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ABSTRACT

The synergy between catalysis and plasma chemistry often enhances the yield of chemical reactions in plasma-driven reactors. In the case of CO$_2$ splitting into CO and O$_2$, no positive synergistic effect was observed in earlier studies with plasma reactors, except for dielectric barrier discharges, that do not have a high yield and a high efficiency. Here, we demonstrate that introducing metal meshes into radio frequency-driven plasma reactors increases the relative reaction yield by 20%–50%, while supported metal oxide catalysts in the same setups have no effect. We attribute this to the double role of the metal mesh, which acts both as a catalyst for direct CO$_2$ dissociation as well as for oxygen recombination.

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I. INTRODUCTION

Using CO$_2$ as a renewable carbon feedstock for making chemicals and fuels is essential in the mitigation of climate change and with it for meeting the goals of the Paris Agreement. Converting CO$_2$ into solar fuels is an important step along this pathway. There are several ways of doing this, including thermal catalysis, electrochemical conversion, and plasma conversion. The last option is especially attractive, as plasma reactors have the promise to exclusively excite the CO$_2$ molecules vibrationally, thus reducing the overall thermodynamic penalty incurred when using CO$_2$ as a reactant. Several studies report that CO$_2$ and/or CH$_4$ can be converted by plasma into CO and syngas (a mixture of CO and H$_2$), which can be used as feedstocks by the chemical industry. Most of these studies use Dielectric Barrier Discharge (DBD) reactors. However, the conversions and energy efficiencies from DBD reactors, in particular for CO$_2$ splitting, are low (conversion ∼30%–45%, efficiency ∼5%–10%) even in the presence of catalysts. Microwave (MW) and radio frequency (RF) plasma can yield higher conversions and energy efficiencies of up to 50%. For such plasma technologies, little is known about the effects of catalysts. Spencer and Gallimore studied the effect of adding a catalyst to a high-power RF discharge and found it to be negative.

Building on our experiments with plasma-assisted reactions, we approached the problem of high-yield CO$_2$ activation in plasma reactors from another angle. Recent experiments on NH$_3$ production from N$_2$ and H$_2$ using RF plasma show that using a catalyst can increase the ammonia yield. This is due to the introduction of different types of metal meshes in the RF reactor. The authors attribute the catalytic effect to the formation of a thin metal film on the reactor wall. The catalytic action mainly takes place in the film. From...
Numerical simulations, the authors concluded that dissociation of N₂ and H₂ is induced by plasma, while the formation of the NH₃ product occurs via a Langmuir–Hinshelwood reaction on the catalyst surface.²⁹ In other studies on ammonia synthesis by plasma, catalysis also significantly increases the product yield. The increased yield was attributed to catalysis on surfaces. Several reactor types were used in these studies.³⁰⁻³⁷ Encouraged by the results reported for ammonia synthesis, we studied the effects of metal meshes on CO₂ conversion in RF plasma reactors. We found that introducing a pure metallic mesh considerably enhances CO₂ dissociation. The present work has a very strong focus to study the increase by catalysis of the CO₂ conversion in a RF plasma reactor.

CO₂ dissociation at surfaces was studied under low pressure and surface science conditions using ultrahigh vacuum (UHV).³⁸⁻⁴⁰ Dissociative adsorption of thermal CO₂ on low index faces of Cu or Ni single crystals is unlikely (1% level or below). Translational activation of CO₂ increases its probability to dissociate to 10%. However, in a non-thermal plasma, translational activation is unlikely because the neutral gas is close to room temperature. It was found that on stepped Cu surfaces dissociation of CO₂ does occur in UHV.⁴¹⁻⁴³ In fact, CO₂ dissociation does occur on a variety of stepped metal surfaces (but not on metal oxides).¹²,¹³ Dissociation and dissociative adsorption may be promoted by vibrational excitation. Modeling of CO₂ plasma using DFT calculations of dissociative adsorption of CO₂ on Ni demonstrates that vibrational excitation assists dissociation into CO and adsorbed oxygen atoms (Oads).⁴⁴,⁴⁵ A recent theoretical study indicates that surface-induced dissociation can be enhanced by adding a strong electric field of typically 10 V/nm.⁴⁶ Such field strengths are possible in electrochemistry but not in a plasma reactor.

The interaction of atomic oxygen with metal surfaces was studied extensively. Several phases of surface oxides are formed on Cu(100) and Cu(110) before bulk oxidation, see, e.g., Refs. ⁴⁷⁻⁴⁹. For Ag and other metal surfaces, Killelea and co-workers recently reported detailed studies in which the surfaces are exposed to atomic oxygen directly.⁵⁰⁻⁵² A number of surface geometries or phases depending on the conditions are again observed in scanning tunneling microscopy. This work demonstrates that the interaction of atomic oxygen, that is present in plasma reactors, can initiate a complex set of reactions on pure metal surfaces. Exposing metals to atomic oxygen leads to a self-limiting growth of a surface oxide. There is no oxidation of the bulk after the formation of a thick surface oxide.⁵³,⁵⁴ There are no studies in the literature to our knowledge in which metal oxides are directly exposed to atomic oxygen.

Besides the classical catalytic dissociation of CO₂ in a Langmuir–Hinshelwood mechanism, surface reaction also may induce dissociation, as proven by Yao et al.⁵⁵ They showed that dissociation of CO₂ on surfaces can occur upon impact, when the translational energy of the ions is around 20 eV or higher. However, non-thermal RF plasmas contain very few positive ions, so this process is unlikely to yield large amounts of CO.

Here, we study the role of catalysts in CO₂ splitting driven by RF plasma. We find that the introduction of purely metallic meshes enhances the dissociation of CO₂, therefore acting as catalysts. XPS and SEM analysis demonstrate that there is no uptake of oxygen by the metal. We propose that the metal enhances the recombinative desorption of O-atoms to yield O₂. In addition, metallic meshes enhance the dissociation of vibrationally excited CO₂, while metal oxides supported on inert materials are inactive under the same conditions.

II. EXPERIMENTAL CONFIGURATION

A. Reactors

Two sets of experiments were carried out in cylindrical RF plasma reactors described earlier.²⁴⁻²⁶,²⁸ Details of the wide tube plasma reactor configuration are given in the supplementary material (see also Fig. S1). Briefly, the plasma is confined by a quartz tube, surrounded by a six-turn coil producing a Radio Frequency Inductively Coupled Plasma (RF-ICP). The composition of the exhaust gas produced in the reactor is measured online, in real time by a quadrupole mass spectrometer (QMS). No attempt was made to optimize the energy efficiency of the reactor as the purpose of this work is to study catalytic effects on the CO₂ splitting process.

Two versions of plasma reactor setups were used. The differences between the wide tube plasma reactor vs the narrow tube plasma reactor are mainly in the actual size of the reactor tubes and the mounting geometry of the catalyst. Both setups are described in detail in the supplementary material (Figs. S1–S6).

B. Catalyst preparation, thermal reactions, and characterization

The supported catalysts were prepared by wet impregnation as described in the supplementary material. These oxide catalysts were introduced into the plasma reactor by two different methods, as described in the supplementary material.

A different type of catalytic material was also tested. It consists of commercially available purely metallic meshes that also can be seen as foam based meshes with high transparency. This Cu mesh is put either in the inner tube inside the plasma region between the windings of the RF coil or downstream behind the coil.

The thermal catalytic tests were carried out under atmospheric pressure in an automated six-flow parallel reactor system. It consists of six individual fixed-bed quartz reactors located in a furnace.³⁸ The reactants and products were analyzed with a gas chromatograph (Interscience microGC, with FID and TCD detectors).

The supported catalyst pellets inserted in the catalyst holder were in situ reduced via Ar–H₂ plasma (i.e., 20% H₂:80% Ar plasma with a total flow of 250 sccm). The Ar–H₂ plasma for the reduction of the catalyst pellets lasted 1 h where the input power was constant at 300 W. The pressure in the narrow tube plasma reactor was 100 Pa.

Details on the characterization techniques of the catalysts, the catalyst holder and the metal mesh capsule are presented in the supplementary material.

III. RESULTS AND DISCUSSION

Results obtained with the wide tube plasma reactor are shown in Fig. 1. Plotted is the CO₂ conversion toward CO, defined by I(COout)/I(CO₂, in). Here, I(COout) is the corrected CO QMS intensity measured at the exhaust of the reactor and I(CO₂, in) is the...
CO₂ intensity measured with the plasma off, i.e., the incident CO₂ flow. It should be noted that the conversion into other products such as carbon or C₂ was not observed and is very low. The CO₂ conversion is plotted as a function of the specific energy input: the RF power per molecule in the flow. This quantity is varied by varying the RF power or the CO₂ flow. Experimental conditions are given in Fig. 1. It should be noted that in the case of a changing CO₂ flow, the CO₂ conversion scales with the specific energy input.²⁵ This is apparent from the fact that the results for an empty reactor are the same for flows of 100 and 200 sccm CO₂. Therefore, the results with metal meshes can be directly compared to results for supported catalysts measured at the same specific energy. When plasma alone was tested (i.e., a CO₂ plasma in an empty plasma reactor without catalyst), the CO₂ conversion was around 30% at a specific energy input of 20 eV. The conversion was higher when placing the copper mesh downstream in the plasma region. Remarkably, an even higher CO₂ conversion was obtained when the Cu mesh was placed directly within the plasma field (see the green triangles curve in Fig. 1). At a specific energy input of 20 eV, the CO₂ conversion reached 50%, showing a synergistic effect of plasma and metal mesh in enhancing CO₂ splitting.

A. Supported oxidic catalysts

We now focus on the conversion obtained with supported oxide catalysts. In Fig. 1, we can see that when using AgO/Al₂O₃ coated monolith, NiO/Al₂O₃ coated monolith, NiO/Al₂O₃ coated tube, and Al₂O₃ coated monolith in the wide tube plasma reactor, the CO₂ conversion does not increase significantly compared to the plasma alone reference with no presence of a catalyst. For other combinations of metal in the oxide and support materials also, no significant reactivity is seen. One possible explanation is that most molecules in the flow do not interact sufficiently with the catalyst surface, especially in the case of the coated inner tube structure, see Fig. S2 in the supplementary material. To check if the way of introducing the catalyst in the plasma reactor is relevant, we carried out experiments with the narrow tube plasma reactor. Here, the plasma flow percolates through the catalyst bed inside the catalyst holder, held in place between two Cu meshes perpendicular to the plasma flow. In this way, the catalyst is in close contact with the plasma flow. The results are shown in Fig. 2.

Figure 2 shows that adding Cu meshes to the empty narrow tube plasma reactor increases the CO₂ conversion by a factor of about 1.2. Adding MgO pellets in the catalyst compartment of the catalyst holder between the Cu grids decreases the CO yield with respect to the empty metallic cell within the catalyst holder but increases the CO yield with respect to the empty narrow tube plasma reactor. This indicates that MgO is slightly catalytically active. Adding the 5 wt. % Co₃O₄/MgO supported catalyst only decreases the CO₂ conversion with respect to CO₂ plasma at the MgO catalyst in the narrow tube plasma reactor. This might be due to the deactivation of active sites on the clean MgO catalyst by
deposited Co. Other Co/MgO supported metal oxide catalysts with a higher metal content show similar results. From the data in Figs. 1 and 2, we conclude that adding a supported metal oxide catalyst (MOx) does not enhance the CO yield by RF-ICP. The experiments with the narrow tube plasma reactor show that the lack of enhancement cannot be due to limited interaction between catalyst and CO2 plasma flow.

In this set of experiments, we determined the temperature of the metal grids using a pyrometer. The highest temperature observed was 420 °C at a power level of 350 W. Such temperatures are sufficient to remove hydrocarbon contamination from the surfaces but are far too low to induce thermal decomposition of CO2.5,11

Operating the RF-ICP at 1000 Pa does not introduce significant changes in the CO2 conversion. Therefore, the lack of enhancement regarding the conversion of CO2 for oxide catalysts cannot be explained by the low operation pressures of typically 100 Pa. For a unimolecular dissociation reaction, the low pressure should not be important. In this case, the only function of the catalyst is to break an O–CO bond, which is independent of pressure. However, vibrational excitation of the CO2 may be required to enhance the dissociation. In the case of a metallic catalyst, the excited molecules will directly impinge on the metal and dissociate. In the case of a supported catalyst, the active metal will be inside the metal oxide structure. In this case, the excited CO2 will be quenched by the oxide before it can interact with the active sites inside the catalyst. Another possible reason could be that the metal oxide catalyst has not been properly reduced. We have reduced the metal oxide catalyst by exposure to an Ar–H2 plasma. This plasma-driven reduction contains atomic H, which should be very efficient in reducing the metal oxide. However, no effect of reduction of the catalyst was observed. Therefore, we conclude that supported metal oxide catalysts do not enhance CO2 dissociation in a RF plasma.

Different from thermal catalysis, the total (internal + external) surface area of our supported catalysts is most likely not relevant. We have found from BET measurements that our surface areas for N2 are typically 200 m²/g. Typical pore sizes are below 50 nm. Detailed information is added in the supplementary material (Table S1). A plasma cannot penetrate these nm-size pores, and vibrationally excited molecules are expected to be quenched very quickly when entering the pore.59 Without plasma, all these materials are completely inactive. See, for instance, studies on thermal CO2 dissociation with different catalysts, but where in all cases temperatures exceeding 600 °C are required to run a CO2 decomposition reaction.60–62 So, the plasma should not be quenched in a pore before interacting with the catalyst.

### B. Metal mesh catalysts

By contrast to the Co3O4/MgO supported catalyst, inserting metallic catalysts like Cu meshes into the RF reactor does increase the CO yield. For the experiments with the wide tube plasma reactor, the metal meshes of Cu do increase the CO2 conversion by a factor 1.2 when the metal is behind the RF coil. The increase is higher by a factor of 1.8 when the metal mesh is between the windings of the RF coil as seen in Fig. 1. Similar effects are seen in the narrow tube plasma reactor in Fig. 2. An enhancement of the CO2 conversion is seen for two metallic grids by a factor 1.2.

Conversion close to 60% was obtained at a specific energy of about 24 eV. In conclusion, we observe that metal oxide supported catalysts do not enhance the CO2 conversion at all, while purely metallic structures significantly enhance the CO yield. The precise amount of the enhancement depends on the morphology of the inserted metal and its position in the reactor.23,25,28 We tested Cu, brass, Co, and Fe, and the results are that inserting any of these metals in a CO2 plasma will enhance the yield of CO. This is an encouraging observation, and it offers within RF-ICP new opportunities for research in plasma-driven CO2 splitting.

We also used the same metallic mesh catalysts in a thermal reactor.7 There was no CO2 conversion detected at all for partial CO2 pressures of 20 000 Pa and temperatures up to 900 °C.

To get more insight into the catalytic behavior of the metal meshes, they were examined by SEM and XPS. The SEM images in Fig. 3 show that surface modification has occurred on the CO2 plasma exposed Cu grid. Especially, Fig. 3(c) shows the zoomed-in SEM image; after CO2 plasma exposure, the surface of the metal grid has become rough. The roughed Cu oxide area contains sharp angled shaped crystal structures. EDX analysis of the images shows the presence of Cu and O uniformly distributed over the sample. The formation of these structures can be caused by the bombardment of the surface by low energy plasma ions.63

Figure 4 shows the XPS spectra of fresh and plasma exposed metal meshes. In the C 1s spectra [Fig. 4(a)], the intensity of the peak is lower for the plasma exposed Cu mesh compared to the fresh one. This is due to the removal of carbonates on the metal grids by the CO2 plasma. This decrease in the amount of carbon also shows that in the CO2 dissociation no elemental carbon is formed, which is deposited on the metal grids in the reactor. We attribute the C signal observed for the CuO and CuO powders to ambient carbon and residual carbonates in these powders, which were analyzed as received. X-Ray Diffraction (XRD) analysis of the
The results presented in Sec. III can be summarized by

- Conversion into CO + O₂ does not occur in thermal catalysis at partial CO₂ pressures of 5000 Pa and up to 900 °C.
- In a RF-ICP reactor, there is a dependence of the CO₂ conversion on reactor geometry and specific energy. Conversions of more than 50% can be observed in an empty catalyst holder (equipped with metal meshes and without catalyst pellets) inside the narrow tube plasma reactor at a specific energy of about 22 eV (Fig. 2).
- Inserting a metal grid or mesh increases the conversion rate significantly.
- Inserting a metal oxide supported catalyst does not increase the conversion rate.

The absence of thermal CO₂ conversion under 1000 °C is not surprising. The decomposition reaction is too endergonic to run at these temperatures. vibrationally excited CO₂ will dissociate more easily at Ni surfaces. Such excited molecules are absent in a thermal gas. Therefore, if any dissociation is observed in a plasma reactor, with or without catalyst, this is driven by a non-thermal plasma action.

The conversion scales with the amount of energy introduced into the plasma per molecule flowing through the plasma channel. We have observed previously that by diluting the CO₂ in Ar, very high conversions (exceeding 90%) can be obtained. The same conversion is seen when increasing the specific energy beyond 1000 eV. However, consequently the energy efficiency will be for both cases too low for any practical application. Insight into the plasma dynamics can be obtained from such experiments, for instance, that the electron temperature of the plasma should be kept low.

Inserting a metal mesh in our plasma reactors does increase the CO yield by at least a factor 1.2. There are several possible explanations for this. At first, plasma parameters may be changed by the presence of the metallic object. However, the visual inspection did not point to any change in the intensity of emitted light or the flow pattern. Optical emission spectroscopy data, shown in the supplementary material, show the same spectrum as seen for a RF CO₂ arc without any catalyst. So, we conclude that a surface reaction on the surface of the mesh is responsible. The first possibility we considered is that the mesh acts as an oxygen scavenger. It is well known that recombination of CO + O + M → CO₂ is a significant loss channel for CO₂ conversion. If the metal would absorb the reactive O-atoms, they are not available for recombination, thereby increasing the conversion. This would lead to a weight gain of the metal structure but this is not observed. Also, in our XPS analysis, concerning Fig. 4 the most important observations are a loss of C and O upon exposure to the metal. Our SEM images show a restructuring of the metal, similar to that of thermal oxidation of, for instance, Cu. We conclude that the surface of the metal mesh re-structures but it does not take up a large amount of oxygen. This is corroborated by the well documented fact that the diffusion of oxygen into a Cu lattice is limited.

Although XPS analysis shows that the surface is oxidized, this does not imply that the surface is oxidized during operation. During the transport of the metal from the reactor to the XPS machine, the sample is exposed to air for a long time and will be
The SEM picture in Fig. 3(b) shows that the surface has restructured so the surface may have been (partially) metallic if oxygen is actively removed by the plasma and recombination via $O + O \rightarrow O_2$. This can be due to the direct adsorption of free O-atoms at the surface of the metal or metal oxide. This will lead to a buildup of an oxygen atom coverage on the surface. Since in-diffusion of O-atoms is limited, the adsorption of O-atoms will lead to recombinative desorption, resulting in the ejection of $O_2$ molecules. The reaction can be both a Langmuir–Hinshelwood type or an Eley–Rideal reaction. Recently, it was demonstrated that N-atoms created in a plasma are very efficient in removing O-atoms from a Ru surface by an Eley–Rideal reaction. The $O_2$ molecules formed in turn can be dissociated in the plasma but the rate is rather low and they will block recombination of CO + O leading to CO$_2$. So, the presence of the metal structure acts as a catalyst for molecular recombination to $O_2$. This process keeps the O-coverage rather low and agrees with our XPS, XRD, and SEM studies, demonstrating the growth of a surface oxide without loss of O-atoms into the bulk. We note again that the O-atoms are available in the gas phase, in contrast to a thermal catalytic reaction. In addition, the SEM images show erosion and restructuring of the surfaces by the plasma. It suggests that the solid metal catalyst is stable in a dynamic equilibrium with the plasma, while a supported metal oxide catalyst is destroyed.

Another possibility for metal-induced CO yield increase is catalytic dissociation of CO$_2$ on metal surfaces (see Fig. 5). We have indicated that at least part of the surface will be metallic during operation. The SEM pictures show that the surface is very rough and will contain many steps, facilitating CO$_2$ dissociation. It is known that CO$_2$ may dissociate upon the impact of a vibrationally and translationally excited molecule on a metal. This is evident from an inspection of potential energy surfaces for CO$_2$–metal interactions. This will lead to O-atoms bound to the surface and weakly bound CO will desorb. Although experimental and theoretical studies have focused on interactions at clean metal surfaces, this option is likely. Another option to enhance CO$_2$ dissociation is field induced dissociation, which was explored in a theoretical study. The SEM images show that sharp structures develop on the metal meshes during operation. However, it is unlikely that these structures can directly lead to dissociation of CO$_2$ because the field strength required for field induced dissociation is very high.

There is a strong similarity of the experimental results of all supported metal oxide catalysts in spite of their different physicochemical properties such as adsorption properties. Therefore, it is likely that a supported Cu catalyst would not enhance CO$_2$ conversion either. In fact, Spencer and Gallimore have done experiments with Rh deposited on a monolith. Only a decrease in CO$_2$ conversion was observed, which demonstrates that only solid metallic catalysts have a clear catalytic action. If we would have taken a real thick film (micrometer size thickness) on a bead one can expect that behavior to be similar to the solid Cu meshes. Beads with such a coating were unavailable to us.

For ammonia production in plasma, it was suggested that adding metal meshes leads to sputtering by the plasma of metal films on to the quartz walls of the reactor. We consider this to be unlikely in the present case, because the onsets for CO formation in the QMS are very sharp, whereas an induction time can be expected if a catalytic film has to be built up in the process. This induction period can be seen in Ref. 29.

Finally, looking at the plasma, we see that not all plasma particles come in contact with the catalyst. The mean free path is small (less than 0.1 mm) so diffusion away from the flow direction will be limited. Designing structures with better contact between metal mesh recombination catalyst and flow may improve the conversion of CO$_2$ further.

Strong synergistic effects between plasma and catalysts have been found for DBD plasma. We attribute the absence of such strong effects in the present work to the very different natures of the plasma for RF and DBD. The DBD consists of very inhomogeneous local high energy discharges. In the DBD, the excitation of molecules is done by fast electrons, whereas in our case, slow electrons drive the plasma. This leads to different active plasma species in the case of the two plasmas. Also, as demonstrated in a recent paper, localized heating of the catalyst by the plasma could contribute to the synergy. Finally, there is a big difference in pressure. DBD’s work at atmospheric pressure, whereas the RF reactor works at a factor of 100 lower. Therefore, it is interesting to increase the pressure in the RF or quite similar MicroWave plasma to atmospheric. This has been done by Spencer and Gallimore, where a monolith was also used. However, these authors have not seen any catalytic enhancement. These are absent in the RF plasma for supported catalysts.

IV. CONCLUSION

We show that placing metallic structures such as meshes into the RF plasma reactor increases the CO$_2$ conversion by a factor of

FIG. 5. Diagrams showing the proposed difference between the interaction of CO$_2$ (left panels) and O-atoms (right panels) with a metal mesh (upper panels) and a metal oxide catalyst (lower panels). It shows that metal meshes break the CO–O bond and allow recombinative of adsorbed atomic oxygen whereas for the metal oxide catalyst this is less probable.
1.2–1.8. The XPS analysis indicates that the metal does not absorb a significant amount of oxygen but rather acts as a recombination catalyst toward molecular oxygen. In this way, the recombination of oxygen atoms and CO to form CO₂ is suppressed in the plasma. In addition, the metallic surface of the Cu mesh will contain many CO–O bonds. Both mechanisms are much less likely on an oxidic catalyst. The mechanisms are summarized in Fig. 5. Although the metal-induced enhancement was demonstrated in our RF-ICP reactor, metal-induced enhancement will be active in other types of plasma reactors which provide primarily high energy efficiency, such as microwave plasma and thermal arc plasma. These results open a pathway to efficient plasma reactors for CO₂ conversion.

SUPPLEMENTARY MATERIAL

See the supplementary material for experimental setup configurations, catalyst preparation, catalyst testing by a thermal reactor, catalyst characterization, and optical emission spectroscopy of the plasma.

AUTHORS’ CONTRIBUTIONS

E.J.D. and M.R.-L. contributed equally to this paper.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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