Plasma assisted photocatalytic CO_2 decomposition in a micro DBD reactor

Deema Khunda[1], Sirui Li[2], Evgeny Rebrov[1,2]

[1] *School of Engineering, University of Warwick, CV4 7AL, Coventry, United Kingdom;*

[2] *Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, 5612 AZ, Eindhoven, the Netherlands*

**Corresponding author: e.rebrov@warwick.ac.uk; e.rebrov@tue.nl*

Highlights

- CO_2 decomposition was studied in a micro DBD reactor.
- A thin 10 μm titania coating were deposited onto the ground electrode.
- The maximum CO_2 decomposition rate was observed at 90 ºC over the titania catalyst.
- The illumination with UV light improved the CO_2 decomposition rate by 1.6 times.

1. Introduction

A combination of a photocatalyst with plasma emerged as a novel method to increase reaction rates in plasma assisted catalytic reactors. Process intensification is of particular importance for CO_2 splitting reaction because it is highly endothermic. Pure CO_2 splitting in dielectric barrier discharge (DBD) reactors has been extensively studied, and energy efficiency above 60% was shown to be possible, resulting in a solar-to-syngas conversion efficiency of at least 20%. In several studies, a sharp maximum in CO_2 conversion was observed at a gas temperature of around 90 °C because of two competing phenomena: increasing the rate of CO_2 dissociation via the vibrational ladder climbing process at lower temperatures which competes with a decrease of the reaction rate via the Arrhenius law [2]. In this study we further investigated the effect of illumination of titania films with UV light to further increase the rate of CO_2 decomposition at mild conditions. In addition, the effect of geometric shape of the electrodes on energy efficiency was evaluated.

2. Methods

A plate-to-plate microreactor with a gap size of 0.25 or 0.50 mm was used in the experiment. The ground electrode constituted of a brass plate with a diameter of 19.5 mm and was engraved with a cooling channel to maintain the desired temperature with a coolant flow. Then a 0.2 mm thin dielectric mica layer was attached to the electrode. Finally, the electrode was coated with a thin (20 micron) titania layer (Figure 1a). The titania coating was studied with SEM, TEM, XRD. A pyramid-shaped high voltage (HV) electrode was made of a titanuim disk of 23 mm diameter. In selected experiments, the catalyst was illuminated from the side via a quartz window with a UV LED (total light intensity: 261 mW m^{-2}).

The gases (CO_2 and H_2) were fed to the reactor with a set of MFCs at a flow rate of 20-100 ml min^{-1}. The temperature of the outlet flow and the ground electrode was measured with thermcouples. The voltage was measured by a high voltage probe (100 MΩ, 3.0 pF) connected to an oscilloscope (Picoscope) as described elsewhere.[3] The product analysis was performed with an on-line GC (Shimadu 2010) equipped with a flame ionization and thermal conductivity detectors. N2 was used as an external standard.

3. Results and discussion

The titania coating increased the CO_2 conversion in the micro DBD reactor compared to the empty reactor as it was expected from the electrical analysis. The latter demonstrated a higher number of microdischarges as well as their longer lifetime when the titania coating was deposited onto the ground electrode. While switching the UV light resulted in a remarkable increase in CO_2 conversion at all flow rates and in particular from 7.6 to 11.0% at a CO_2 flow rate of 50 mL min^{-1} and a power input of 8.4 W (Figure 1). Also the CO_2 conversion increases by a factor of 1.4-1.6 across the whole power range studied (2-8 W).

The narrow gap (0.25 mm) increases power consumption, especially at low voltages in the range between 5.0 and 6.3 kV. The narrow gap allowed the reactor to operate at lower voltage, starting

discharge at 5.0 kV, whereas it needs 6.0 kV at a gap of 0.5 mm. When the discharge gap increases, the power density of the reactor (discharge power/discharge volume) decreases because the reactive plasma volume doubles and this results in partial discharging rather than fully bridged discharging, hence less charge formation and lower power consumption.

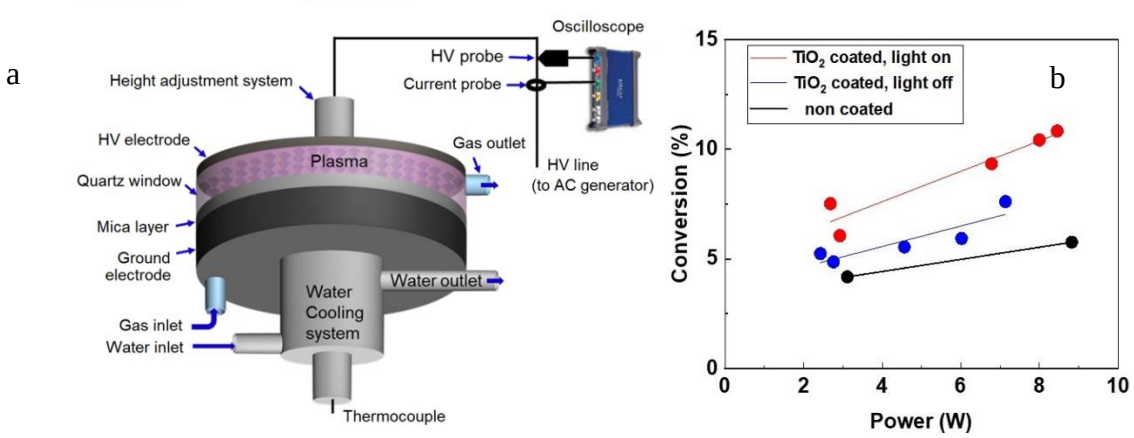

Figure 1. (a) Schematic view of micro DBD plasma reactor, (b) Conversion of CO_2 in the micro DBD reactor over TiO_2 coatings vs input power with and without UV light. The blank experiment is also shown for comparison.

In the micro DBD reactor, the temperature difference between the electrode temperature and the gas temperature remains at least two times smaller due to the increased value of heat transfer coefficient in the narrow gap size. The corresponding heat transfer coefficient was calculated from the Nu number for a channel with a rectangular cross section.

High viscosity of plasma as compared to non-ionized gas may create preferred pathways for the fluid flow in the micro DBD reactor. In the plasma, if the mean velocity of a certain plasma component is space inhomogeneous, there are the momentum currents to move from a high velocity layer to a low velocity layer, leading the viscosity. As a result, more gas passing through the area with low viscosity corresponding to low intensity plasma, while less gas goes via the areas with strong ionization. This explains the fact that CO_2 conversion decreases at lower gas flow rates. We may conclude that hydrodynamics and momentum transfer effects are responsible for such behavior rather than reaction kinetics.

4. Conclusions

The operation in the lower power range of about 3 W provides a CO_2 conversion of 16% with an energy efficiency of 20% which may be seen as the optimal operation point for the microelectrode DBD reactor. This combines the advantage of stronger electric fields and higher concentration of electrons, thus combining the advantages of microreactors and microplasma formation. The conversion further increases by 1.6 times via illumination with UV light of rather low intensity. Thus the energy efficiency in this reactor exceeds the state-of-the-art in DBD reactors used for CO_2 decomposition.

References

[1] R. Snoeckx, A. Bogaerts, Chem Soc Rev, 2017, 46, 5805–5863.
[2] D. Khunda, S. Li, N. Cherkasov, et al. React Chem Eng. 2023, 8, 2223-2233.
[3] D. Khunda, S. Li, N. Cherkasov, et al. Plasma Chem Plasma Process 2023, 43, 2017–2034.

Keywords
Process intensification; non-thermal plasma; microreactor; CO_2 decomposition; heat transfer