined by calculating reaction rates at fixed temperature and gases concentrations, by using kinetic equations describing well the integral experiments performed in presence and absence of both calcium oxide and plasma.

Synergy is observed at low operational temperature (640 °C) with a rate-enhancement factor of 1.7. The rate enhancement steadily decreases with increasing temperature until synergy disappears at 750 °C, independently of the composition of the gas mixture. Synergy is caused by opening a new reaction pathway involving plasma activated species on the CaO surface. The apparent activation barrier of the plasma-catalytic pathway is 40 kJ mol⁻¹, much lower than the apparent activation barriers of thermal-catalytic reaction (140 kJ mol⁻¹) and of the pathway with Al₂O₃ and plasma (90 kJ mol⁻¹). The apparent orders for CO₂ and H₂ are 0.9 and 0.8 respectively, suggesting that the rate-determining step is the reaction of surface CaCO₃ with a plasma-activated H₂, presumably H radicals.

6. Notes

The authors declare no competing financial interest.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Fig. 7. RWGS reaction rates as function of concentration of CO₂ (a), H₂ (b) and H₂O (c) on “CaO” in thermal operation (●), “Al₂O₃” in plasma operation (▲), sum of “CaO” thermal and “Al₂O₃” plasma operation (▼) and “CaO + Al₂O₃” in plasma operation (●); enhancement factor (■); the fixed concentrations are 10% H₂, 0.2% CO₂ and 0.1% H₂O in Ar, temperature is 750 °C, flow rate is 90 ml min⁻¹.

Fig. 8. Dominant reaction pathways for the conversion of CO₂ and H₂ into various products, in a 50/50 CO₂/H₂ gas mixture. The thickness of the arrow lines is proportional to the rates of the net reactions. The stable molecules are indicated with black rectangles. Reproduced from [64], permission pending.
Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2019.123806.


