Plasma enhanced CaCO₃ hydrogenation for direct fuel production

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Abstract: This study addresses the effect of a hydrogen Dielectric Barrier Discharge plasma on $CaCO_3$ decomposition by using a comparative method to distinguish between thermal effect, i.e. increase of temperature, and plasma chemistry effects. Thermal effect dominates on CO_2 formation, while both temperature and plasma chemistry influence CO production, which may occur via CO_2 hydrogenation or directly from $CaCO_3$. Plasma applied during CO_2 hydrogenation shows a decrease of CO_2 and H_2 reaction orders and of the activation barrier.

Keywords: CO_2 conversion, Plasma Catalysis.

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]. Dielectric Barrier Discharge (DBD) plasma is a promising technique for plasma-catalytic conversion, since the non-equilibrium plasma has very high electron temperatures ($10^4 - 10^5$ K), rather high vibrational temperatures (10^3 K) and rather low rotational and translational temperatures, typically in the order or smaller than 100 K. The low gas temperature allows the application of a catalyst directly in the plasma generation zone without fast deactivation, maximizing the interaction between active species and the catalytic phase.

Interaction between plasma and catalyst can proceed in many ways. Obviously, the plasma will introduce new chemical species including activated species, radicals and ions, which all may adsorb on the catalyst opening new reaction pathways and influencing the products distribution. Plasma can also induce photocatalytic effects by UV irradiation, impingement of charged particles and thermal fluctuations. The surface and sub-surface 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, creating local field enhancement with roughness of the surface, but also modifying the free volume and the residence time in the plasma zone. Unfortunately, plasma also increases the temperature of the system, obviously influencing reaction rates of chemical reactions.

This study assesses the potential of using H_2 plasma to enhance $CaCO_3$ decomposition. $CaCO_3$ is a relevant material for CO_2 separation. Calcium Looping Cycle is widely discussed in literature [2], consisting of carbonation of CaO for capturing, followed by calcination of $CaCO_3$ in order to recycle calcium oxide and to produce pure CO_2. However, the calcination reaction requires high temperatures in order to achieve high CO_2 concentrations in the outlet, i.e. at least 950°C to achieve 1 bar 100% CO_2. Such temperatures results in sintering, decreasing the CO_2 capture capacity when calcium oxide is recycled multiple times Using a DBD plasma during the calcium carbonate decomposition might circumvent the need for such high temperatures, and in addition CO_2 will be converted by plasma into CO, converting electrical energy into chemical energy and producing an added-value product. Using hydrogen as a co-reactant to enhance $CaCO_3$ thermal decomposition leads to a decrease in the decomposition temperature of ca. 50°C and production of CO and H_2O [3].

The decomposition is studied by using a method to distinct between thermal effect and plasma chemistry effects in fixed bed DBD plasma reactors, based on the fact that plasma cannot exist in the pores inside particles if they are smaller than a few micrometers, as can be understood from the Paschen's Law, which is generally accepted [4]. The internal surface area, caused by the presence of small pores in the material is not exposed to the plasma, but would be influenced by any thermal effect, whereas the external surface area is exposed to both plasma and thermal effects. Consecutive reactions, i.e. CO_2 hydrogenation will be also addressed.

2. Materials and methods

CaO samples, obtained by calcination of $CaCO_3$, Ca-L-ascorbate and Ca-D-gluconate precursors, are carbonated to form a $CaCO_3$ layer of ca. 30nm. The particle sizes are varied, i.e. diameters of 100-125 and 250-300 µm. The samples properties are summarized in Table 1 The powder was characterized by N_2 physisorption, XRD, XRF and SEM. Decomposition experiments have been performed in a DBD plasma fixed bed reactor. The decomposition temperature is varied in the range 590°C - 630°C in 10% H_2 in Ar, while the plasma power is varied from 0 to 6 W. The $CaCO_3$ samples weight 10 mg and are mixed in 90 mg α-Al_2O_3 as inert material in order to fill completely the plasma zone. The product stream is analyzed by Mass Spectrometry.

Table 1. CaCO$_3$ samples properties

Sample code	Precursor	Carbonation time (h)	CaCO$_3$ S.S.A. (m^2 g^{-1})	Particles diameter (µm)
A	Ca Gluc.	5	1.7 ± 0.1	250-300
B	Ca Asc.	4	0.8 ± 0.1	250-300
C	CaCO$_3$	5	< 0.5	250-300
D	CaCO$_3$	5	< 0.5	100-125

3. Results and discussion

Figure 1 presents the result of an isothermal CaCO$_3$ decomposition (sample C) in presence of plasma, showing the products concentration as function of time.
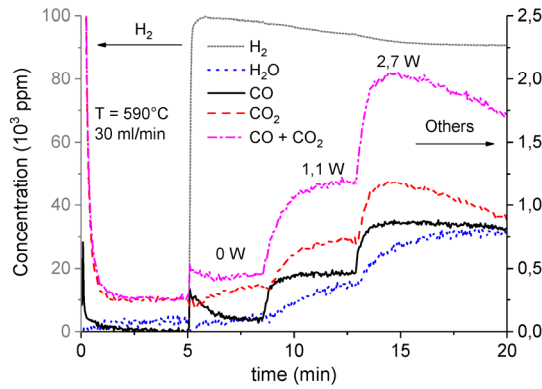

Fig. 1. Concentration of the gases during CaCO$_3$ decomposition (sample C) as function of time at 590°C, flow rate of 30 ml/min, gas composition of pure Ar for 5 min and 10% H$_2$ in Ar afterwards, plasma power is 0, 1.1, and 2.7 W.

Introduction of H$_2$ causes a doubling in the reaction rate and a formation of CO and H$_2$O, while the introduction of plasma causes an increment of all the products concentration with increasing power. Changing the plasma power causes a fast response of the CO concentration in the order of seconds, while the CO$_2$ concentration needs typically a minute to stabilize. H$_2$O concentration shows a delay, suggesting adsorption in the last section of the lines. The CO and CO$_2$ concentration have been calibrated. Figure 1 clearly shows that steady-state decomposition was achieved for all the plasma power values, while exhaustion starts to take place after 15 minutes.

Figure 2 shows the concentrations of CO (figures 2a,b) and CO$_2$ (figures 2c,d) measured during the steady state as function of plasma power for samples with different surface area (figures 2a,c) and for samples with different particles size (figures 2b,d). The results show that the increase in CO$_2$ depends on the internal surface area of the CaCO$_3$ sample, which is not exposed to plasma, but is affected by temperature changes induced by the plasma. On the other hand, CO$_2$ concentration appears independent of the external surface area, which is exposed to plasma. Thus, CO$_2$ formation is influenced only by the gas temperature, and no plasma-chemistry is contributing. Figure 2 shows also that the increase in CO formation is influenced either by internal and external surface areas at constant plasma power, implying that both increase of temperature and plasma chemistry are involved.
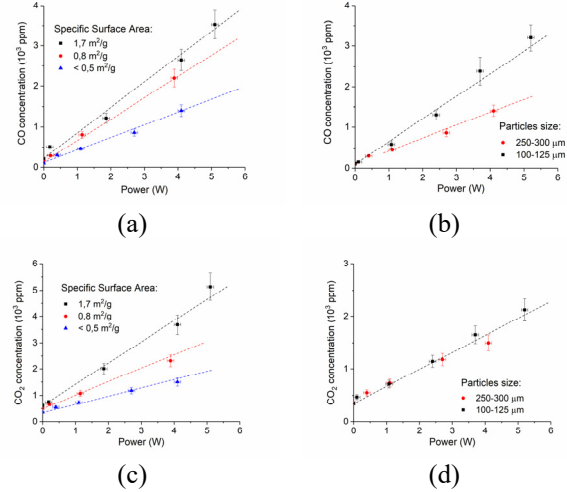

Fig. 2. Concentrations of CO (2a,b) and CO$_2$ (2c,d) as function of power during decomposition of CaCO$_3$ samples with different surface areas (2a,c; samples A, B, C) and different particles size (2b,d; samples C, D); the experiments are performed at 590°C, in 10% H$_2$ in Ar, flow rate of 30 ml/min.

Figure 3 shows the apparent temperature increase, as estimated based on the temperature that would be required to account for the increase in decomposition rate, based on the kinetics of the decomposition reaction [5]. Remarkably, all observations converge to a single line, independent of both surface area and particle size. Figure 4 shows also the apparent temperature increase obtained during CaCO$_3$ decomposition in pure Ar plasma, suggesting that the presence of 10% H$_2$ doesn't influence the plasma thermal effect. The order of magnitude of the temperature increase is quite similar to results reported in literature [6].

The reaction proceeds according to scheme 1. CO may be produced either via direct formation from CaCO$_3$ (R2) or via consecutive CO$_2$ hydrogenation (R3). The excess of H$_2$ always ensures that the CO produced is much lower than the equilibrium concentration, allowing to neglect the backward reactions. The kinetics of the consecutive reaction will be addressed in the following section.
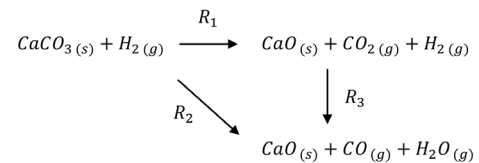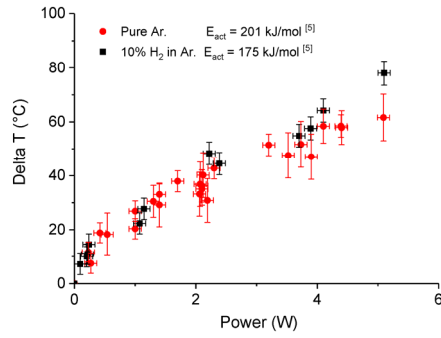

Scheme 1

Fig. 3. Average increase of temperature in the plasma zone as function of power during the CaCO₃ decomposition in pure Ar (circles) and 10% H₂ in Ar (squares).

3.1. CO₂ hydrogenation kinetics

Figure 3 shows the result of a CO_2 hydrogenation experiment in a packed bed of 100mg α-Al₂O₃, performed adding concentrations from 0.1 to 0.4% CO_2 and 2 to 10% H_2 in Ar at temperatures from 400°C to 630°C in absence of plasma. Two similar experiments are performed in presence of plasma, by applying a constant power of respectively 0.4 W and 1 W during the whole duration.
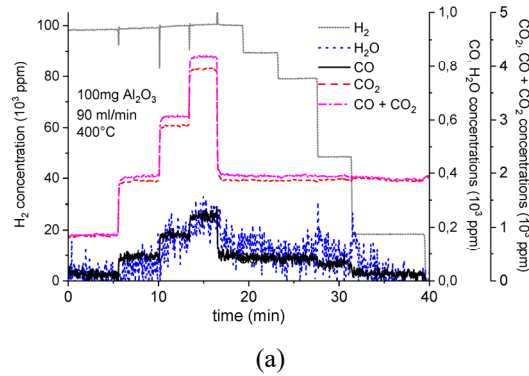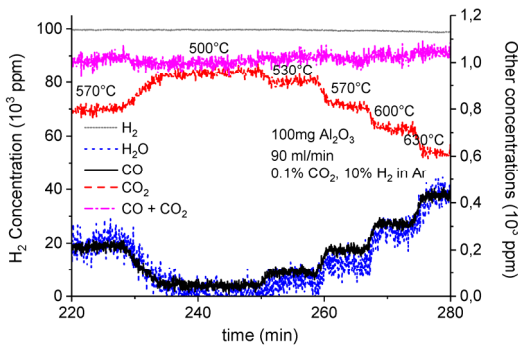
Fig. 4. Concentration of the gases during CO_2 hydrogenation in 100mg α-Al₂O₃ sample with particles size between 250 and 300 μm. The temperature is 400°C, CO_2 concentration is between 0.1 and 0.4%, H_2 concentration is between 2 and 10% (4a); the temperature is between 500 and 630°C, CO_2 concentration is 0,1%, H_2 concentration is 10% (4b); flow rate is 90 ml/min, no plasma is applied. In figure 4a the H_2 concentration is shown on the left axis while the other concentrations are shown on the right axis.

The kinetic equation can be approximated as follows

$$R_3 = k \cdot [CO_2]^\alpha \cdot [H_2]^\beta \qquad (1)$$

The calculated reaction orders for CO_2 and H_2 are shown in figure 5 for the three experiments. It has to be stressed that in presence of plasma such orders are only apparent, since each one of them are involves not only CO_2 and H_2 respectively, but all the active species produced in the plasma. Figure 5 shows that the reaction rate increases with plasma power in all the conditions used. The CO_2 reaction order steadily decreases with increasing power, while the H_2 reaction order becomes negative and steady in presence of plasma, suggesting that the presence of hydroxyl groups formed by rapid reaction of hydrogen and oxygen species react with CO producing CO_2 as claimed by Snoeckx et al. [7].

(a)

(b)
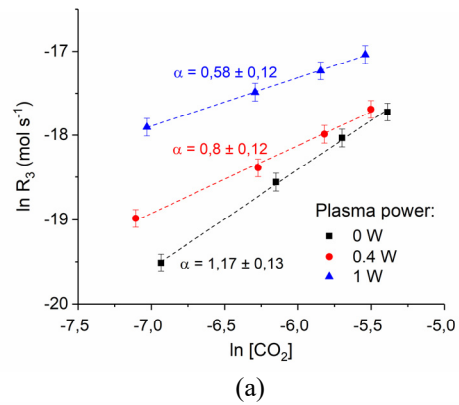
(a)
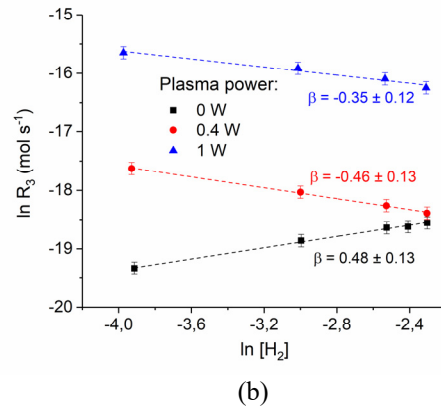
(b)

Fig. 5. Reaction rates obtained during CO_2 hydrogenation on 100mg α-Al_2O_3 as function of CO_2 concentration at H_2 concentration of 10% (5a); and as function of H_2 concentration at CO_2 concentration of 0,2% (5b). Plasma powers are 0, 0.4 and 1 W, temperature is 400°C for 0 and 0.4 W and 100°C for 1 W, flow rate is 90 ml/min.

The kinetic constants are calculated and shown in the Arrhenius plots on figure 6, resulting in a decrease of activation energy from 95 to 13 kJ/mol with the increase of plasma power. In presence of plasma, the activation energy is higher at temperatures above 500°C, suggesting two regimes: 1) "low" temperatures where CO_2 is only hydrogenated by plasma chemistry and 2) "high" temperatures where the thermal reaction starts to play a role in parallel to the plasma chemistry. It has to be stressed that the kinetic constants absolute values for different power cannot be compared, since the apparent reaction orders are different.
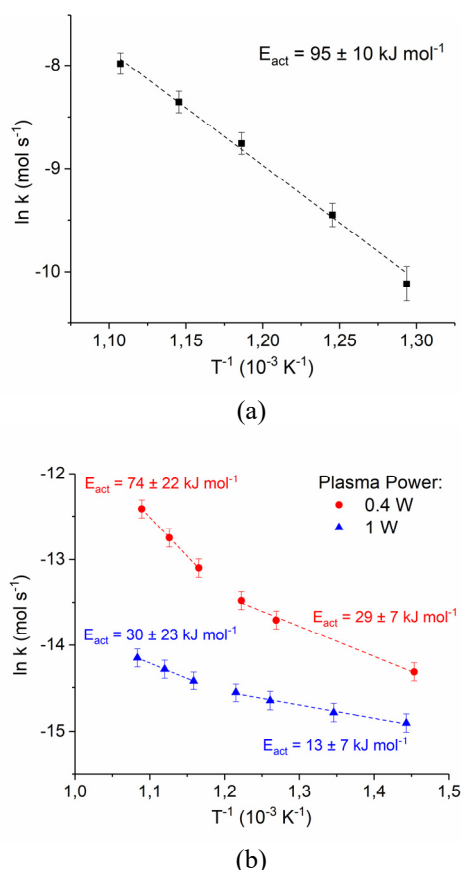

(a)

(b)

Fig. 6. Kinetic constant obtained during CO_2 hydrogenation on 100mg α-Al_2O_3 as function of reciprocal temperature at plasma power of 0 W (6a), 0.4 and 1 W (6b). Temperature is between 400 and 630°C, H_2 concentration is 10%, CO_2 concentration is 0.1%, flow rate is 90 ml/min.

Ongoing experiments will show whether the addition of $CaCO_3$ in the system enables a direct pathway for CO formation and aim to clarify the role of plasma. Early results suggest that the presence of $CaCO_3$ substantially increases the CO production, but a more detailed study is needed.

4. Conclusion

The effect of 10% hydrogen in argon plasma on calcium carbonate decomposition has been assessed by means of a comparative method allowing to distinguish between thermal effects and plasma chemistry, based on reaction rates and dynamics. It represents a systematic method to distinguish between thermal effects versus plasma-chemistry effect in fixed DBD plasma applications. The application of H_2 plasma causes two effects when decomposing $CaCO_3$.

First, the rate of CO_2 desorption increases. We conclude that this effect is purely a thermal effect, based on the fact that the rate of decomposition is enhanced when the total surface area is increased, whereas the external surface area has no influence. If the contact of plasma with $CaCO_3$ would dominate, the opposite would be expected. Furthermore, the dynamics of CO_2 desorption follow the dynamics of heat transfer in $CaCO_3$ particles.

Second, the increase in CO formation is a combination of thermal and plasma chemistry effects, since CO formation is enhanced when both internal and external surface areas increase and based on the observation that dynamic changes are very fast, as expected for plasma effect. Whether the CO is formed by consecutive CO_2 hydrogenation or directly from $CaCO_3$ is still an open question.

A kinetic study on CO_2 hydrogenation shows that a plasma of 1 W has three effects: 1) the reaction for CO_2 decreases from 1.2 to 0.6, 2) the order for H_2 shifts from positive to negative, suggesting that H_2 plays a role in CO and O recombination to CO_2, and 3) the activation barrier decreases from 95 to 13 kJ/mol, confirming the important role of the active species. Ongoing experiments will show the role of $CaCO_3$ on CO production.

5. References

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