Fuel synthesis through CO_2 reduction in a plasma expansion

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The plasma-assisted reduction of CO_2 to hydrocarbon molecules in an argon-hydrogen plasma expansion is reported. CO_x is injected into the expansion part where the dissociation mechanism might be radical- and/or ion-driven. The (steady state) gas composition obtained by infrared laser absorption spectroscopy and mass spectrometry indictates an inherent syngas step as known from conventional catalysis. Experiments with different catalytically active surfaces suggest that the use of materials which are tailored to the plasma-environment can enhance the conversion yield.

1.   Motivation

Two of the world's most daunting problems, the global warming due to excessive emissions of carbon dioxide and the depletion of transportation fuels can have a solution in a universal carbon-cycle provided an efficient CO_2 reforming step is included. The efficiency of harvesting electrical energy from renewable sources is constantly increasing. However, efficient energy storage options are still absent and would be highly desirable in a chemical form [1]. Using the electrical energy for plasma processing of the carbon dioxide to convert it into conventional fuels with requisite energy density is an alternative approach. While reducing the green house gas emissions significantly, these fuels can be integrated in the existing transport infrastructure. The formation of CO from CO_2 as a precursor is considered to be the most important and rate limiting step [2, 3] in further hydrocarbon or oxygenate forming reactions. This paper discusses CO_2 reduction, i.e. dissociation and hydrogenation, in a low temperature plasma expansion. The aim is to evaluate conversion efficiencies in plasma-assisted CO_2 processing and assess the potential of plasma catalysis in this context.

2.   Experimental

The expanding thermal plasma was produced from a cascaded arc fed with mixtures of Ar and H_2 (fig. 1). The gas mixtures through the arc were varied from pure Ar to pure H_2. The gas expands supersonically from sub-atmospheric pressure in the remote arc into the background vessel which was at low pressure (1 mbar total pressure) and magnetized (14 mT). A constant CO_2 flow of about 10% of the total flow (3360 sccm) was added to the expansion part of the setup where electron temperatures are usually as low as 0.3 eV. Hence, the inital partial pressure of CO_2 was about 0.11 mbar. The gas flow in the background vessel forms recirculation zones which cause distinct surface interactions due to the imbalance in timescales of expansion and pumping [4]. Thus, the chemistry may be altered by providing different surface materials. Apart from the native stainless steel (SS), aluminium (Al) and copper (Cu) foils were used in close contact to the vacuum vessel to evaluate the influence on the steady-state gas composition and hence the conversion yield.
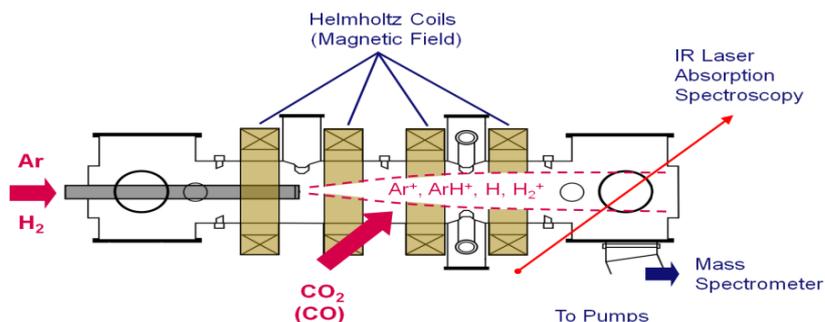

Fig. 1: A schematic of setup with gas flows and diagnostics

Infrared tunable diode laser absorption spectroscopy (IR-TDLAS) along with a multi-pass absorption cell was used to quantify the CO_2 depletion and the reaction products formed. Quadrupole mass spectrometry (QMS) was applied as complementary method to estimate the densities of molecular components which are not accessible by IR-TDLAS, e.g. O_2. To obtain quantitative result from QMS ion currents, careful calibration was carried out. Both diagnostic methods, IR-TDLAS and QMS, were used at distances from the arc where the gas temparature was clearly lower than 500 K (fig. 1). The calibration of the QMS was confirmed through a comparison of selected interference-free m/z-ratios and the corresponding results from IR-TDLAS (e.g. fig. 2).
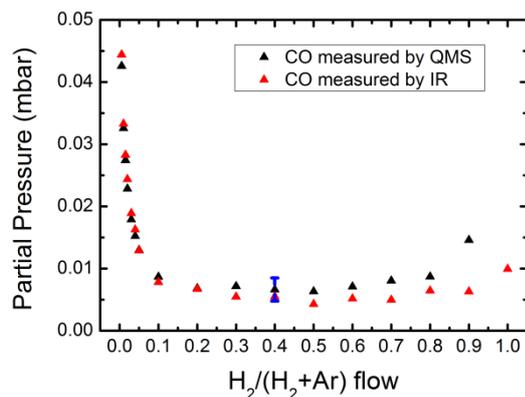
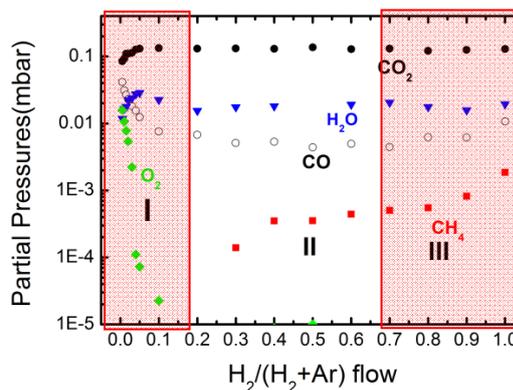Fig. 2: Carbon monoxide measured by both QMS and IR-TDLAS showing good agreement.

Fig. 3: Steady-state gas phase composition during the CO_2 reduction. The three different regimes can be distinguished and are outlined in the text.

3.   Results and Discussion

Fig. 3 shows the stable products measured for different Ar/H_2 gas mixtures. C_2H_y hydrocarbons were in most cases absent while H_2O and CO turned out to be the main stable products. No oxygenates were observed in the products. Three distinct regimes can be observed. In the first regime (I), where usually Ar^+ ions are dominantly formed, a high dissociation of CO_2 of up to 50% is observed (figs. 2+3). Charge exchange between CO_2 and Ar^+ ions followed by dissociative recombination of CO_2^+ - as observed for other molecular gases in this type of plasma - may be the dominant process. Ar^+ is quenched quickly with addition of few percentage of H_2 to the flow [5]. CO_2 dissociation levels off while the formation of O_2 is hampered (regime II, fig. 3). This regime also shows gradual methanation and the CO concentration remains at low level. In regime III the chemistry is mainly driven by H radicals which leads to a slight increase in methane production.

From the aforementioned trends it was concluded that the plasma-assisted CO_2 hydrogenation (also) essentialy requires a gas composition similar to synthesis gas (CO/H_2). This hypothesis was corroborated by experiments performed with CO in place of CO_2 where the production of CH_4 starts at much lower addition of H_2. Additionally, hydrocarbon yields up to 25 % were achieved whereas this value was 10 times lower during CO_2 experiments (fig. 3).

A significant difference in the gas composition, when different surface materials were used, was only evident for a Cu surface. However, in contrast to conventional catalysis the CO concentration was reduced and so was the CH_4 formation. On the other hand, carbon deposits were clearly visible on the surface. Hence, plasma-catalysis may certainly provide another handle over achieving higher effeciency in fuel formation. However, the selection of suitable catalytic materials in a plasma environment needs further work.

References

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