

CO₂ reduction reactions: general discussion

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Jonathan Albo opened the discussion of the paper by Gabriele Centi: Our group recently found the formation of methanol (as the major CO₂ electro-reduction product) at Cu-based surfaces in a similar two-compartment cell configuration.¹ Actually, the production of methanol at Cu-based electrocatalysts is commonly reported in the literature.² How do you explain (in terms of reaction mechanisms) the formation of acetic acid and only trace amounts of methanol in your liquid phase system?

1 J. Albo, A. Saez, J. Solla-Gullon, V. Montiel, A. Irabien, *Appl. Catal. B-Environ.*, 2015, **176**, 709-717.

2 J. Albo, M. Alvarez-Guerra, P. Castaño, A. Irabien, *Green Chem.*, 2015, **17**, 2304-2324.

Gabriele Centi replied: We believe that due to the type of electrodes we use (gas diffusion electrodes, with the electrocatalyst at close contact with the Nafion membrane), methanol forms but further reacts under these experimental conditions to give acetic acid, with the tentative mechanism reported in the paper.

Jonathan Albo continued: Could the differences in pH explain the productivity and selectivity variations between the liquid and gas phase CO₂ electroreduction?

Gabriele Centi responded: No, we do not believe it is a problem of pH, but rather of effective concentration of CO₂ at the electrocatalyst surface. It is the higher concentration in the gas-phase approach (as it is not limited from the

solubility and electrical double layer) which explains the formation of products > C1.

George Dowson queried: During the description of the proposed mechanism for the formation of acetic acid during your reaction, you suggest that methanol, the product of formaldehyde hydrogenation, is not observed, however the very next section describes how the methanol may essentially be being scavenged by formic acid in the generation of methyl formate. Would it not therefore be more reasonable to conclude that only some of the formaldehyde is converted into acetic acid, with the rest being converted to methanol for methyl formate production?

Additionally, in your paper, the reaction profiles in Fig. 5 suggest that the methyl formate is being consumed during the latter stages of the reaction. As this coincides with the increased formation of acetic acid in both cases, could this indicate that perhaps methyl formate is being consumed to form acetic acid? This reaction is known to occur in the literature, both *via* insertion of CO and by rearrangement on the metal surfaces. Finally, is any methyl acetate observed as a product?

Gabriele Centi replied: Yes, we believe that methanol and methyl formate further react under our experimental conditions to produce acetic acid. This is one of the possible mechanisms of C-C bond formation during the CO₂ reaction, and also may be of interest in terms of application. We are currently analyzing this mechanism in more detail, as it is currently only in a tentative stage. Methyl acetate, on the contrary, is currently only observed in minor amounts. For now, we have focused our attention on the main products.

Csaba Janaky asked: Could you comment on the amount of water transferred with H⁺ ions through the Nafion membrane (electroosmotic water drag)? What is the temperature in the cathode side in the "gas-phase" reactor?

Gabriele Centi answered: We feed, in the gas phase configuration, some water vapor together with CO₂. If the electrocatalytic side joins with a photocatalyst, water vapor is also coifed on the other side (for the chemical reported in the paper, a water solution is present on the cathode side). The water feed (on the anode side, together with CO₂) is necessary to maintain a wet Nafion membrane and (likely) has a thin water film over the electrocatalyst (in contact with the Nafion membrane). This helps in enhancing the H⁺ surface transport.

Csaba Janaky enquired: You mention the role of the O-functions of the carbon nanotubes on the electrocatalytic effect towards CO₂-reduction. I don't know the exact potential of your working electrode, but it is very likely that at the applied cathodic potential, these O-functions are electrochemically reduced. Can you comment on this issue?

Gabriele Centi replied: After the oxygen functionalization of CNT (with HNO₃) there is a thermal annealing to remove less stable oxygen species. The remaining oxygen functionalities are stable in the potential range studied.

Gonçalo V. S. M. Carrera commented: Unlike the gas phase cell configuration, when the reaction is carried out in aqueous electrolyte the products are mainly carboxylic acids. I wonder if this difference in behaviour is caused by the stabilization of the carboxylates by water in relative alkaline medium, as this type of stabilization is not possible in a gas phase cell configuration. Of course, other parameters influence the reaction outcome; nevertheless the results in my opinion suggest this explanation. What is your perspective on this issue?

Gabriele Centi responded: In our experiments, we use gas diffusion type electrodes, thus the electrocatalyst is at close contact with Nafion both in the liquid and gas phase operations. Under these conditions, the environment close to the catalyst is strongly acidic, which also determines the type of products we observed. However, I agree that under different pH conditions, there may be a different reaction path and type of products.

Michael North extended the discussion by addressing both Alexander Cowan and Gabriele Centi: How do the electrochemical processes described in each of your papers cope with being turned on and off repeatedly? The ability to cope well under these conditions is essential if they are to be linked with renewable energy.

Alexander Cowan answered: This is an interesting point. Our electrochemical system is stable if left in the dark, turned off, and it can be used for several cycles. Indeed most electrochemical systems for CO₂ reduction that I am aware of are able to operate intermittently. In some of the electrodes presented here we actually find that a period of in-operation can be advantageous as it provides a period for the CO₂ concentration at the electrocatalytic sites to increase - we believe that the diffusion of CO₂ through the polymer is one of the limiting factors in the experiment.

Gabriele Centi replied: The fixed costs of plants in electrochemical processes is typically over 50%, thus continuous operations are necessary to decrease amortization costs. When coupled with renewable energy sources (except for in few cases, such as hydropower), a storage of electrical energy would be necessary. Therefore continuous operations (with adequate energy storage) are requested to minimize the costs and the device should not operate with a fast on/off switch.

Ian Ingram addressed Alexander Cowan and Gabriele Centi: High Aspect Ratio Nanoparticles (HARNs), and carbon nanotubes in particular, are the subject of growing concern and regulation because of their toxicity. Konarka, an organic photovoltaics company, went out of business in 2012 partly because their process used large quantities of chlorobenzene and other toxic solvents which proved to be very expensive to handle safely in a production environment, even though they are of very little concern in the research laboratory. Could you both comment on the viability of using carbon nanotubes at scale in an industrial process, given the concerns about their safety?

Alexander Cowan responded: We note that CNTs are already in use in several industrial processes, however, this is of course not sufficient evidence for us to propose that they can be safely used on very large scales. A full assessment of the

health impacts of CNT manufacture would be required if these materials, developed for fundamental studies, were to be deployed on a large scale. Of relevance to this question is the stability of the polymer/CNT films, which is relatively good. We do not see evidence for CNT loss into the electrolyte which would decrease the potential exposure to CNTs.

Gabriele Centi answered: Health and safety aspects are clearly critical and definitively we should avoid using toxic solvents or dangerous materials. However, the toxicity of CNTs has often been overestimated, being made on materials which are not those in practical use. By themselves, CNTs are not toxic, for example they are used for drug delivery, but it is the surface radical-chemistry or the adsorption of some organic compounds which may make them problematic. However, in practical materials where high conductivity is necessary, these aspects are not different from those of many other materials used to prepare electrodes.

Csaba Janaky commented: When discussing the scalability of CO₂ electrolysis, one should consider that water electrolysis (H₂-evolution) was already performed on an industrial scale in the USA in the 1970s. This shows that the technology itself can be scaled, it's just that more research is needed to find efficient and selective electrocatalysts.

Gabriele Centi responded: Yes, we agree. There are also large electrochemical processes in operation (besides Cl₂, adiponitrile, *etc.*), even if the technology is somewhat different. However, the key problem of cost should be addressed by increasing the productivity of the electrodes, *i.e.* by developing 3D-like electrodes.

Peter Styring addressed Gabriele Centi and Alexander Cowan: I agree with the good point raised by Professor Centi regarding the use of 3D electrodes. Related to scalability, we've talked about the materials but what about the process itself? Cells operate in a laboratory environment, but how do you scale out into tonnes of product?

Gabriele Centi replied: The cost of the cell is the critical element in electrocatalytic reactions, and it is therefore necessary to increase productivity per surface of the electrode in order to decrease the costs to the levels required for industrial exploitation. Developing 3D-like electrodes is therefore a priority in order to proceed in this direction. There are problems of scalability, related to homogeneous utilization in large electrodes, but these technological problems are already solved in part for other applications.

Alexander Cowan answered: This is an interesting point. I would like to start by noting that even at the laboratory scale significant technical challenges still need to be overcome. Overpotentials for many systems are still larger than many would consider practical, furthermore, obtaining selectivities towards a particular CO₂ reduction product is challenging, especially when aqueous electrolytes are used. Finally, the role of potential contaminants in CO₂ is very rarely even studied and this must be addressed if we are to utilise industrial CO₂ sources. However, work is underway to address these problems and the potential of this approach is

enormous. I can think of no insurmountable reason why the sort of materials discussed could not be scaled up to these levels. As discussed, particular attention will need to be paid to the development of 3D high surface areas that are able to maintain suitably high current densities, and additional effort will be required to develop suitable reactor designs. Many very high tonnage electrochemical synthesis processes already exist which does provide confidence that such issues can be addressed.

Niklas Meine asked: In industry, safety is one of the major issues, and for this reason we are training people all around the world to guarantee very high safety standards. With respect to electrochemical cells, I wonder how you consider up scaling this process, and how the choice of electrode materials is therefore considered?

Gabriele Centi answered: I fully agree that high safety standards are important in the manufacture of electrodes. The electrode we discussed could be manufactured in quite a similar manner to those for fuel cells, by screen printing or similar methods that can also be automated to avoid direct contact of operators with the materials used. There are therefore currently no specific issues over their industrial manufacture.

Jonathan Albo remarked: The transport of protons across the membrane may be key in this process. Have you tested other ionic transport membrane materials for your system? I also wonder if you detected CO₂ reduction products in the anodic compartment (membrane crossover)?

Gabriele Centi responded: The transport of protons from the two electrodes is the element limiting productivity, and likely the transport from the photocatalyst to the membrane and from the membrane to the electrocatalyst (rather than across the membrane). While transport in the Nafion membrane is well established, the measure of the other two aspects is not easy, but it's greatly influenced by the reaction conditions (a thin liquid film is likely necessary) as well as the electrode characteristics (hydrophilicity). We feed CO₂ gas into both the anode and cathode compartments to avoid crossover.

Michael North commented: Regarding the benefits of water *versus* acetonitrile as the electrolyte, polar aprotic solvents, including acetonitrile, are on the EU REACH at risk list and could soon be banned. Furthermore, cyclic carbonates would be a suitable alternative to polar aprotic solvents, and have the advantage of being made from CO₂.

Michele Aresta replied: Organic carbonates are already used as support electrolytes, also if at a low volume. Their use is driven by the operation conditions: they cannot be used in acidic conditions as they would be converted back into alcohol and CO₂.

Peter Styring continued the general discussion of the paper by Gabriele Centi: A general comment on using acetonitrile is that it would have to be used in a closed system for safety reasons. However, there are economic concerns as it is

getting harder to source acetonitrile. Are there any other solvent systems that could be used that are more sustainable and safe?

Gabriele Centi responded: It is unlikely that an organic electrolyte like acetonitrile could be practically used in industrial operations under strong acid/base conditions. For this reason, our experiments are undertaken in aqueous solutions.

Michele Aresta enquired: Cu electrodes have been reported as being able to produce ethene from CO₂. Have you observed any formation of this alkene under your experimental conditions?

Gabriele Centi answered: No, we have searched for them but they were not detected, although traces of hydrocarbons were detected. Alkenes form at a high potential, in conditions where fast deactivation occurs.

Daniel Reed asked: Can you comment on the durability/life span of the cells, and do you have any special handling requirements for them? For example, are they brittle and do they require careful handling? Furthermore, how easily can they be scaled up?

Gabriele Centi responded: The cell itself does not have any special requirements for handling and the electrodes are quite robust. One of the problems, however, is that some of the product may remain adsorbed on the electrode, causing deactivation. One of the reasons for operating above r.t. is also to increase the rate of desorption of some of the reaction products from the electrode. Productivity is still the main issue, so we have not made long-term durability tests (beyond the usual lab scale). In terms of scale up there are no main concerns, at least up to 10 x 10 cm size.

Alexander Cowan replied: Once formed, the polymer/catalyst/CNT films are quite stable in the dark. The biggest issue regarding stability arises through operation at very high current densities, when excessive gas production can cause film rupture. We are working on new electrode designs in an attempt to alleviate this issue. One of the advantages of the proposed approach is its simplicity. Film fabrication involves preparation of a polymer/catalyst/CNT ink that is either drop-cast or doctor bladed onto the carbon electrode. The ability to simply print the electrodes appears to be quite amenable to scale up.

George Dowson continued the general discussion of the paper by Alexander Cowan: Comparing the previous literature performance of catalyst 2 against the performance you see post-immobilisation, there is an extremely large drop in turnover frequency. Since the higher voltage used in the non-immobilised form was partially responsible for this discrepancy, do you think that perhaps there is an economic argument that it is worth increasing the voltage used to achieve these higher frequencies? Concordantly, would it not be worth testing your catalyst system at the same and even higher voltages as used in the previous literature?

Alexander Cowan responded: Thank you for your question. One of the reasons for the lower turnover frequency here is that the numbers are based upon the inclusion of all of the Mn centres within the film, of these we know that only a small subset are actually electroactive, so if we quoted the turnover frequency for electroactive centres it would be far higher. You are also correct in noting that we study the system at a different applied potential. We agree that ideally the potential dependence of the turnover frequency would be fully reported in both cases so that the catalysts can be fairly compared, however, in our experiments we find that at higher applied potentials the selectivity towards carbon dioxide decreases and increased hydrogen production occurs. So although higher TOF may be achievable we believe that the system is of less interest at greater applied potentials.

Richard Heyn remarked: Rather than performing the electrochemical CO₂ reduction in water, is there any benefit to be gained if one could do the reduction on aqueous carbonate or bicarbonate species?

Alexander Cowan answered: Many studies are indeed carried out using bicarbonate based electrolytes as you suggest. We chose to use a phosphate buffer in this particular study as it simplifies the analysis of the control experiments done in the absence of carbon dioxide. During experiments using bicarbonate/carbonate, the electrolyte is a potential carbon source for reduction, which in practical applications may be advantageous, but for fundamental studies such as this one, complicates the analysis.

Katie Lamb communicated: I have a question regarding the manganese complexes used for electrochemical carbon dioxide reduction. I understand that many manganese complexes are light sensitive, and therefore many of the reactions in this study were performed in the dark. I was therefore wondering whether you see this as a potential hindrance in the future for these catalysts, and if this will also hinder potential industrialisation of these catalysts?

Alexander Cowan communicated in reply: The complexes employed are all handled in air and are quite stable in air. The question is completely correct that they are however very light sensitive and all experiments are carried out in the dark. This is a potential disadvantage. If this system, which is still at an early stage of research, was to be developed into an industrial process then the reactors and electrode preparation areas would have to be darkened.

William Webb communicated: I was wondering if you observed, or had measured, the leaching of your Mn system from the electrode into solution during the course of the reaction? Given that, if any leaching is present can you comment on the lifetime of the catalyst system within the electrode and do you know of a way to improve this?

Alexander Cowan communicated in response: This is an important question. We examine the electrolyte solutions after the experiment using a range of techniques (UV/Vis, NMR and electrochemically) to check for catalyst leaching. In all of the systems tested we have not observed any catalyst leaching. To date, the

longest experiments have been on the timescale of hours, and in the future if this system were to be developed further it would be important to also confirm that leaching does not occur over much longer periods (weeks to months).

Roman Michez communicated: In your paper, degradation of complex 4 and a decrease in the faradaic efficiency for the formation of CO is observed after long time electrolysis is performed in acetonitrile; apparently correlating to the low catalytic activity of this system. However, the same behavior can also be observed during experiments in which the potential of the reference electrode is not stable, due to the accumulation of the reduction products. Have you observed any indications of the stability or non-stability of the reference electrode you used?

Alexander Cowan communicated in reply: You make a good point that we did not fully consider in our original study. I agree that the CO produced may poison the Ag reference electrode that was used in the anhydrous acetonitrile experiments after prolonged electrolysis. Since our discussion at the meeting we have also carried out some studies using a Ag/AgNO₃ reference electrode. However, unfortunately we still find that the catalytic activity decreases during prolonged electrolysis experiments.

Jennifer Dodson addressed Gabriele Centi and Alexander Cowan: Separation of dilute concentrations of products from solutions can be a huge processing challenge. Can you comment on the process for recovery and separation of the products from your solution-phase electrocatalytic cells?

Gabriele Centi responded: The main reason for the electrolyte-less cell design we used (*i.e.* gas phase) is the possibility of easy recovery of the reaction products, which is energy intensive when it requires recovery from an electrolyte.

Alexander Cowan answered: In this study we produce CO and H₂ as the products. The relatively low solubility of CO in water means that the product can be recovered from the reactor headspace relatively easily. At the moment the headspace gas consists of CO, H₂, CO₂ and some water vapour.

Troy Manning asked: How sensitive are these electrocatalysts and electrocatalytic processes to the composition of the CO₂ feedstock? How do impurities in the CO₂ affect the process?

Alexander Cowan replied: Thank you for the question. The potential inactivation of the catalyst through impurities within the CO₂ feedstock is an important issue. For this early stage fundamental study we use a high purity CO₂ source where water is the primary impurity. Unpublished experiments from our lab indicate that our catalysts are also reasonably tolerant to the presence of oxygen. To date, we have not tested other likely impurities such as SO_x and H₂S, and this will be addressed in future work.

I would like to note that the use of a molecular electrocatalyst for CO₂ reduction may have distinct advantages when considering competition between the desired substrate and impurities. If the mechanism of catalyst inactivation

can be identified then it may be possible to design new synthetic analogues with improved tolerances.

Gabriele Centi responded: We do not use a rather pure CO₂, but one compatible with that which may be derived from fermentation processes or from biogas after methane recovery. We do not believe that there is a need to recover CO₂ from flue gases, in which case some of the impurities may become critical for stability.

Ian Ingram opened the general discussion of the paper by Peter Edwards†: The boiling points of propane and propene are very close together, which makes separation difficult and more expensive. As propene is a relatively low-value product, you are making it from a fossil source and your process is thermodynamically limited to low conversions. Is the significant environmental and economic cost of separation justified?

Xian Du answered: The physical separation of propylene from propane is of course challenging, as you point out, but there are indeed well-established (and indeed new) technological processes for such separations. Regarding the price, from alkane to olefin, the price can be nearly doubled as you can see from a quick check online: from the market in China, I can see that propane is currently 3500 CNY/ton while the price for propylene is 6000 CNY/ton. In industrial terms over large volume production, this is a highly significant difference indeed! Many industrial concerns are now aggressively targeting new routes to propene production and this has been a major focus for the King Abdulaziz – Oxford Centre of Excellence in Petrochemicals, which is a part-funder of this research. More robust, higher performance catalysts are now the subject of our own studies. The major aim of our research in this paper is to find a way to minimize the by-product and coke effect, and of course this method can be easily applied over other higher performance catalysts.

Eryk Remiezowicz asked: You produce carbon monoxide, what is your idea for the usage of this product of your reaction?

Xian Du responded: We haven't yet made a complete calculation, but of course both CO and hydrogen as the synthesis gas is the route to many fuels. Of course, at the very heart of our 'vision' is the use of thermal energy in so-called 'intermediate' temperature regimes (ca 3–500 °C), where such solar thermal energy is accessible by cheap, robust collectors rather than the high technologies required for say 1000 °C thermal collectors and processes.

Gabriele Centi asked: The system is essentially the combination of two reversible reactions, propane dehydrogenation and RWGS. How fair are the results with respect to equilibrium? Did you analyse the amount of H₂ formed to demonstrate that RWGS is shifting the equilibrium in propane dehydrogenation?

† Peter Edwards' paper was presented by Xian Du, University of Oxford, United Kingdom.

Xian Du replied: According to our modelled simulation results with Aspen Plus (a software which can calculate the composition of a gas mixture at equilibrium state), at 500 °C, propane will be totally converted, no propylene would be observed in the system, and only methane, CO and CO₂ are left. When comparing this result with the calculated results of traditional propane dehydrogenation (without CO₂, which should be around 30% at 500 °C), we can see that the ultimate equilibrium of the system was effectively shifted by CO₂ addition. It's not easy to confirm that H₂ production can immediately demonstrate the existence of RWGS. H₂ was generated *via* multiple side reactions (such as cracking of propylene), and therefore it'll be tricky to prove the RWGS by only calculating H₂ production. The ideal and most straightforward way, we believe, is to observe H₂O production; so far, the amount of H₂O is nearly immeasurable, and that's why we will try to scale up the reactor to seek more details on this.

Michele Aresta enquired: The use of CO₂ as the dehydrogenating agent has different properties (thermodynamics, rate, selectivity) with respect to dioxygen. Can you comment on the different behaviours of the oxidizing agents?

Xian Du answered: So far, besides CO₂, only O₂ and H₂O have been published as oxidising agents in dehydrogenation reactions. O₂ is effective in improving the propane conversion, but the selectivity is massively reduced due to the enhancement from O₂ in the complete combustion process. We are seeking a high selectivity of propylene even though the propane conversion would be sacrificed a little bit, so we think O₂ is simply too strong in this delicate system. H₂O has similar usage to CO₂, and the generated coke can be more easily removed when using H₂O rather than CO₂, thermodynamically. However, because H₂O cannot consume H₂, the equilibrium of propane dehydrogenation ($C_3H_8 = C_3H_6 + H_2$) can hardly be shifted. This is the main reason why we are using CO₂ as the mild oxidising agent, as a potential route to these solar thermal reactions, at these more accessible temperatures, rather than highly energy intensive dry reforming processes.

Kusman Dossumov communicated: Do you take into consideration the problem of catalyst carbonization during utilization of CO₂?

Xian Du communicated in reply: Actually we didn't consider it, and also we didn't see any evidence of carbonate species generated on the post-reaction catalysts.

James Comerford remarked: Why do you specifically use a 2 : 1 ratio of CO₂:propane in your paper? Have you tried varying this?

Xian Du responded: Yes we have; varying the ratio will apparently affect the conversions and selectivity due to the competitive adsorption between CO₂ and propane. However, in this paper, we maintain the ratio at 2 : 1 due to a similar ratio being published in other papers, and we would like to make the data comparable with others.

James Comerford asked: The total concentration of propane and CO₂ used in your system is low. As such, how much propene can be produced (*i.e.* grams per hour), considering that this paper is essentially focused at developing an industrial process? Additionally, does catalytic activity diminish after 300 min?

Xian Du replied: The production of propylene is indeed very low due to the experimental scale in our lab. Actually, as you can see in the paper, we were mainly focusing on how to inhibit by-product generation, and industrialisation, as in most of the schemes presented during this meeting, is about an outlook for the future. In fact, we do not think the production rate will be a big issue when we finally, successfully, scale this reaction up and proper heat and mass transfer are being carefully considered.

Michael North asked: Is CO₂ the actual oxidant for propane, or is the chromium oxide oxidising the propane and CO₂ reoxidising the chromium?

Xian Du answered: First, I don't think that CO₂ is the major oxidant for propane immediately, because nearly no conversion of propane can be observed if we don't use any effective catalyst. This result can also prove that the activation and dehydrogenation of propane can only happen on a suitable catalyst surface. Here we believe that CO₂ acts as a sacrificial agent of hydrogen, which is from the dehydrogenation of propane. CO₂ can also act as a reoxidising agent for the chromium catalyst. This needs further study.

Gabriele Centi opened a general discussion of the paper by Moti Herskowitz: Can you give a little more information about your catalyst, for example, whether there are supported iron particles segregated on the surface and which dimensions they have, as they are relevant for the FT reaction. Likely, it is not a true spinel phase, but a partially decomposed phase which then further transforms during the reaction.

Moti Herskowitz responded: The catalyst is a potassium promoted pure Fe-Al-O spinel Fe(II)(Fe(III)_{0.5}Al(III)_{0.5})₂O₄ in its as-prepared form. It is transformed after activation (carburization) and self-organization under the reaction conditions to iron carbide phases (mainly Fe₅C₂) and Fe-poor spinel phase with an Fe(III)/Al(III) ratio of 0.2–0.3. Their particle size is 20–50 nm. No metallic iron nanoparticles supported on these phases were detected in the steady state catalytic material (XRD, XPS, HRTEM-EELS).

Vera Meynen communicated: The experimental section, in your paper, indicates that the catalysts have only been calcined to 450 °C, while the TPD has been done up to 900 °C. Can you comment on the stability of the catalysts over the entire temperature profile of the TPD? Did you check the stability with a blank measurement with the same heating profile, with only a helium flow, or evaluate the presence of structural and/or physico-chemical changes after the TPD measurements?

Moti Herskowitz communicated in reply: The CO₂-TPD spectra were recorded within the temperature range of 100–900 °C in order to detect both weak and

strong basic sites. It is known that the reflections representing strong basic sites in Fe-oxide based materials appear at $>500\text{ }^{\circ}\text{C}$, as illustrated in Fig. 4. Heating of the K/Fe-Al-O spinel to $900\text{ }^{\circ}\text{C}$ did not change its structure (as measured by XRD), it only increased the size of the primary nanocrystals.

Vera Meynen communicated: Can you also indicate if degassing or stripping of the sample was done before the TPD measurement and if so, under which conditions they occurred?

Moti Herskowitz communicated in response: During the TPD measurements the catalyst surface was saturated with CO_2 at $40\text{ }^{\circ}\text{C}$, and before recording the TPD spectra the samples were heated in a He flow at $40\text{--}100\text{ }^{\circ}\text{C}$ for stripping.

Vera Meynen communicated: In your discussion of Fig. 4, you write that two additional CO_2 desorption peaks appeared centered around 550 and $850\text{ }^{\circ}\text{C}$. However, in my opinion there are 3 or even 4 peaks, as I see two additional smaller desorption peaks at 120 and 135 min (so in between the two peaks mentioned). Or are they not significant? Also, the first peak appearing in both the samples with 2 wt% and 4 wt% K content is not just one peak, as you have indicated in your paper, as it is asymmetric. Could you please correct this. Do they have any characterization towards physico-chemical information on which type of bonding sites these peaks coincide with?

Moti Herskowitz communicated in reply: Firstly, the level of CO_2 signal recorded during 120–135 min was significantly lower than that of the peaks mentioned in the article, and therefore they were indeed neglected. Secondly, the purpose of the CO_2 -TPD measurements performed in this section was to study the effect of potassium on the surface basicity of the catalyst, differentiating between weak and strong basic sites. As a matter of fact, the peaks of the three samples centered at $\sim 150\text{ }^{\circ}\text{C}$ are asymmetric indicating that there could be more than one peak. The total area was integrated providing the relative amount of weak basic sites, while the strong basic sites are found at $>500\text{ }^{\circ}\text{C}$. Finally, the characterization of the physico-chemical information is beyond the scope of this work.

Gabriele Centi enquired: What is the effect of K, for example how does it affect the product distribution? CO_2 has a stronger oxidizing effect with respect to CO and this typically affects the productivity. In your case, what is the productivity of the catalyst feed CO_2/H_2 rather than syngas (with a little amount of CO_2)? What is the role of Al in determining the catalyst performances, particularly the resistance to water inhibition?

Moti Herskowitz answered: The addition of potassium shifts the products distribution to higher carbon hydrocarbons. Productivity is lower for CO_2 hydrogenation compared with CO hydrogenation. Our spinel material is a good FT catalyst yielding almost complete conversion of CO. The role of aluminum in the composition of the K/Fe-Al-O spinel is to reduce the reduction-carbidization of iron at the activation step, thus controlling the amount of Fe-carbides. Excess Fe-carbides formed by activation of magnetite spinel in the absence of aluminum leads to deep carburization. As a result, a large amount of graphitic carbon is

formed due to oxidation of carbides at the catalyst self-organization stage. This significantly reduces the catalyst surface area.

Dina Churina communicated: 1) What is the stability of the catalyst for utilizing CO₂ as a chemical feedstock? 2) What is the cost of this catalyst?

Moti Herskowitz communicated in response: 1) The catalyst was tested for 500 h with no apparent deactivation. 2) The catalyst cost was not evaluated, however, given the low cost of the reagents and the simple preparation method, it is expected to be low.

Alexander Cowan remarked: Your paper states that hydrogen production for electrocatalysts is not competitive when compared to hydrogen from fossil derived resources. The use of biogas is instead proposed here – have you done a comprehensive analysis looking at the relative costs for biogas as well?

Moti Herskowitz replied: We are working on the economic evaluation of various sources of hydrogen, biogas among them.

Jennifer Dodson commented: To add to the discussion about biogas availability, I think this would be extremely limited as a feedstock. I wrote a recent overview on Anaerobic Digestion for the UK Parliament and we estimated that the country's biogas potential was less than 1% of the UK energy supply. This is already used directly as a fuel both for cars and electricity production.

Moti Herskowitz responded: Biogas availability is limited, but this may change in the future, certainly in specific locations where it could be an abundant feedstock.

Michael North opened the discussion of the paper by Koen Michiels: Did you see any evidence for phenol formation in your reactions, as there is some evidence in the literature for the formation of phenol under similar conditions? Furthermore, as you use large amounts of water, could corrosion of the reactor be a potential problem?

Koen Michiels replied: All obtained liquid samples were analysed with proton NMR spectroscopy. In all cases, no evidence was found for the presence of aromatics such as phenol. Large amounts of water and hydrogen gas create corrosive conditions, therefore, it is important to select the materials of which the autoclave and related components are made of. We chose stainless steel 1.4435 as the 'reactor' material. This type of stainless steel is known to be highly resistant to corrosion. Until now, we have not faced any corrosion problems.

Eryk Remiezowicz asked: How do you justify a CO₂ utilization process making iron, which generates a lot of CO₂ during production, knowing that the iron waste is being used by the steel industry and is valuable?

Jeroen Spooren answered: Iron production indeed generates CO₂. Therefore, it is our intention to utilise waste fine grained iron materials, such as waste

generated during shaving, milling, and drilling at iron works. The fine fractions of these waste materials cannot be directly used in the iron or steel industry as secondary raw materials due to the creation of hotspots upon introduction in the oven, and even a danger of explosion. In fact, through industrial contacts, we are aware that currently a small fraction of fine grained iron waste is still introduced in furnaces by mixing it with other scrap materials. However, acceptance criteria with regard to the fine grained waste iron are getting more strict, so that blast furnaces and smelters are refusing to take in these waste materials. Therefore, it would be a good solution to recycle such waste in an alternative way and turn it into higher added value products.

Niklas Meine enquired: I think it is quite an interesting idea to use the fine iron powder as a raw material. Can you form only magnetite or would it be possible to oxidize iron to hematite as well? How could you do so?

Koen Michiels responded: The developed hydrothermal process to produce hydrogen gas is based on the oxidation of zero valent iron into magnetite Fe_3O_4 . Experiments performed at different conditions of temperature, initial CO_2 amount, *etc.* – which were performed in the context of the optimisation study of hydrogen production – do not suggest the formation of hematite Fe_2O_3 . In the literature, the commonly described hydrothermal iron oxidation reaction is the conversion of zero valent iron into magnetite.¹ Therefore, until now, we were not able to convert metallic iron directly into hematite *via* a hydrothermal process.

1 F. Jin, X. Zeng, Z. Jing and H. Enomoto, *Ind. Eng. Chem. Res.*, 2012, **51**, 9921–9937.

Niklas Meine asked: Does the particle size remain small after oxidation so that the iron oxide could be used as a pigment?

Koen Michiels replied: During the hydrothermal production of hydrogen gas particle aggregation occurs. In the case of applying zero valent iron grains of 5 μm as the starting material, aggregates of different sizes were obtained, ranging from 10 μm up to 1000 μm , which was confirmed by laser diffraction particle size analyses. The formation of aggregates probably has a negative effect on the formation of hydrogen gas due to incomplete conversion of metallic iron present in the inner core of the larger grains. We are indeed looking at ways to re-utilise the oxidised iron after reaction as the intention is to valorise the oxidised iron phase. Use as a pigment is indeed one of the routes that we are currently investigating. To our knowledge, Fe_3O_4 is applied as a black pigment in concrete and has a value of about 500–750 € per ton. But of course, other options are also possible.

Peter Styring returned to the general discussion of the paper by Moti Herskowitz: You say that the production of hydrocarbons from CO_2 using Fischer–Tropsch-type processes are un-economical. Have you come across the German company Sunfire's process? They are producing synthetic diesel at a cost claimed to be less than 1 euro per litre. Do you have any comments on this?

Michael North stated: CRI now have a commercial plant for methanol synthesis in Iceland which uses very cheap geothermal electricity to electrolyse water – process economics are very location dependent.

Moti Herskowitz responded: I definitely agree that there are opportunities to produce low-cost hydrogen by electrolysis if indeed very low cost electricity is available.

Gabriele Centi commented: To make economical methanol, you need to have a cost of H_2 at about 0.12–0.14 € Nm³ H_2 – this low cost is possible in some areas where cheap electrical energy is available. This is different if you apply for an excess of energy, it is necessary to store the energy, because the fixed costs of a plant for electrolyzer/catalytic conversion account for about 70% of the overall cost (thus the amount of time it is being used should be high).

Jennifer Dodson continued the general discussion of the paper by Koen Michiels: You presented a scheme indicating that your process involves the direct reaction of CO_2 and H_2 to form formic acid, however, in reality you are reacting bicarbonate ions. Have you tested the direct reaction of CO_2 and H_2 over your catalyst?

Koen Michiels answered: Our experimental results suggest that the reduction of CO_2 , mainly present as dissolved hydrogen carbonate ions, with H_2 takes place in the water phase and not in the gas phase. In the paper, we explained our choice to use potassium bicarbonate, $KHCO_3$, as the CO_2 source – in order to make a comparison with other similar one-step hydrothermal methods, which are described in the literature and which also make use of HCO_3^- ions. In the case of applying Milli-Q water as the reaction medium, we did not perform experiments with gaseous CO_2 . We believe extra parameters, such as the solubility of CO_2 , will become important in that case. However, when applying 1 M KOH as the reaction medium, we have performed experiments with gaseous CO_2 . After producing 42 mmol H_2 via the developed hydrothermal method (step 1), in which 15 mmol of gaseous CO_2 dissolves in 40 mL of a 1 M KOH solution to obtain mainly carbonate CO_3^{2-} ions, we investigated different experimental options to convert ' CO_2 ' (step 2), as described in the paper. Firstly, the temperature was increased to 280 °C for 24 h. In this case, a carbon conversion amount of approximately 9.7 wt% was observed. One-step hydrothermal methods described in the literature make common use of a hydrogen carbonate salt, such as $NaHCO_3$, which is dissolved in water as the CO_2 source.¹ In the above described experiment, on the other hand, the CO_2 source is mainly CO_3^{2-} ions. In order to obtain mainly HCO_3^- ions, the addition of extra CO_2 is necessary after the first step of hydrothermal H_2 production. However, performing an exactly quantified addition of CO_2 without losing the produced amount of hydrogen gas is complicated due to the high pressure already present in the reactor, as we experimentally encountered. Therefore, we did not include the obtained results in the paper.

1 B. Wu, Y. Gao, F. Jin, J. Cao, Y. Du and Y. Zhang, *Catal. Today*, 2009, **148**, 405–410.

André Bardow continued the general discussion of the paper by Koen Michiels: Your title indicates that you are producing formic acid but you appear to actually be producing formate. I worry about the separation of the product which is crucial for the energy efficiency of the process but is not discussed in your work. Could you comment on a) your current final product and b) on the separation?

Koen Michiels responded: The obtained main product is potassium formate, dissolved in an aqueous solution, therefore, the title might be misleading. In order to tackle any possible confusion, we replaced the word 'formic acid' by 'formate' in the title and throughout the paper. However, in the case of acidifying the obtained aqueous solution, *e.g.* by adding hydrogen chloride, HCl, potassium formate will be converted into formic acid (and potassium chloride). We agree that product separation is an important aspect which should be taken into account when making the process economically feasible. We believe that the optimal process conditions should match the separation procedure. More concretely, for example, the separation of formate/formic acid and water might become more difficult in the case of low formate/formic acid concentrations. Low formate/formic acid concentrations might be obtained in the case of applying a high degree of filling with water. However, a high degree of filling has, according to our research, a positive influence on the amount of carbon conversion due to the increase of the (absolute) amount of dissolved hydrogen gas. Potassium formate and water can be separated by evaporation.¹ Mixtures of formic acid and water are, due to their similar properties, more difficult to separate. For example, the boiling point of formic acid is 100.7 °C, which implies that performing a distillation process is difficult. However, certain current commercial production processes of formic acid also have to deal with the separation of mixtures of formic acid and water, since these processes make use of large amounts of water in the last (hydrolysis) step. Therefore, separation methods of mixtures of formic acid and (large amounts of) water are already commercially available. A possible solution is described hereafter. Firstly, formic acid and water are separated based on a liquid–liquid extraction method with an organic base. Formic acid will dissolve in the organic base. Eventually, formic acid and the organic base are separated by distillation (http://www.intermediates.basf.com/chemicals/topstory/ideen_tradition).

1 Patent WO2008091186 A1, 2008.

Michael North continued the discussion of the paper by Moti Herskowitz: Potassium is introduced to the catalyst as potassium carbonate, then the solid is calcined. What is the chemical nature of the potassium in the active catalyst? Does it stay as carbonate or form potassium oxide or hydroxide, which may be relevant to the strongly basic sites on the catalyst.

Moti Herskowitz replied: Potassium carbonate is decomposed at the catalyst calcination step and does not form nanoparticles of oxide or hydroxide phases (XRD, HRTEM-EELS), rather atomic or small cluster species that are uniformly distributed and interact with the surface of Fe-oxide and Fe-carbide nanoparticles. The strong basic sites detected by CO₂-TPD at high potassium loadings are probably a result of this interaction.

Anthony Coogan asked: In your paper, you state: 'Carbon dioxide and water are the most abundant and low-cost sources of carbon and hydrogen needed for the production of hydrocarbons.' I understand that the cost of water may be expensive in certain places due to the cost of desalination. Have you considered this?

Moti Herskowitz responded: The cost of water produced by desalination of seawater is by far lower than the cost of electrolysis thus it is negligible compared with other costs associated with water splitting to produce hydrogen.

Alexander Foote opened a general discussion of the paper by Annemie Bogaerts: The asymmetric mode vibrational states of CO₂ play a very important role in the dissociation to CO. There are many vibrational states of CO also included in the model. Do the vibrational states of CO also play an important role in dissociating CO into C, and if so does this significantly reduce the yield of CO obtained?

Annemie Bogaerts answered: No, the vibrational states of CO play a less important role in dissociating CO into C and O, because of the higher energy needed for excitation.

Alexander Foote remarked: Why doesn't the plasma produce a significant amount of C from CO? Is it due to the energy required to break the C-O bond or high recombination of C and O, or both?

Annemie Bogaerts responded: It is mainly because of the energy required to break the C-O bond.

Gerard van Rooij said: Dissociation of CO *via* vibrational excitation, analogous to the mechanism that is put forward to explain the efficient CO₂ dissociation in the plasma phase, is inherently less efficient than CO₂ dissociation due to the higher dissociation energy and a larger vibrational constant of CO.

Annemie Bogaerts answered: Yes, that's right.

Thomas Butterworth commented: Your experimental data for CO₂ splitting in a packed bed DBD shows that with smaller particle sizes the conversion of CO₂ decreases. In your work this is attributed to a reduction in residence time. However, this reduced conversion with particle size may also be attributable to the applied electric field strength being insufficient to initiate an electrical breakdown in the void spaces of the particles *i.e.* the reactor is not completely discharging. This phenomena can be demonstrated through the use of Lissajous figures, and measuring the burning voltage at different particle sizes. This is a result that I have demonstrated in my own, currently unpublished, work. I have attached a graph (Fig. 1) showing the change in reactor burning voltage at different particle sizes from my thesis. Although the data shown in this graph very specifically applies to my experimental equipment, the general trends are likely to apply to all packed bed plasma reactors *i.e.* burning voltage increasing with decreasing particle size. In addition to this, it is worth noting a recent publication from Duan *et al.*,¹ which has demonstrated that CO₂ conversion increases with

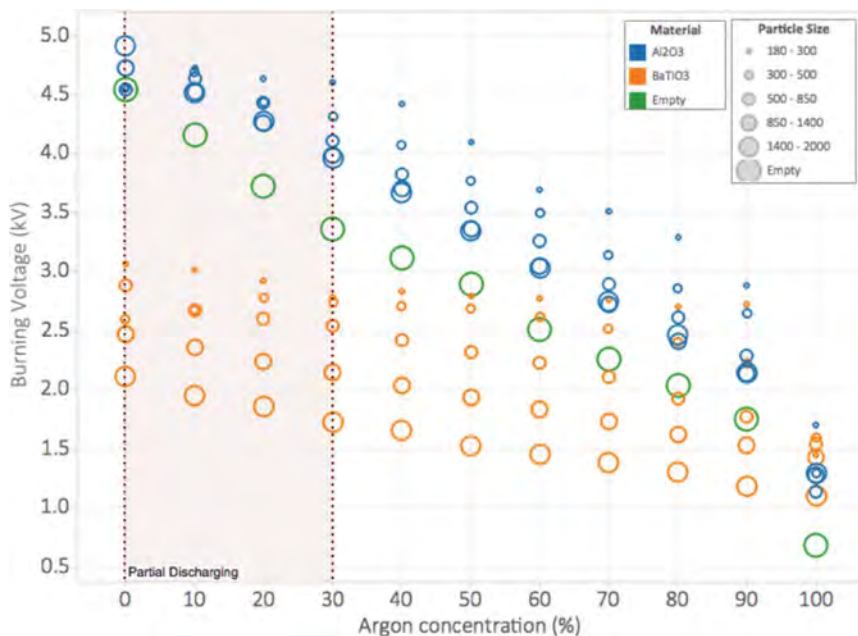


Fig. 1 A graph showing the change in reactor burning voltage at different particle sizes.

decreasing particle sizes, with the application of electric field strengths approximately 7 times greater than those used by Bogaerts *et al.*

1 X. Duan, Z. Hu, Y. Li, B. Wang, 2015, *AIChE Journal*, **61**, 898–903.

Annemie Bogaerts responded: This is a very interesting comment. To investigate this in more detail, we are analyzing the Lissajous plots for different bead sizes. The publication of Duan used a much smaller gap (0.6 mm, while we used 4.5 mm). In this smaller gap, for the same applied voltage, the electric field will be higher so the breakdown will be easier, also for smaller bead sizes. That might explain the difference with our results. This kind of DBD microplasma might be of interest for CO₂ conversion.

Matthew Moss asked: Vibrational states play an important role in the dissociation of CO₂ in a plasma, less so in a DBD but nonetheless they do play some role. As plasma modellers we aim to create accurate models yet we wish to do so within a reasonable timescale. What is a reasonable level of simplification in a typical plasma model, that still accounts for the role of vibrational levels, which reduces the computational time to a reasonable level?

Annemie Bogaerts answered: The answer depends on the type of model (0D chemical kinetics model or multi-dimensional fluid model) and on the type of plasma (DBD vs. microwave (MW) plasma or gliding arc (GA) discharge). In a 0D chemical kinetics model, the calculation time is not so much of an issue, as the calculations do not take too much time. In this case, it is better to include all vibrational levels of CO₂ that contribute to CO₂ splitting (*i.e.*, the levels of the

asymmetric stretch mode), as we did in our model.^{1,2} For the other CO₂ vibrational modes, as well as for the other molecules present in the plasma (like CO₂ and O₂), it is sufficient to include only a limited number of vibrational levels, as they play some role, but no major role, in the CO₂ splitting.

This applies especially to a MW plasma and a GA discharge, but as the calculation time is not such an issue, the same levels can also be included for a DBD (although it is not strictly necessary, as the vibrational kinetics is of minor importance in a DBD).³ In a multi-dimensional model (1D, 2D, 3D), calculation time is much more of an issue, and an extensive reaction chemistry, as included in a 0D model, would lead to prohibitively long calculation times. My recommendation then is to reduce the vibrational kinetics scheme as much as possible for a MW and GA (*e.g.*, by combining some levels), and to neglect it completely for a DBD.

1 T. Kozák and A. Bogaerts, *Plasma Sources Sci. Technol.*, 2014, **23**, 045004.

2 T. Kozák and A. Bogaerts, *Plasma Sources Sci. Technol.*, 2015, **24**, 015024.

3 R. Aerts, T. Martens and A. Bogaerts, *J. Phys. Chem. C*, 2012, **116**, 23257–23273.

Michele Aresta commented: In the 1980's–1990's there was great interest in the plasma technology applied to the conversion of poor natural gas, possibly at the well mouth, instead of undergoing separation. This approach was also considered valid for biogas, rich in CO₂ (40–60%). Can you comment the state of the art in this area? What is the conversion and energy efficiency in DRM with plasma?

Annemie Bogaerts responded: There is still a lot of interest in methane conversion and specifically also dry reforming of methane (DRM) by plasma technology. The conversion and energy efficiency again depends on the type of plasma (*i.e.*, DBD, packed bed DBD, microwave (MW) plasma, or gliding arc (GA)), as for pure CO₂ splitting, as well as on the CH₄/CO₂ mixing ratio.

In a DBD, conversion up to 60%, with energy efficiencies of a few % (up to 8%) have been reported. For a packed bed DBD, a conversion of 27% with a corresponding energy efficiency of 23% was reported. For a MW plasma at atmospheric pressure, a conversion of 70%, along with an energy efficiency of 39%, was reported. Finally, for a GA, a conversion of 37% with an energy efficiency of 31% was reported, as well as a conversion of 10% with an energy efficiency of 75%.

A detailed overview of the state-of-the art for plasma-based DRM for different types of plasmas, including a table of all the data and all the corresponding references, can be found in the literature.¹

1 R. Snoeckx, Y. X. Zeng, X. Tu and A. Bogaerts, Plasma-based dry reforming: Improving the conversion and energy efficiency in a dielectric barrier discharge, *RSC Adv.*, 2015, **5**, 29799–29808.

Michele Aresta asked: When you have a mixture of CO₂ and CH₄ in the plasma, is the CO₂ splitting and methane dehydrogenation simultaneous, or they can be separated in time?

Annemie Bogaerts replied: When we have a mixture of CH₄ and CO₂, the methane dehydrogenation and CO₂ splitting occur simultaneously. Indeed, the electrons in the plasma cause dissociation, ionization and excitation of the gas

molecules (both CH₄ and CO₂), forming radicals, ions and excited species, which can recombine into new compounds. These electron impact collisions occur more or less at the same time (although CH₄ dissociation is a bit easier than CO₂ dissociation, so the CH₄ conversion will typically be a bit higher than the CO₂ conversion after a certain residence time).

Michele Aresta enquired: The DBD technology may allow the use of catalysts. Can you discuss some results of processes under plasma-catalytic conditions? Which catalysts have you used?

Annemie Bogaerts responded: DBD technology is indeed very suitable for use in plasma catalysis. We just started our work on plasma catalysis, and up to now, we mainly focused on introducing a packing in the plasma reactor, and looking at the enhancement in both CO₂ conversion and energy efficiency, which is mainly attributed to physical effects, like local electric field enhancement, and an increase in the electron energy. Up to now, we used SiO₂, ZrO₂, Al₂O₃ and BaTiO₃ as packing materials. We also did some first experiments for Cu and Ni catalyst coatings on the packings, but the results are still too preliminary.

In fact, the chemical effects of plasma catalysis are not yet well understood. This is partially because the physical and chemical effects are often correlated, as the catalysts are mostly introduced in a packed bed, so it is not easy to distinguish between the two effects. However, Scapinello *et al.*¹ reported an enhanced selectivity towards the production of carboxylic acids in the case of DRM, when using copper or nickel electrodes instead of stainless steel, which may be attributed to a chemical catalytic effect of these metals, as no packing was involved here.

Another reason why the chemical effects of plasma catalysis for CO₂ conversion are not yet fully understood, is that a wide variety of catalyst materials are being explored, including metals (Au, Pd, Pt, Rh, Cu),² zeolites (NaY, NaOH treated Y, HY, Na, NaX, Na-ZSM-5 and Linde type 5A zeolite),^{3,4} La₂O₃/g-Al₂O₃, CeO₂/g-Al₂O₃,⁵ n-type oxide semiconductors (ZnO, CuO), and Al₂O₃ foams with Ni, Rh or Ca catalysts.⁶ Commercial Ni/Al₂O₃ catalysts, which are also used in thermal catalysis, are currently the most popular catalysts for DRM, but they are not necessarily the most suitable ones under plasma conditions. We believe that there is still a lack of insight into which catalysts should perform best in a plasma. Therefore, there is a clear need for more systematic studies on both the physical effects (of the structural packing and the support materials, *e.g.*, their dielectric constant, acid/base properties, porosity) and the chemical effects of the catalyst material (including type and coordination of the active element).

- 1 M. Scapinello, L. M. Martini, P. Tosi, CO₂ hydrogenation by CH₄ in a dielectric barrier discharge: catalytic effect of Ni and Cu, *Plasma Proc. Polym.*, 2014, **11**, 624.
- 2 S. B. Brock, M. Marquez, S. Suib, Y. Hayashi and H. Matsumoto, Plasma decomposition of CO₂ in presence of metal catalysts, *J. Catal.*, 1998, **180**, 225–233.
- 3 K. Krawczyk, M. Mlotek, B. Ulejczyk, K. Schmidt-Szalowski, Methane conversion with CO₂ in plasma-catalytic system, *Fuel*, 2014, **117**, 608–617.
- 4 C. J. Liu, R. Mallinson, L. Lobban, Methane conversion to higher hydrocarbons in a corona discharge over metal oxide catalysts with OH groups, *Appl. Cat. A: General*, 1999, **178**, 17–27.
- 5 X. Zhang, A. Zhu, X. Li and W. Gong, Oxidative dehydrogenation of ethane with CO₂ over catalyst under pulse corona plasma, *Catalysis Today*, 2004, **89**, 97–102.
- 6 J. Amouroux, S. Cavadias and A. Doubla, CO₂ reduction by non-equilibrium electro-catalysis plasma reactor, *IOP Conf Ser.: Mat. Sci. Eng.*, 2011, **19**, 012005.

Michele Aresta remarked: In the experiment made using beads, there is no apparent linear correlation between the size of the beads and both the conversion and the efficiency. Is the scattering due to an error in the measurements? Are the data replicated? Can you show the error bar for each single experiment?

Annemie Bogaerts responded: The scattering might indeed be (partially) due to an error in the measurement. These were only our first experiments. The data shown in the paper were not yet replicated, but now we are performing more experiments, with repeated packing for the same conditions, so that we will be able to add error bars in our new experimental results.

Gerard van Rooij commented: Concerning plasma production within a packed bed system; as the volume in which the plasma is to be produced becomes smaller, the ionization life time becomes lower. This increases the average electron temperature and may compromise energy efficiencies.

Annemie Bogaerts responded: This may be true. On the other hand, the polarization of the dielectric beads also gives an enhanced electric field, so that the electrons can more easily become heated, and they have a higher energy, which will facilitate the electron impact ionization and dissociation of CO₂, so that the applied power (or energy) is more efficiently used for the CO₂ splitting. Therefore, this can also increase the energy efficiency.

Alexander Foote asked: There is a lot of recombination of atomic oxygen, does this occur largely in the effluent, and how much of the atomic oxygen recombines into molecular oxygen and how much into ozone? Furthermore, what is the density of these species compared to CO?

Annemie Bogaerts answered: Most of the atomic oxygen recombines into molecular oxygen. That is also confirmed by our experiments, as we do not detect significant fractions of O₃ in our effluent (although the latter can also be attributed to the high reactivity of O₃; and other people do see some significant fractions of O₃, typically up to a few %).

In general, there is a delicate balance between O, O₂ and O₃, as explained by R. Aerts *et al.*¹ The O₂ molecule density is typically about half of the CO density (because 2 CO₂ molecules split into 2 CO and 1 O₂), while the O₃ molecule density is significantly lower.

1 R. Aerts, W. Somers and A. Bogaerts, *ChemSusChem.*, 2015, **8**, 702–716.

Alexander Foote asked: How stable is ozone in the effluent? Do you see a large drop off in the density shortly after exiting the plasma?

Annemie Bogaerts replied: In our experience, ozone is not very stable in the effluent, and that's probably one of the reasons why we don't detect ozone in our gas chromatography measurements, although other people do detect ozone, in concentrations up to a few %.

Eric Fraga opened a general discussion of the paper by Gerard van Rooij: Alexander Navarrete mentioned the issue of scale up in his paper. I would like to know if there are any issues caused by scale up in your technologies, for instance, in the uniformity of the properties of the plasmas created.

Gerard van Rooij responded: Similar to the DBD reactor, the microwave approach could be scaled up by placing larger numbers of reactors in parallel. A more attractive way (in terms of footprint) seems to be scaling up the power in a single reactor. This does involve uncertainties in maintaining favourable plasma property profiles, however, these are difficult to predict as long as these have not been solved in the present 1 kW reactors.

Annemie Bogaerts commented: In a DBD plasma, scale up is straightforward. It is realized by placing a large number of DBD reactors in parallel. This has already been successfully demonstrated many years ago for the commercial production of ozone in a DBD.¹

1 U. Kogelschatz, *Plasma Chem. Plasma Process.*, 2003, 23, 1.

Alexander Navarrete remarked: I assume that the penetration length of microwaves in plasmas cannot be very large (at least at atmospheric pressure), thus in principle electrons near the wall will have more energy than those in the center of the vessel containing the plasma. Therefore, I wonder if constraining the plasma to small diameters (close to or below the penetration length) could provide a more homogeneous (and perhaps efficient) absorption of the energy by the electrons throughout the plasma volume. If that assumption is true, perhaps it could be possible to design systems consisting of several parallel small cylinders, where reactions can be carried out more efficiently?

Gerard van Rooij responded: Indeed, depending on the plasma density, the penetration depth of the microwaves may become very small and power will be absorbed in the skin. There, the absorption of microwave power, as well as the electron energy, will be the highest. Electron heat conduction to the centre of the discharge will drive the discharge there, so that power transfer to the heavy particles will still occur throughout the discharge. Nevertheless, our working hypothesis, based on the Boltzmann solver results in the paper, is that mean electron energy should be decreased in order to promote vibrational excitation. Promotion of high electron energy regions, by increasing the total skin volume in a multiple discharge channel approach, has the opposite effect.

Gabriele Centi continued the general discussion of the paper by Annemie Bogaerts: Under thermal conditions in CO₂ dissociation, the back reaction has a critical role. Is this also a key issue under plasma conditions?

Annemie Bogaerts responded: This might be important, but only at high CO₂ conversions. This is evidenced by the fact that CO₂ conversion tends to saturate at high conversion values (reached at long residence times or high plasma power). A way to solve this problem could be to separate the oxygen formed.

Gabriele Centi asked: In MW plasma, the loss in energy efficiency could be reduced by having a restriction of vibration modes, which may occur under confined spaces in a catalyst (like in C-nanotubes or in zeolites)?

Annemie Bogaerts replied: Indeed, the energy efficiency could be optimized when selectively exciting the asymmetric stretch mode of CO₂, as this is the most important vibration mode for CO₂ splitting.

Csaba Janaky opened a general discussion of the paper by Alexander Navarrete: Could you comment on the mechanism of how plasmons contribute to the enhanced catalytic activity in your experiment?

Gabriele Centi asked: What is the mechanism that you have in mind for this plasmonic catalyst? Generally, in plasmonic catalysts you have small metal nanoparticles (Au, Ag) which are able, with visible light, to promote charge separation in a semiconductor. Your case seems different. Could it be possible that there is an effect of local overheating of the metal nanoparticles?

Alexander Navarrete responded: Copper based catalysts are known to be active for CO₂ hydrogenation. On the other hand, ZnO has proven to be good at providing dispersion and stability to the copper catalyst (amongst other things). Therefore, Cu/ZnO catalysts are commonly found in research dealing with methanol synthesis (200–250 °C and 20–50 bar usually). In our research, we were looking for local activation of the metallic copper nanoparticles by means of the plasmon phenomena. The related effects reported include an increase of local temperature by the generation of hot electrons, near field effects and scattering. We can therefore use this "heating" to locally activate the reaction instead of heating the complete vessel (*i.e.* it is more efficient). Thus, our work looked towards the integration of the plasmonic composite together with the reactor in order to have one single entity acting in response to visual light (not UV in our tests). Therefore, the idea was to carry out the reaction at mild temperatures (possible in a solar collector) and locally activate the copper. Now, we need to really explore the actual mechanisms taking place and know which (if any) is most prominent in order to better design these devices. I therefore propose to characterize our composite with optical and *in situ* techniques. We are presently studying the appropriate techniques to achieve this.

Alexander Cowan asked: I wonder if you could give us an insight into the activity of the material without the metal nanoparticles. ZnO is known to be photoactive under UV light. Has a control without the metal nanoparticles been carried out?

Alexander Navarrete replied: I agree we need a control. Therefore, I propose the use of different wavelengths to those where the plasmon effect is activated. We have already got blue, red and yellow LEDs in order to make those tests. Yet, we have lots of work to do! Linic *et al.* have written an interesting review dealing with the plasmon effect and its application, if you would like to read about it further.¹

1 S. Linic, P. Christopher and D. B. Ingram, *Nat. Mater.*, **10**, 911–921.

Michele Aresta said: One of the factors affecting the net CO₂ reduction in a process based on CO₂ conversion is the emission attached to the preparation of the catalysts. Your interesting catalytic system looks quite complicated from the point of view of its preparation. Have you estimated the energy expenditure for making the catalyst? It looks like it will require high TON to compensate for the emissions attached to the catalyst preparation. Can you comment on the life of the photocatalyst?

Alexander Navarrete replied: These are initial results and we believe there is much room for optimization in terms of the composite nanostructure and composition together with the reactor operation conditions itself. Thus, we have not yet made a LCA analysis of our synthesis process. However, we are confident that the life time will be similar to the industrial Cu/ZnO based catalysts already on the market. This of course needs to be proven, and will therefore be considered among the next steps that we take.

Thomas Butterworth continued the general discussion of the paper by Gerard van Rooij: If by the addition of earth metals to the microwave plasma you limit electron energy to 1 eV specific energy, does that mean you're theoretically limiting conversion to ~30%? Am I correct?

Gerard van Rooij answered: This is not correct. The electron energy determines the excitation rates in the plasma but does not relate to the amount of power that is transferred to the feedstock. Whilst adding alkalis to the discharge will likely change the momentum loss rate of the electrons to the heavy particles, this will be compensated by a change in (integrated) electron density so that the total power transferred to the feedstock remains constant. Conversion is connected to specific input power and energy efficiency.

Thomas Butterworth asked: If your maximum conversion is only ever going to be 30% and you're operating at low pressures, isn't this a problem when using microwave plasmas in industry? Do you think that it can ever be an industrially viable technology under these conditions?

Gerard van Rooij replied: It is evident that the goal of our research is to reach energy efficient operation at higher pressures and higher conversion. In my opinion, conversion and operating pressure are not the prime indicators for success. These are energy efficiency and the total power to which the approach can be scaled. Limited conversion demands separation, and low operating pressure demands high flow speeds. Industrial viability would still heavily depend on the cost of separation and pumping.

Annemie Bogaerts enquired: It is important to improve the energy efficiency in a MW plasma to keep the gas temperature low. What is the best way to accomplish this? Keep the pressure low? Use a high gas flow rate (thus short residence time)? Pulsing the plasma? Or other possibilities?

Gerard van Rooij responded: The reasoning in our paper is that presently the effect of a high average electron energy driving the direct dissociative excitation

processes is dominating. This efficiently heats the heavy particles and subsequently quenches any vibrational excitation. Gas flow rate (residence time) and pressure are connected, and were varied in the experiments reported in our paper. It strongly affected central gas temperatures but was less effective in achieving strong non-equilibrium conditions. Nevertheless, record energy efficiencies reported in the literature invoked supersonic flows, a regime far beyond the parameter space covered in the present paper. Pulsing of the plasma is surely an interesting option to investigate, although this would periodically increase electron energy even further (as has been shown in your papers on dielectric barrier discharges).

Alexander Foote asked: Is the thermal region in the plasma causing a very high degree of ionisation which, in turn, is causing dissociative recombination to be dominant over vibrational excitation, which is not desired for high energy efficiencies?

Gerard van Rooij replied: This is indeed what we believe is happening.

Alexander Foote remarked: Do you have any idea of the electron density and temperature in the thermal region of the plasma? Is there a very high electron density in the thermal region due to a high degree of ionisation?

Gerard van Rooij responded: Estimates of the electron temperature are given in the paper on the basis of Boltzmann solver calculations. Estimates of the density could be based on a simple power balance: the product of plasma volume, electron density, gas density and electron energy loss rate should match the input power. These are very sensitive to assumptions on radial profiles. Simply assuming a plasma volume of let's say $\sim 5 \times 10^{-6} \text{ m}^3$ for the measured central neutral densities of $\sim 10^{23} \text{ m}^{-3}$ would give an electron density of $\sim 5 \times 10^{18} \text{ m}^{-3}$. Without gas heating, the electron density would have been 1–2 orders of magnitude lower.

James Comerford remarked: In your paper you refer to the term 'input energy', could you please define what you mean by this. My understanding is that with traditional plasma apparatus, the input energy from a generator is very different to the plasma energy. As such, the difference between the two can have a substantial effect on energy efficiency calculations.

Gerard van Rooij responded: The paper refers to the terms 'input power' and (dividing input power by gas flux) 'specific input energy'. In situations where matching circuits are used between the power generator and plasma reactor, it is often difficult to determine the input power. In our microwave experiment this is relatively straight forward. We measure the power that is launched by the microwave source as well as the power that is reflected back from the plasma reactor and absorbed in the water load. In both cases, additional power losses will decrease performance, and the latter will thus not be overestimated.

Michele Aresta asked: The formation of Group 1 cations may also cause interactions with CO_2 and, depending on the cation, a possible change of

geometry (towards a bent molecule). Have you observed any effects due to such interactions?

Gerard van Rooij answered: We have not observed any such interactions. I expect that the interaction between the cations and the CO₂ will mainly have an effect on the ionization life time and therefore on the plasma properties, which is the subject of our present research. Given the low amounts of cations (well below 10⁻⁴) the effect on vibrational excitation dynamics will be low.

Thomas Butterworth communicated: How do you intend to incorporate alkali metal ions in the plasma? Considering that you emphasise the importance of having 0.01% sodium ions for optimum plasma properties. How do you control the distribution of these ions in the discharge?

Gerard van Rooij communicated in reply: In our current approaches we use commercially available alkali metal dispensers. These allow controlled rates of evaporation of the metal. The exact amount and distribution of alkali atoms in the discharge is in the first instance not important. There simply should be sufficient alkali atoms present to provide the ionization. In other words, the quoted 0.01% sodium content is the minimum amount to allow an ionization degree of 10⁻⁴. In this way, the plasma properties are tuned by the ionization energy of the alkali atom and not by the amount of alkali.

Richard Heyn addressed all the speakers: I understand very well that we are still at the early stages of research in the field, but I would like to be a bit provocative and ask for a frank assessment and future vision of these "alternative" techniques for CO₂ reduction: electrochemistry, photochemistry, and plasma. What are the main challenges or limitations? Which one(s) might be considered the most promising at this stage? Which one(s) have the best chance of eventually achieving some sort of commercial realization?

Alexander Cowan responded: This is a challenging question. I have experience of electrochemical and photochemical systems but it would not be appropriate for me to comment on how these compare to plasma techniques due to a lack of knowledge. Photochemical approaches are potentially very low cost, doing away with the need for separate PV panels, electrolyzers and all of the costs associated with the wiring of these together, hence in my opinion the long term photochemical approaches are highly attractive. However, direct photochemical carbon dioxide reduction is currently inefficient. Typically, solar to fuel conversion efficiencies are below 1% and advances in catalyst design will be necessary in the forthcoming years. In the shorter term, electrochemical approaches offer a more viable solution. Utilising available PV panels and state of the art electrodes, other research groups have managed to convert up to 7% of the incident solar energy in the form of a carbon based fuel produced *via* carbon dioxide reduction. Further advances in the development of new low cost electrocatalysts are likely to make these systems more attractive from an economic viewpoint as well.

Gabriele Centi answered: For plasma, the real challenge is to have a different approach in the integration with the catalyst, because the catalyst should be able

to work with excited gas phase species. There are still very limited attempts in this direction, but some new ideas are emerging. It is mainly a question where today's researchers have not really addressed the key problems.

Furthermore, for the photochemical approach, I believe that the problem is still not understood well. Again, it is still not clearly defined exactly what the essence of the problem is. On the other hand, electrocatalysis is somewhat more advanced, and likely within a few years (let me say 5), we will see the first commercially relevant applications, although this depends on the effective R&D efforts in this direction.

Michele Aresta continued: Plasma technology is quite old, maybe 40 years or so. Previously, in the 1970's and 1980's, discharge using CO_2 or CH_4 have already been investigated. Today, the technology is more advanced, but the fundamentals have been known for a long time. Electrochemical reduction of water to produce hydrogen for CO_2 reduction is on a commercial scale. It is a matter of cost of H_2 with respect to reforming. Photoreduction of CO_2 is in its growth phase and catalysts are designed and show interesting efficiencies of a few units %. Carboxylation is a new baby. We need to discover the band gap of semiconductors to match the potential of the reactions, depending on the substrate. Much work is still necessary, so let's wait until it grows up. The common denominator is that all technologies may use perennial primary energies – such as solar, wind or geothermal energies for producing electricity. Fossil carbon is saved anyway. I am an optimist, I was optimistic in 1975 when we discovered the first nickel complex of CO_2 and said that it opened the way to the utilization of CO_2 , and now my dream has come true.

Annemie Bogaerts responded: I cannot really comment on electrochemistry and photochemistry, as I am not a specialist, but I can comment on the challenges and limitations of plasma. In my opinion, the most important challenges are to improve the energy efficiency and the selectivity towards specific chemicals.

The energy efficiency strongly depends on the type of plasma. The highest energy efficiency up to now was already reported in 1983 for a microwave (MW) plasma, *i.e.*, up to 90%, but this was at very specific conditions; *i.e.*, supersonic gas flow and reduced pressure (~100–200 Torr), and a pressure rise to atmospheric pressure, which would be desirable for industry, yields a drop in energy efficiency to 40%. Moreover, this high value of 90% has never been reproduced since then. The highest energy efficiency for a MW plasma reported recently was 55%, but again at a reduced pressure and supersonic flow. A GA plasma also exhibits a high energy efficiency, even at atmospheric pressure, *i.e.*, around 43% for a conversion of 18% in the case of CO_2 splitting, and even around 60% for a conversion of 8–16%, for DRM. The energy efficiency of a DBD is more limited, *i.e.*, up to 10% for a conversion of 30% for a DBD without packing, but by inserting a (dielectric) packing in a so-called packed bed DBD reactor, the energy efficiency can be improved. An improvement up to a factor of 12 was indeed demonstrated already, but this was for other applications (air purification) while for CO_2 conversion only improvements up to a factor of 2 were reported recently. However, the advantages of a DBD are that it also operates at atmospheric pressure, and has a very simple design, which is beneficial for up scaling, as demonstrated many years ago for the

large scale production of ozone, and therefore it also has potential for industrial applications.

The other challenge, as mentioned above, is the selective production of specific chemicals. In my opinion, this is still a larger challenge. Up to now, mostly syngas is formed, and the direct production of oxygenates (methanol, formic acid, *etc.*) is very limited. The reason for this is that a variety of reactive plasma species is formed, but not in a selective way. To improve the selectivity towards specific value-added compounds, we need to combine the plasma with a catalyst, *i.e.*, so-called plasma catalysis. The latter is most easy to realize with a (packed bed) DBD reactor, as often shown already for air pollution control, and to a limited extent for CO₂ conversion. However, currently the underlying mechanisms of plasma catalysis are not yet fully understood, and it is not yet known which catalysts are most suitable for this purpose. Clearly more research is needed here.

Eric Fraga commented: The question of which technology is *best* may not be the right question. Often, the premise of the existence of a best solution is based purely on economics and often with an assessment of the local properties of the technology. However, design choices are often multi-criteria and include more than just economics. For instance, criteria may include environmental impacts, societal perception and policy directions. It is also necessary to consider the full life cycle, as much as one can, so that the impact of aspects of pretreatment or precursor preparations and also waste disposal on all the various criteria are taken into account.

Michele Aresta responded: Economics is not a factor that may be used for defining the "best" technology in the case of CO₂. We are targeting CO₂ emission reduction and therefore the quality of a process must be judged on the basis of CO₂ reduction parameters: Carbon Utilization Fraction (CUF), Carbon Footprint (CF), Waste production (E factor), Energy Utilization Fraction (EUF). Moreover, if we discuss in terms of economics the question will be "who has to pay ": consumers or producers? This is not a selective criterion in terms of environmental benefit. If the CO₂ reduction is targeted, then a more complex frame derives with implications of collective and individual responsibilities with respect to an efficient use of resources.

Gabriele Centi commented: Up to now, we have mainly worked on selectivity, putting little attention on the energy point of view – from this point of view we learn that if you just have thermal energy it's not selective – we need to find alternative solutions (like electrocatalysis, plasma catalysis, photochemistry) to supply energy selectively, but we still do not know how to create a selective catalytic path with the excited species created by these approaches. This is the challenge we face.

Pedro Abrantes commented: The solutions and technologies shown during this CO₂ meeting may come to be an industrial reality in 10–20 years time. I ask you to have in mind that in 20 years the conditions (requirements, sources of materials) will not be the same as today (see <http://www.terresacree.org/>)

ressourcesanglais.htm); so you need to be careful and visualise how easy it will be in the future to buy some of the products required to run the process.

Keep in mind that a simple solution, which is cheap and easy to run will find its users easily. If it's more expensive and complex to operate than existing solutions, it has less chance of being industrially deployed.

Alexander Navarrete responded: I agree, as you say the technologies presented, included ours, are in the initial stages. However, thinking that there is potential in the integration of solar energy and CO₂ transformation, we have chosen to work in microreactors. This technology allows more efficient energy and mass transfer and can be scaled up by "parallelization". Furthermore, the continuous flow operation makes it adaptable and flexible enough for industrial requirements. However, we have lots of work to do yet.

Carmine Capacchione responded: The use of an iron-based catalyst to promote the cycloaddition of CO₂ to epoxides has been designed with the aim to use an abundant, cheap and biocompatible metal for this reaction. The reactions were carried out without the use of organic solvents and with low catalyst loading. Of course, there are still issues regarding energy input due to the temperature and pressure required to obtain good conversions, but we believe that we are going in the right direction to reach a financial affordable process in the near future.

Derek Harris enquired: I would like to ask whether most of the techniques we are talking about are on real situations or ones that you have recreated in the lab? I believe in real situations and that when you start with pure chemicals it doesn't work, but when you put it in real applications it works well. It may take some time before we are able to achieve good results in real situations, particularly when chemicals are prepared in distilled water.

Gerard van Rooij commented: The focus of CO₂ utilization discussions is often on emissions mitigated for each CO₂ molecule that is re-used. The plasma work aims to produce solar fuels by sustainable electricity to aid in peak shaving, by addressing intermittency issues. By enabling long term electrical energy storage and energy sector integration, it aids in reaching large scale sustainable energy deployment. Concerning realism of the plasma approach, the essential ingredients are available – particularly demonstrated by high energy efficiencies and availability of the required microwave technology. The challenge is the demonstration of it as a viable concept.

Peter Styring noted: An interesting point has been raised regarding the technological readiness of CDU technologies, and why most are presented at the fundamental stage. This is because we are looking to develop these new technologies and the level to date is appropriate for laboratory studies. You have to start from somewhere, on the fundamentals. You have to start with pure CO₂, then add impurities such as nitrogen, before going on to more simulated glue gases with more impurities. Only when this laboratory screening has been carried out can you go into the field to work on real systems. Going in to the field from the start is very difficult and expensive.

Gabriele Centi said: We are still at the stage of exploring the many possibilities which exist, but care should be taken in extrapolating the actual growth of knowledge as it is still too far from an industrial point of view. 60 years ago, the situation was similar with the transition from acetylene to olefins. The transition was extremely fast, and companies not rapidly prepared become out of business. In a PV cell, the International Energy Agency predicted in around 2000 that commercial introduction of these cells in the market would be negligible, 1–2% in 2020, however we are already above 10%. There is not a linear, but an exponential growth, when conditions (including the knowledge necessary) are ready. The same may be applied for the field of CO₂, and I would predict that within a few short years there will be quite an explosion of commercial uses, even if we are still not in the position now to indicate exactly which technology will be a priority. However, I believe that electrocatalysis is one of these technologies, which is at the foundation of the future of sustainable energy/chemical production.