
Process conditions study via design of experiments for dry reforming of methane

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During the past decades, there has been increasing global concern over the rise in carbon dioxide emissions into the atmosphere. Therefore, utilization of CO₂ is being intensively researched, with dry reforming (CO₂) of CH₄ as a prospective process to integrate CO₂ as carbon source into chemical value chains. For this purpose, Ni-based catalysts are used as they are affordable and economical.¹ On the other hand, they suffer from deactivation. We studied the effect of different process conditions on the performance and stability of a commercial Ni-based catalyst (denoted here as Com-Cat). Additionally, all catalysts, fresh and spent, were characterized with a wide range of analytics. Therein, the potential of a Plackett-Burman design of experiments for fast evaluation of major factors governing the system was explored.² The design of experiment exhibits 3 factors with 2 levels each summarised in Table 1.

Table 1: Dry Reforming Conditions

Experimental Run	Reaction Temperature (°C)	Gas Hourly Space Velocity (h ⁻¹)	CH ₄ :CO ₂	Reaction Rate at 4h TOS·10 ⁻⁵ (mol·g ⁻¹ ·s ⁻¹)
Com-Cat PB #1	950	52000	0.5	3.5
Com-Cat PB #2	800	52000	2	3.3
Com-Cat PB #3	800	26000	0.5	1.9
Com-Cat PB #4	800	52000	0.5	3.8
Com-Cat PB #5	950	26000	2	Clogged
Com-Cat PB #6	950	26000	0.5	2.0
Com-Cat PB #7	950	52000	2	Clogged
Com-Cat PB #8	800	26000	2	2.5

*PB stands for Plackett-Burman

Reaction conditions with GHSV values of 52000 h⁻¹ perform better in terms of reaction rate of both CH₄ and CO₂. Reaction conditions with CH₄:CO₂ ratio equal to 0.5 present higher yields of both CO (based on total carbon) and H₂. At reaction conditions represented by Com-Cat PB #5 and #7 experiments, with CH₄:CO₂ ratio equal to 2 and temperatures of 950°C the reactor got clogged due to severe coking.

Therefore, we can conclude that the GHSV and feed ratio are the most important factors, with temperature effects mostly dependent on the aforementioned parameters (coupled interactions). Generally, high GHSV and low CH₄:CO₂ are beneficial for the overall catalysts performance. This finding is in good agreement with literature and confirms the potential of a Plackett-Burman design of experiments for fast evaluation of the major impact of process parameters.

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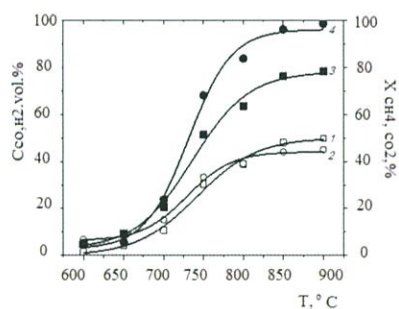
Carbon dioxide reforming of methane

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Carbon dioxide conversion of methane to the syngas is ecological importance, as it allows to utilize two simultaneous greenhouse gases - CO₂ and CH₄ and is a promising way for the production of hydrocarbons by Fischer-Tropsch synthesis [1-3]. Catalyst, based on metal oxides of the transition series (Ni, Cu, Nd and Mo) was investigated during CO₂ reforming of methane. Process was carried out in a laboratory flow reactor at conditions: 0.1 MPa, the temperature range of 600-900 °C, the ratio of CH₄/CO₂ - 0.25-4.00, the total gas flow rate - 60 ml/min. The reaction products were identified by chromatography on "Chromos GC-1000". The supporting of the active phase (Ni, Cu, Nd and Mo) was carried out by co-impregnation with solutions of nitrates of the carrier - 20% Al₂O₃-HZSM-5 (surface area 308.6 m²/g), subsequent drying at 350 °C (2 hours) and calcining at 550 °C for 3 hours. Effect of reaction temperature on the activity of the catalyst was studied in the range 600-900 °C at a space velocity of 3600 hr⁻¹ and a ratio of CH₄/CO₂ = 2 (Figure 1). With increased temperature from 600 to 900 °C the conversion of CH₄ increases from 4 to 78 %, and CO₂ - from 5 to 98%; concentration of H₂ formed increased from 1.6 to 49.8 vol. %, and CO- from 6.9 to 45.0 vol. %. That is, despite the fact that the ratio of the starting components of CH₄/CO₂ = 2, the conversion of CO₂ is markedly higher than that of methane.



1-H₂; 2- CO; 3- CH₄; 4-CO₂

Figure 1 - Effect of the reaction temperature on the conversion of CH₄ and CO₂ and concentrations of the main reaction products over the Ni-Cu-Nd-Mo/ 20% Al₂O₃-HZSM-5 catalyst

At 850 °C the concentration of H₂ and CO reach a plateau, so, a study of influence of the ratio of CH₄/CO₂ from 0.5 to 4 on the catalyst activity was carried out at this temperature. The dependence of the conversion of methane on the ratio CH₄/CO₂ is of extreme with a maximum located in the area close to 1 and corresponds to 92.6%. Increase the value of the ratio CH₄/CO₂ leads to a fairly rapid reduction of CH₄ conversion.

Unlike methane conversion of carbon dioxide at a ratio close to 1 reaches 92.3% with subsequent yield plateau to values of 96%. Curves of formation of the desired product - H₂ and CO are also has the maximum (H₂-49 vol. % and CO-50 vol.%) in a ratio of CH₄/CO₂ close to 1.

Thus, the most favorable ratio for the process of CO₂ reforming of methane is stoichiometric, at which is the maximum yield of reaction products and the largest conversion of initial reagents. Increasing the ratio of CH₄/CO₂, based on the received dependency leads to a drop in methane conversion and concentration of reaction products. The optimal conditions for the process are: the ratio of CO₂/CH₄ = 1, T-850 °C, W- 3600 h⁻¹ at which a concentration of the formed hydrogen - 48.9 vol. %, CO -50.9 vol. %, conversion of methane - 92.6% and carbon dioxide - 93.2%. It was determined that in the temperature range 650-900 °C observed the equilibrium yield of H₂ and CO.

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Structure-dependent electroreduction of CO₂ at Au-Pd core-shell nanostructures

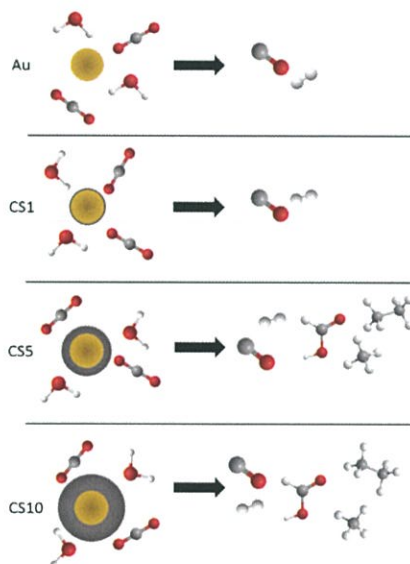
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Au-Pd core-shell (CS) nanoparticles, with shell thicknesses between 1 and 10 nm, were employed as catalysts for the electrochemical reduction of carbon dioxide.¹ Electrochemical behaviour was assessed by cyclic voltammetry in aqueous Na₂SO₄ at pH 4. Liquid and gas phase products of bulk CO₂ electrolysis were detected by highly sensitive ¹H NMR and on-line electrochemical mass spectrometry (OLEMS), respectively. Results show that the catalytic activity and, more interestingly, the selectivity can be tuned by the thickness of the Pd shell: the catalysts with 1 nm shells (CS1) present a product distribution similar to that of pure Au, with CO and H₂ being the only products generated, while catalysts with 5 (CS5) and 10 nm Pd shells (CS10) produced HCOO⁻, CH₄ and C₂H₆.



The concentration of HCOO⁻ detected in the electrolyte was dependent not only applied potential but, crucially, on catalyst composition; 27 % faradaic efficiency for CO₂ reduction to HCOO⁻ was achieved for CS10 electrocatalysts. The observed trends in selectivity were rationalised in terms of the H-absorption and CO adsorption properties of the nanostructures, which are strongly related to the shell thickness and lattice strain invoked by the epitaxial growth of Pd overlayers on Au.^{1,2} The results provide valuable information regarding how catalyst compositional and geometric properties can be modified to tune activity and selectivity towards CO₂ reduction.

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Methyl esters as efficient and green water suppressors in the synthesis of dimethyl carbonate from CO₂

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Dimethyl carbonate (DMC) has attracted much attention as a nontoxic and biodegradable reagent. DMC is used as methylating agent, octane booster in gasoline and starting material for the production of polycarbonate polymers¹⁻³. The direct synthesis of DMC from the reaction of CO₂ with methanol is the most attractive route. On the other hand, the reaction has thermodynamic limitations, which impair the formation of DMC in high yields. The removal of water from the reaction system is a way to shift the equilibrium^{4,5}. We report the use of methyl esters as water suppressor. We particularly studied the use of methyl formate (FM), methyl trifluoroacetate (TFM) and methyl trichloroacetate (TCLM) in the presence of dibutyl tin (IV) oxide (Bu₂SnO) as catalyst (Figure 1). These esters were selected based on steric and electronic effects toward hydrolysis.

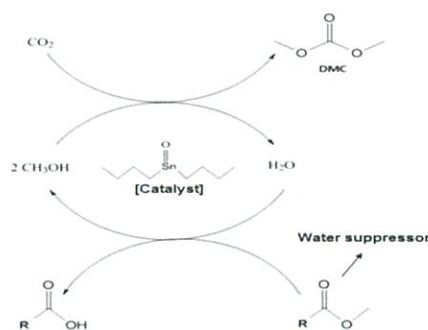


Figure 1. Synthesis of DMC from methanol and CO₂ in the presence of Bu₂SnO as catalyst and methyl esters as water suppressors.

The reactions were studied in a Parr® batch reactor, varying the initial pressure of CO₂ (700 or 900 psi), time (3 or 6 h), temperature (170 or 200 °C) and the molar ratio of the esters suppressor to methanol (0.1, 0.25, 0.5 or 1.0). The product was analyzed by gas chromatography and the yield of DMC, expressed in terms of turnover number (TON), was calculated using a standard calibration curve.

The best results were obtained at 1:1 molar ratio of the esters to methanol. For instance, at 170 °C, 700 psi of CO₂ and 6 h of reaction time, the TON for the blank reaction (without the esters) was 1.4. The presence of the esters increased the yield of DMC. With FM as water suppressor the TON was 1.8, whereas with TFM the TON was 4.3. The highest DMC yield was achieved with TCLM, with a TON of 21.5.

The electron withdrawing effect of the CF₃ and CCl₃ groups led to a increased reactivity of the respective methyl esters toward hydrolysis, compared with DMC itself. In addition, the product of ester hydrolysis was methanol, which may contribute in the formation of DMC, and a carboxylic acid, which can be easily separated from the medium and reused later, after transformation in the ester. Hence, there is virtually no waste, no secondary useless product formed.

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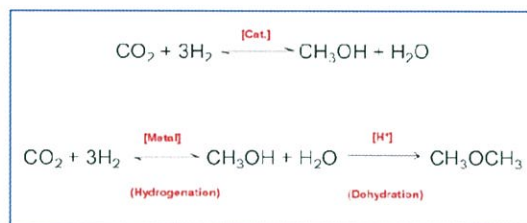
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Production of Methanol and dimethyl ether from CO₂ hydrogenation over bifunctional catalysts

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Carbon dioxide (CO₂) capture and utilization as feedstock to manufacture fuels and chemicals is an alternative to reduce the CO₂ concentration in the atmosphere¹. Hydrogenation of CO₂ to methanol (MeOH) and the subsequent dehydration to dimethyl ether (DME) is one of the most promising alternatives² (Scheme 1). There are many studies on that CO₂ conversion to MeOH³ and a pilot plant was built in Japan, as well as an industrial plant in Iceland⁴. Concerning the CO₂ conversion to DME the studies are still less advanced. The synthesis of methanol from CO₂ often use copper (Cu) and zinc (Zn) unsupported catalysts with different promoters^{2,5}. By the fact that two catalytic reactions are necessary, a bifunctional catalysts is necessary for the conversion of CO₂ in DME.



Scheme 1: Hydrogenation of CO₂ to MeOH and the subsequent dehydration to DME.

In this work we report the synthesis and catalytic evaluation of CuZn-based catalyst supported on Al₂O₃, as an acidic material, to study the CO₂ hydrogenation. The catalysts were prepared by co-precipitation of the metals over the support. Different molar ratios of Cu to Zn (1:1 and 3:1) were used. The catalysts were characterized by different techniques, such as XRF, BET surface area, TGA/DTA, XRD and TPR. Catalytic tests were performed in an automated catalytic unit (PID Eng&Tec) coupled to a gas chromatograph with FID and TCD detectors. Different conditions of temperature and pressure were studied.

It could be observed that the different molar ratio of Cu:Zn modifies the selectivity to the products of the CO₂ hydrogenation, at the conditions used in this work. MeOH was the sole product when the molar ratio of the metals was 1:1. However, when the ratio was 3:1, besides MeOH, DME could be also observed. Therefore, higher amounts of Cu are necessary to produce sufficient concentration of MeOH, which upon contact with the acid sites of the support, can be dehydrated to DME. Other catalysts, based on modified Al₂O₃ support, to create Bronsted acid sites are under investigation.

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Processing of methane to synthesis gas over the fiberglass catalysts

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In recent years, a growing interest in research attracts the partial oxidation and CO₂ reforming of methane, as they extend the capabilities of the efficient use of natural gas^{1,2}.

The present work devoted to investigation the catalytic activity of polyoxide catalysts on the basis of fiberglass in the process of CO₂ conversion of CH₄. Samples of the catalysts were prepared on the basis of fiberglass brand KT-11-TO, can maintain a temperature of 1200 °C. The active components of the catalyst deposited on the surface of the fiberglass matrix by method "solution combustion"³. The catalysts activity was tested on-line using a gas chromatographic method on the device "CHROMOS GC-1000". The effect of temperature of catalytic process on the conversion of the initial components (CH₄ and CO₂) and the yield of target products (H₂ and CO) for a catalyst containing 1% MgO, 0,8% NiO, 0,2% Cr₂O₃ was studied.

An increase in temperature of the process increases the conversion of the initial components. The maximum values of the conversion of CH₄ and CO₂ is observed at 857 °C and = 93.2% for CH₄, 99.1% for CO₂, respectively. With increasing the process temperature yield of hydrogen and carbon monoxide gradually increases and at 857 °C reaches a maximum value. Yield of H₂ - 40.26%, CO - 45.42%.

It was shown when the temperature increases in the range 626-857 °C the ratio [H₂] / [CO] reaches the value (0.89) is close to 1. It is necessary for the synthesis of hydrocarbons by Fischer-Tropsch method and production of dimethyl ether.

Varying the composition of the catalysts showed that the content of chromium oxide on the base of sample does not affect the conversion and yield of the final reaction products. Changing the concentration of nickel oxide from 0.5 to 1.5% leads to an increase in conversion and an increase in CO and H₂ output, however, was observed the growth of carbon deposits from 10 to 13%. It is also established that increasing the content of MgO in the samples from 1 to 3% leads to a decrease in both the conversion of the starting components and reaction products yield.

Thus, it was found that increasing the temperature of the carbon dioxide reforming of methane results in increasing the conversion of the starting components and yield of desired products. X-ray diffraction revealed that the samples of synthesized catalysts generally are monophase compounds MgO • NiO. The experimental data also confirmed that the concentration of the introduced into sample the Cr₂O₃ does not affect the conversion of the initial components and the yield of the desired products.

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Carbon dioxide conversion of methane over the polyoxide catalysts

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CO₂ conversion of CH₄ is one way of allowing to convert natural gas - methane to valuable desired products, which are a gas mixture of H₂ and CO in a ratio close to 1¹. This reaction is the most secure process, in contrast to the partial oxidation of methane with air oxygen and steam-oxygen conversion. However the main problem is the carbonization of catalyst and so many efforts in this area directed to the development of catalysts stable to coking²⁻³.

In this study were synthesized systems on the basis of NiO and Al₂O₃ supported on a fiberglass and oxide catalysts Ni/Al₂O₃, Ni-La/Al₂O₃. The catalysts were tested in a CO₂ reforming of methane in the temperature range 600-850 °C at atmospheric pressure, and the ratio of CH₄ : CO₂ = 1: 1. Testing of the catalysts effectivity was carried out on an automated flow catalytic unit (PKU -1). The reaction products were identified by chromatography on the apparatus "CHROMOS GC-1000". Study of the catalytic activity of the system based on fiberglass in the reaction of carbon dioxide conversion of methane with the introduction of the oxides of Al and Ni (Table 1) was carried out. The difference between these systems is that at the synthesis of the first two catalyst samples produced by separately supporting of Al₂O₃ and NiO to the base of fiberglass by "solution combustion" method with using urea as the reductant ((CO) 2NH₂). Namely, initially on fiberglass was deposited alumina and only after its complete layer formation was deposited on it a second layer of NiO. In the second case, oxides of Al and Ni were deposited on fiberglass simultaneously from a common solution.

Table 1 - Composition of samples based on fiberglass the separate synthesized (№1, 2) and joint (№3,4) applying the active ingredients and the characteristics of the catalytic activity of the catalyst at 850 °C

Sample № №	Composition	K(CH ₄), %	K(CO ₂), %	Output of H ₂ , %	Output of CO, %	Carbon formation
1	1,5 % NiO/1% Al ₂ O ₃	58.65	56.42	24.43	28.64	-1.468
2	1,5 % NiO/2% Al ₂ O ₃	70.39	74.16	31.89	37.19	-1.537
3	1,5 % NiO-1% Al ₂ O ₃	80.56	87.42	35.51	42.22	-4.320
4	1,5 % NiO-2% Al ₂ O ₃	85.35	94.22	39.14	45.68	-3.262

The experiments showed that the catalytic activity of the samples synthesized by co-application to fiberglass alumina and nickel oxide was higher as in the conversion of the initial components and on the yields of the desired products. The table shows that the greatest catalytic activity for the conversion and the yield is characterized by a sample №4, and on the deposition of carbon on the surface of contact - samples №1 and 2. Next, NiO was supported on Al₂O₃ and modified with and LaO. The synthesized oxide catalysts (Ni/Al₂O₃, Ni-La/Al₂O₃) were tested in the reaction, the results showed that over the catalyst Ni-La/Al₂O₃ degree of conversion of methane increases from 28 to 67% with increasing reaction temperature from 600 to 850 °C. Conversion of CO₂ is increased from 69 to 96% under the same conditions. The yield of H₂ = 44, CO = 48%. The ratio of the synthesis gas at 750-800 °C =1: 1.

After the test reaction catalysts were investigated by scanning electron microscopy (Figure 1). a) Ni / Al₂O₃; b) Ni-La / Al₂O₃

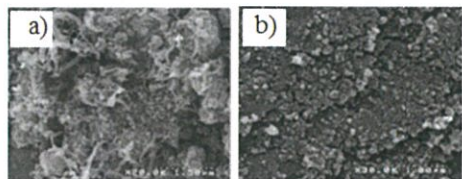


Figure 1 – Microphotographs of catalysts

After the test in the reaction on the Ni/γ-Al₂O₃ catalyst surface is formed of carbon filaments. Modification of nickel catalyst by lanthanum leads to an increase in dispersion of the catalyst surface and also to reduce of carbon deposition.

Thus, these results showed that, compared with nickel catalysts, supported on glass fiber oxide catalysts exhibit relatively high activity.

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Carbon dioxide reforming of methane

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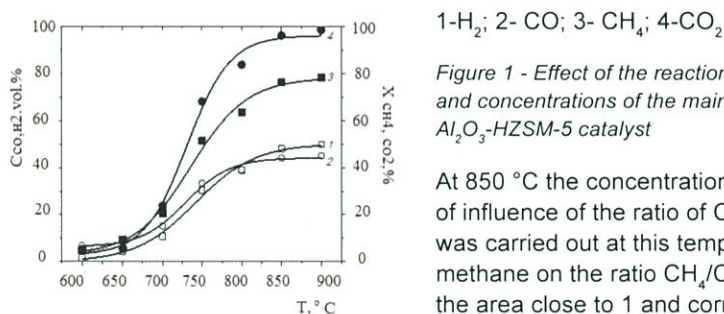


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The direct carbonation of glycerol with CO₂ using heterogeneous catalysts

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Glycerol is a by-product of biodiesel production through transesterification of triglycerides, with an increasing surplus in the world¹. Therefore, there are many studies concerning the use of glycerol as a renewable feedstock for the production of different chemicals²⁻⁴. Glycerol carbonate (GC) is an important product in this category. It is gaining increased applications every year. Today, it is mostly used as solvent, emulsifier and chemical intermediate. The preparation of GC is usually carried out via the reaction of urea with glycerol in the presence of zinc salts⁵. Since urea can be obtained from CO₂, this is an indirect route to obtain GC from this greenhouse gas. On the other hand, the direct carbonation of glycerol is still poorly studied.

We wish to show the use of heterogeneous catalysts for the reaction of glycerol with CO₂ to produce glycerol carbonate (Figure 1).

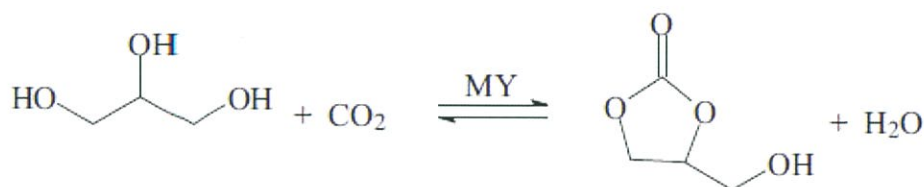


Figure 1. Production of glycerol carbonate from glycerol and CO₂ in the presence of metal-impregnated zeolite Y (MY).

Metal-impregnated zeolite Y catalysts were prepared by treatment of a NaY zeolite with an aqueous solution of AgNO₃, Zn(NO₃)₂ and SnCl₄, followed by water evaporation. The materials were then calcined in air. The catalytic activity in the reaction of CO₂ with glycerol was evaluated in a Parr® reactor at 180 °C and 100 Bar for 3 hours. The product was analyzed and quantified by gas chromatography coupled to a mass spectrometer through the use of a calibration curve. The parent NaY zeolite was inactive under these conditions, but the metal-impregnated zeolites, as well as the calcined salt precursors, showed yields of glycerol carbonate up to 5.8%, which is within the thermodynamic equilibrium for this reaction at similar conditions⁶.

The zeolite catalysts presented a significantly higher TON, expressed in mol% of GC formed divided by the mol of metal in the reaction medium, than that of the calcined salts, suggesting the formation of a highly active metal oxide phases at the external surface of the zeolite. For instance, AgY showed a TON 12 fold higher than calcined AgNO₃.

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High pressure CO₂ reduction: *In operando* heterogeneous catalyst characterisation setup

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The increasing global energy demand resulted in extensive use of fossil fuels and inflation of anthropogenic carbon dioxide (CO₂) emissions. The latter's leading position as greenhouse gas spurred the development of non-fossil fuel energy sources to address the issues of climate change and meet the fossil feedstock deficiency. CO₂ exploitation and recycling appears then as a valuable carbon source in the form of an unlimited feedstock available for a range of industrial products.

In this perspective, we use heterogeneous catalysis for CO₂ waste conversion into hydrocarbon fuels by means of high-pressure hydrogenation in continuously operated microreactors.^{1,2} A high pressure plant for heterogeneous catalytic CO₂ hydrogenation in stainless steel capillary reactors has been used in the synthesis of methanol. Elevated pressures were shown to favour methanol synthesis from a thermodynamic point of view, while the process' energy efficiency was proved to be almost pressure independent.³

Herein we present a setup for the *in operando* analysis of high pressure CO₂ hydrogenation reactions in view of shedding light on the still debated CO₂ reduction mechanism. A micro view-cell was developed to withstand pressures of 500 bar and temperatures up to 300°C. This optical access within the reactor assists in a more rational catalyst and reactor design via the collection of chemical and physical evidences by various microscopy means.⁴ Combined with the precise control of temperature and residence time in microreactors, Raman microspectroscopy is used to monitor intermediate surface chemical species and their dependence on reaction conditions.

The performance of the micro flow-cell as continuous reactor will be put forward as well as its compatibility with a fibre-coupled Raman microspectrometer using as a case study methanol synthesis. The findings shall be applicable to assist in controlled CO₂ reduction to various specific hydrocarbons.

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Polymer derived from biomass and incorporating carbon dioxide as replacements for petroleum based plastics

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Global production of synthetic polymers is close to 300 million tonnes annually. The vast majority of these materials are produced from petrochemical feedstocks and, in fact, polymer production is the greatest consumer of petroleum after fuels. By selecting bio-derived "platform molecules" containing alkene functionalities and converting them to their corresponding epoxides we have the ability to access a large synthetic space for the development of bio-based polymers incorporating carbon dioxide which could replace petrochemical materials. The relatively long lifespan of plastics (decades at least) makes them especially attractive as a candidate for carbon dioxide utilisation as this is orders of magnitude longer than the lifespan of other CCU options such as fuels, which typically capture carbon dioxide for only days or weeks before being burned.

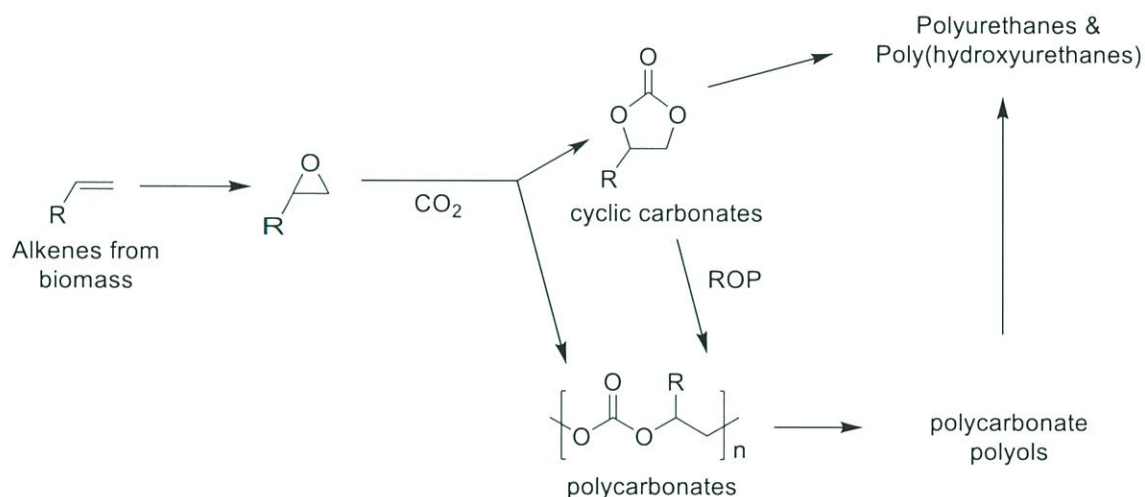


Figure 1: Simplified scheme illustrating some of the opportunities for carbon dioxide utilisation in polymers.

Our approach is to concentrate on a key biobased alkenes, which can be obtained economically at scale from biomass, and from them generate a wide variety of polycarbonates, polyurethanes and polyhydroxyurethanes incorporating carbon dioxide as well as other classes directly from the alkenes or epoxides themselves including biobased polyethers, polyalkenes etc.

The generation of epoxides from challenging biobased alkenes, and their reactions with carbon dioxide will be reported, as well as preliminary results on the production of bio-based polymers incorporating carbon dioxide.

Synthesis of cyclic carbonates from diols and carbon dioxide

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With atmospheric carbon dioxide thought to be increasing to record high levels over the past decade, much attention is being focussed on reducing CO₂ waste and embracing the use of CO₂ as a renewable chemical feedstock. Carbon dioxide's benign nature and low cost, along with its high abundance has created a significant field within chemical research. In particular, cyclic carbonate synthesis has had considerable industrial focus due to their importance and wide range of applications, including, use as a green solvent, electrolytes for lithium-ion batteries and intermediates for pharmaceuticals and polymers.

The large majority of preparations of cyclic carbonates are based on reacting carbon dioxide with various epoxides. Although many highly efficient catalysts have been reported for this 100% atom economical synthesis, the necessitated preparation of epoxide starting material from peroxyacids (such as mCPBA) or halohydrins adds additional reaction steps prior to the 'target' carbonate synthesis. A more attractive and sustainable route is preparation from 1,2 or 1,3 diols¹. However, due to the relative stability of both the CO₂ and diol moiety, such syntheses seldom achieve high conversions or employ a single 'one pot' catalyst, making preparations non trivial. Examples include the use of electrogenerated N-heterocyclic carbenes or cyanomethyl anions², urea³, ionic liquids⁴, or through transesterifications⁵, (other papers utilise carbon monoxide, which can be obtained from carbon dioxide, in a carbonylation reaction⁶).

Herein, we report of several zinc complexes and their parent salts able to catalyse the direct addition of carbon dioxide to 1,2 diols with much improved conversions compared to the literature, giving a single component catalyst system. Further to this, attempts have been made to tether the species to inorganic silica frameworks in an effort to make a heterogeneous catalyst that can simply be filtered, reactivated and reused multiple times over.

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Conversion of CO₂ via the utilisation of atmospheric pressure plasmas

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The generation of CO from CO₂ on demand could provide a much safer means of generating just the required amount of CO, by removing the need to store CO in pressurised cylinders. Low temperature plasmas can be used for the in situ generation of CO¹, from relatively non-toxic CO₂.

The key challenges in using this method, for CO production, are optimising the energy efficiency, maximising the conversion of CO₂ into CO and then separating the CO from the other species produced in the plasma. Many reactions occur within a plasma and not all of these are desirable². Understanding the reaction mechanisms in both the core and the effluent of the plasma will enable greater optimisation of the system to favour the desirable reactions and suppress the undesirable reactions.



To generate a plasma at atmospheric pressure the CO₂ is fed into a carrier gas, helium or argon, because a pure CO₂ plasma cannot be generated at atmospheric pressure by radio-frequency discharge. The CO₂ admixture is usually around 1% of the total gas flow and therefore the gas feed that comes out of the plasma is mostly the inert carrier gas, He or Ar. Hence, the CO produced has to be separated from the carrier gas as well as the other species produced by the plasma chemistry. The conversion of CO₂ can be as high as 92% in the argon carrier gas and is lower in helium, with a maximum conversion of 62%. The energy efficiency however is greater in helium, but is still not high and can be greatly improved.

CO is known to be soluble in polar aprotic solvents such as DMF and DMSO³. Therefore by bubbling the gas mixture that leaves the plasma through a solvent the desired CO can be selectively removed from the products. However other products of the plasma chemistry, such as ozone, can react with these solvents. Therefore the use of the green polar aprotic solvent propylene carbonate has been investigated.

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Ionic liquids as catalysts for CO₂ transformation in dimethyl carbonate

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The carbon capture and utilization CCU is one of the major challenges nowadays. In this concept the captured CO₂ is not considered a waste but a C1 building block for different chemicals¹. The main goal of this work was to obtain dimethyl carbonate using CO₂ as a raw material and mild pressure conditions of 4 MPa. Different ionic liquids were tested as catalysts in the dimethyl carbonate formation reaction such as the imidazolium and pyridine cations combined with the anions [Cl]⁻, [BF₄]⁻, [PF₆]⁻ and [NTf₂]⁻. Besides the use of different catalyst also the variation in reaction parameters such as reaction time and temperature were also evaluated. The ionic liquids structures were confirmed by FTIR and ¹H-NMR. The resulting liquid mixtures, after the carbonation reaction, were analyzed using a gas chromatograph with a flame ionization detector. The reaction times of 12 h, 24 h and 48 h were tested as well as the temperature from 413.15 K to 448.15 K. The time of 24 h and the temperature of 448.15 K were elected as giving the best results for selectivity and yield when [bmim][BF₄] and [bmim][Cl] were used as catalysts. Using this conditions the others anions were tested as well as the pyridium cation. The use of both cations provided similar results in terms of yield and selectivity. The anions play an important role in the dimethyl carbonate selectivity in the order of [BF₄]⁻ > [Cl]⁻ > [PF₆]⁻ > [NTf₂]⁻ for both cations. For instance, the selectivity in dimethyl carbonate was 39 % when [bmim][NTf₂] was used as a catalyst and of 81 % when [bmim][BF₄] was the catalyst. The catalyst recyclability was evaluated and after the fifth cycles a small selectivity decrease of 8 % was observed while the yield was unchanged.

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Electrochemically driven carbon dioxide mineralisation

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Sustained removal of carbon dioxide from N_2 - CO_2 mixtures has been achieved using low electrochemical voltages (approximately 1 V) applied between a high surface area graphite-aluminium anode and a platinum cathode in a solution of 1 M $NaCl_{(aq)}$ (figure 1). Highly efficient CO_2 uptake has been achieved with gas feed mixtures of 9% CO_2 (figure 2). The CO_2 is trapped as a solid carbonate material which has been analysed using solid-state NMR, TGA-IR and solution NMR analysis. Further analysis of this solid material, and other results obtained, will be described in the poster.

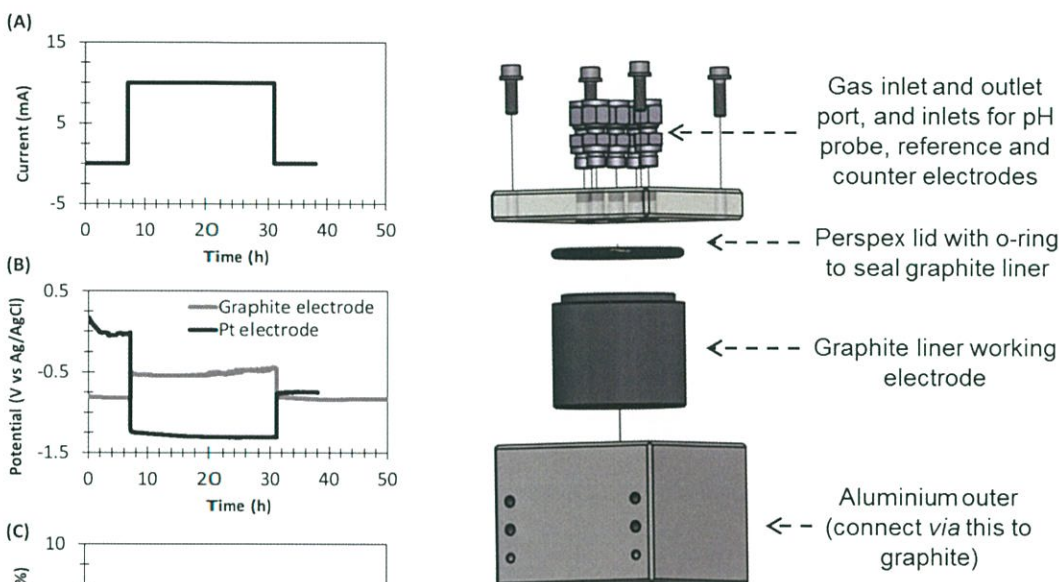


Figure 1 (above): Exploded view of graphite-aluminium electrochemical cell

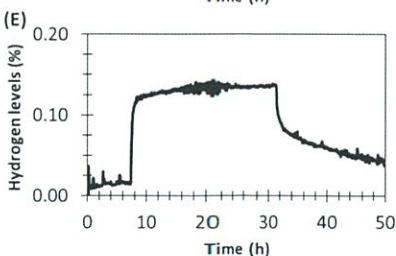


Figure 2 (LHS): Simultaneous CO_2 uptake, during an applied current of 10 mA for 24 hours. (A) Applied current, (B) voltage driving force applied to graphite and platinum electrodes relative to Ag/AgCl reference electrode, (C) resultant CO_2 gas levels, (D) pH levels of electrolyte solution, and (E) H_2 levels from gas outlet of cell. CO_2 flow rate 1.0 mL min^{-1} , N_2 flow rate 13.0 mL min^{-1} , total gas flow rate 14 mL min^{-1} , 30°C , 1 M NaCl.

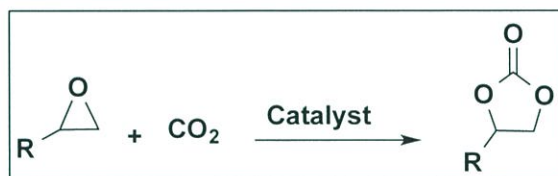
Cycloaddition of epoxide and CO₂ to cyclic carbonate catalyzed by vanadium complexes of amine-bis(phenolate) ligands

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The addition of carbon dioxide to epoxides to produce either cyclic carbonates or polycarbonates is an important reaction allowing the conversion of a renewable, inexpensive and non-toxic feedstock such as CO₂ into useful products with many potential applications. Vanadium compounds have been shown by others to be very active for the catalysis of cyclic carbonate synthesis from epoxides and CO₂.^{1,2,3}

A series of easily prepared oxovanadium complexes with amine-bis(phenolate) ligands possessing different steric, geometric and electronic parameters were prepared and used effectively for cyclic carbonate synthesis from epoxides and carbon dioxide without utilization of any solvents. All reactions displayed excellent selectivity to cyclic carbonate without polycarbonate or other by-products. However, as with many other catalysts, polymer can be formed when cyclohexene oxide is used. The synthesis and structural characterization of the complexes as well as the effects of reaction time, CO₂ pressure, co-catalyst, reaction temperature, and the catalytic results will be presented.



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Hydrothermal conversion of CO₂ into higher hydrocarbons and oxygenates

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As a consequence of the combustion of fossil fuels CO₂ concentration in the atmosphere is continuously and significantly increasing. The strategies proposed to reduce CO₂ concentration in the atmosphere are the reduction of energy consumption, the use of carbon neutral energy sources such as renewable energy, the capture and storage of CO₂ and the use of CO₂ as a raw material. Despite its potential as a C1 building block, the industrial use of CO₂ as a raw material is currently limited to the synthesis of salicylic acid, urea and organic carbonates¹. The conversion of CO₂ into hydrocarbons and oxygenates usually requires the presence of gas-phase H₂ which is energetically expensive to produce. Nevertheless, studies into the potential origin-of-life have demonstrated that hydrocarbons and oxygenates can be synthesised from CO₂ in the absence of H₂ using water as hydrogen source^{2,3}. If such processes can be optimised for industrial application then this can present a novel strategy for CO₂ utilisation. This work reports initial proof-of-concept studies on the synthesis of hydrocarbons and higher oxygenates from the hydrothermal conversion of CO₂ in the presence of iron-based catalysts.

The hydrothermal conversion of CO₂ was carried out under batch conditions in a stirred tank of 100 mL. The influence of temperature, H₂O:CO₂ mole ratio and different iron-based catalysts was investigated. Liquid samples were analysed by GCMS while gas phase products were analysed by online MS. The main products detected in the liquid phase were ethanol and acetone. Heptanal, formic acid and 2-octanone were also found. Figure 1 shows the liquid product distribution for the main products and also 2-octanone at different reaction temperatures. The products detected in the gas phase were methane, carbon monoxide, formic acid, formaldehyde, acetaldehyde and 2-propanol. Figure 2 shows the conversion of CO₂ and selectivity to the three main gas products (CH₄, CO and 2-propanol) at different reaction temperatures. These results demonstrate the feasibility of converting CO₂ into ≥C₂ species in the absence of gas phase H₂ using iron-based catalysts.

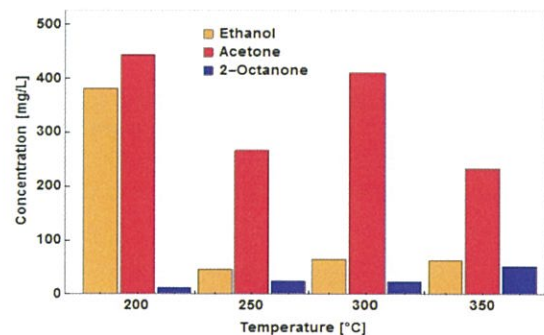


Figure 1. Reaction conditions: 0.56 g Fe powder, CO₂:H₂O mole ratio=0.25, P_{CO₂}=25 bar and reaction time=4 h.

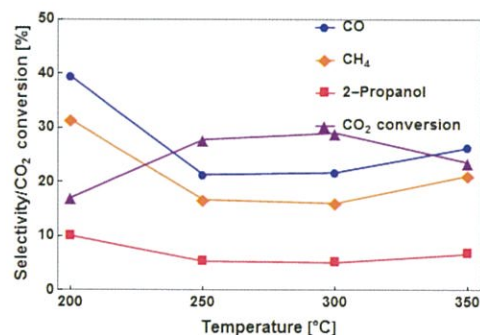


Figure 2. Reaction conditions: 0.56 g Fe powder, CO₂:H₂O mole ratio=0.25, P_{CO₂}=25 bar and reaction time=4 h.

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Fresh water generation by oxidising methane with carbon dioxide to combat the effects of global warming; potential uses of the graphite by-product

Anthony Coogan

Independent Library and Internet Researcher

The literature showed that carbon dioxide could oxidise methane, generating water.

Graphite is a by-product. Possible benefits of adopting this scheme include lowering atmospheric carbon dioxide levels and removal of some dangerous undersea methane hydrate deposits.

Introduction: Inui et al (1) presented an economically viable [in 1998] source of graphite fibre. The competitive acrylonitrile process has since become cheaper.

The object of this library and Internet project has been to utilise (already) captured carbon dioxide to oxidise methane to generate water and graphite either as a consumer product, **or** as a *solid* (therefore much safer) form of carbon storage.

Items studied: major environmental and social harm resulting from global warming arising from carbon dioxide and methane, such as rising sea-level, widespread drought, and ocean acidification. Methane hydrates are blamed for some problems – and in this submission are suggested as a method of helping to overcome them.

Outline of Chemical Reaction Schemes: The industrial process presented by **Inui et al (1)** took place in two stages: 1) Methane decomposition to carbon (graphite) and hydrogen, followed by 2) hydrogen reduction of carbon dioxide to methane (recycled) and water vapour (a by-product in the original scheme).

The second reaction path, suggested by geologists: dire consequences of global warming, expected to take place in three stages: 1) slow warming due to carbon dioxide, followed by 2) release of undersea deposits of methane hydrate. As methane is a powerful greenhouse gas, the temperature rises more rapidly, and 3) oxidation of methane to carbon dioxide to further escalate the warming effect. **Dr. Jason Box (2)** was disturbed by reports of methane rising to the surface.

Other harmful effects: sea-level rise where salt water contaminates *tidal* estuaries and destroys food crops, e.g. the Sacramento Valley in California, and the paddy fields of south-east Asia. Low-lying countries such as Bangladesh will be flooded. Global warming must be tackled urgently. *Ocean acidification* prevents certain sea creatures from forming shells. Entire food chains may collapse. This plan lowers amounts of both CO₂ and CH₄ currently in the atmosphere, or likely to enter it.

Commercial Viability: Water is greatly in demand, as shown by the new \$1 billion desalination plant in San Diego, California. Graphite is less certain to be beneficial, but if need be, it can be stored (CCS) more conveniently and safely than CO₂.

Loss of Heat Output: using Hess' Law, as much as 12% of the heat normally generated through methane combustion can be saved in the water production.

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2. **Dr. Jason Box** reported for Daily Mail Online, by Ellie Zolfagharifard, 8 August 2014, "Climate change will be catastrophic for mankind after study finds methane leaking from the Arctic Ocean, scientist warns"

Effect of NaNO_3 promoter on desorption of CO_2 of MgO absorbent

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Nitrate-promoted MgO is a representative intermediate-temperature (at 300~500°C) CO_2 absorbent. Many researchers have explored the behavior of MgO-based CO_2 absorbent but the role of promoter and the exact operating mechanism of MgO absorbent are still unclear. In order to improve its performance, it is imperative that we understand CO_2 absorption/desorption process of MgO absorbents and the role of promoter.

According to the recent reports [1, 2], it has been established that a nitrate promoter increases the CO_2 absorption capacity and accelerates the CO_2 absorption rate of MgO. Also, in these studies, mechanisms of CO_2 absorption by a nitrate-promoted MgO absorbent have been proposed. Although slightly different in details, the two mechanisms agree that the liquid state promoter functions as the medium for the reaction between CO_2 and MgO. On the other hand, the mechanism of desorption of CO_2 from MgCO_3 , the product of CO_2 absorption by MgO, has attracted far less attention. However, we believe that lowering the desorption temperature and facilitating the desorption kinetics are also important aspects to be taken into consideration in designing CO_2 absorbents. The input energy and cost of operation can be lowered by reducing the gap between absorption and desorption temperatures. Also, the durability of MgO absorbent may be increased by lowering the desorption temperature.

In this study, we demonstrate that the promoter NaNO_3 encourages CO_2 desorption as well. The decomposition temperature of MgCO_3 into MgO and CO_2 is lower by about 100°C in the presence of NaNO_3 than in the absence. In addition, we found that the presence of Li ions in the promoter further lowers the desorption temperature by about 20°C. The effects of the promoter on the desorption of CO_2 can be explained in terms of the changes of relative thermodynamics between MgO and MgCO_3 by having contacts with the promoter. Details of our experiments and their analyses will be presented in our presentation.

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Effect of alkaline–earth metal carbonate salts on CO₂ absorption on NaNO₃–MgO absorbent

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MgO-based CO₂ absorbents have been investigated for the operation in the intermediate temperature of 300–500°C. Typically, these absorbents are composed of MgO and a promoter. NaNO₃ or other alkali nitrates have been explored as the promoter. Although the overall reaction mechanisms have been clarified by previous studies as that the promoter is the medium for the reaction between CO₂ and MgO, many details are not yet clear. We believe that clear elucidation of the details reaction mechanism is the first step for the improvement of the performance of the MgO-based absorbents.

The absorption isotherms of NaNO₃-promoted MgO absorbents in the literature and our own data shows sigmoidal curves. We interpret this as a signature of autocatalyzed kinetics of CO₂ absorption. We further conjectured that this behaviour may arise from the growth kinetics of MgCO₃, which involves nucleation and growth steps. In order to verify this idea, we have prepared various NaNO₃-MgO absorbent samples with different alkaline–earth metal carbonates added. The carbonate salts did not affect the CO₂ absorption capacity of MgO, but they appeared to enhance the CO₂ absorption kinetics. However, the facilitation effects of the added carbonate disappears from the second cycle of the absorption-desorption cycles. These observations are consistent with the proposed mechanism of nucleation and growth of MgCO₃ crystals. Further, our observations indicate that the growth of MgCO₃ is the rate-determining steps.

Details of experimental data and their implications to the CO₂ absorption kinetics by MgO-based absorbents will be presented.

Photoelectrochemical conversion of CO₂ to useful fuels: Opportunities and challenges

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Carbon dioxide is a greenhouse gas with a continuously rising concentration in air, therefore its value-added conversion to useful chemicals or fuels by exploiting sunlight is a very attractive and advantageous method. Photoelectrochemical approaches can be suitable for this purpose, however, CO₂ reduction is a multi-electron process (e.g., 6 e⁻ in the case of methanol), with considerable kinetic barriers. Thus, our main goal is to find p-type semiconductor compounds¹ or assemble nanocomposites which can efficiently catalyze this process. An ideal candidate a) should have its conduction band position at a more negative potential than the selected CO₂ reduction reaction, b) its bandgap should be narrow enough to utilize visible light, moreover c) it should be resistant towards photocorrosion, and finally d) it has to be cost effective.

In the first part of my presentation I am showing the photoelectrochemical behavior of thin films (e.g., silicon carbide, Cu₂O, CuFeO₂, copper-niobate) synthesized in our laboratories.^{2,3} The films were characterized by several techniques, such as: photovoltammetry, stationary measurements (chronoamperometry), Scanning Electron Microscopy (SEM), FT-IR and Raman spectroscopy. The photoelectrochemical reactions were followed using GC and GC-MS, to assess their applicability in hydrogen evolution as well as carbon dioxide reduction.

As the second example, we briefly present examples for the electrosynthesis semiconductor/conducting polymer composite materials for PEC CO₂ reduction.⁴ Through careful control over the composition and morphology of these hybrid materials we aim to make improvements in: light absorption, interfaces (charge separation), and stability. A carefully designed sequential method will be presented, where the oxide component of the hybrid material is in situ generated in the presence of its polymeric counterpart. These methods result and in an intimate contact between the organic and inorganic components, both at the physical and electronic level which is likely to contribute to an improved PEC performance. Structure property relationships will be shown, which may act as guidelines for the rational design of hybrid photocathodes.

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Waste CO₂ and biomass-based chemical synthesis for the green economy

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Anthropogenic use of fossil fuels, releasing carbon dioxide, is a major cause of climate change.¹ Recent research on the utilisation of carbon dioxide as a chemical feedstock shows promise, enabling the lowering of greenhouse gas emissions, the replacement of existing petrochemical derived products and reduction in costs associated with carbon capture and storage.² Brazil has several unique opportunities in this field, particularly due to the availability of waste carbon dioxide from the large-scale fermentation of sugarcane and bagasse combustion. This offers advantages over other sources, as waste CO₂ from fermentation will not require purification and will meet emerging (EU) standards around the bio-content of products. The combination of this waste carbon dioxide with bio-derived molecules, specifically bioethanol and glycerol, to produce organic carbonates would be of huge commercial interest.

A collaboration between the University of York and the Federal University of Rio de Janeiro through the Newton Fund is outlining sustainable paths for the production of new materials and chemicals using carbon dioxide from bioethanol production and bio-derived platform molecules and enabling the exchange of CO₂ utilisation expertise and knowledge. The key successes of this project to develop a new UK-Brazil CO₂ utilisation network will be highlighted including:

- Analysis of the opportunities and challenges for the utilisation of byproduct CO₂ from bioethanol plants
- Research on routes to entirely bio-derived cyclic carbonates
- Knowledge exchange including an interdisciplinary postgraduate course on 'CO₂ utilisation' and building a Brazilian CO₂ utilisation network



Attendees and speakers at the postgraduate course on CO₂ utilisation, UFRJ, April 2015

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CO₂ capture and separation from simulated flue gas using low cost solid sorbents and a pressure swing process

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To realise the potential of Carbon Dioxide (CO₂) utilisation, we first require effective capture processes, which make use of low cost sorbents and have a low energy penalty. Successful tests on low cost, widely available sorbents including some ionic liquids have been carried out with great success. The sorbents tested have shown high stability, selectivity and capacity for CO₂. Optimal tests yield a CO₂ loading of 63 %wt. at 50bar and 296k. However loading is reduced at increased temperatures and decreased pressures. The rate of CO₂ adsorption is considered to be very fast, full sorbent saturation (of CO₂) was reached in less than 10 seconds for lower capacity ionic liquids and within 5 minutes for other sorbents. All sorbents have shown a stable and repetitive use over hundreds of adsorption-desorption cycles with no degradation losses. An example result when simulating a pressure swing separation process has enabled us to take a 25 %vol. CO₂ stream (75 %vol. N₂) and refine it to yield a small volume of gas containing 63 %vol. CO₂ in a single pass of the adsorber. The pressure swing process is in it's early stages and requires some optimisation, but shows very promising results for CO₂ capture and separation from flue gas.

Modelling of CO₂ reduction by pulsed corona discharge

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The work reported is part of a sub-project within 4CU (Comprehensive and Coordinated Approach to Carbon Capture and Utilisation) focusing on carbon monoxide production. Non-thermal plasmas, specifically pulsed corona discharges, are used as they already have proven industrial-scale application in electrostatic precipitators to remove particulates from waste gas streams in, for example power stations and cement factories. The utilisation of high voltage electricity passed through wires or points with a narrow curvature generates a high local electric field from which a corona discharge is established. The objective is to take recognised corona discharge technology and apply it in novel way. Carbon dioxide gas is passed through a strong electrical field wherein electron excitation occurs so that the gaseous feed becomes partially ionised and, upon recombination, a fraction of carbon monoxide is formed along with ozone and oxygen as minor products.

The aim of the presented work is to develop a numerical model that has the potential to scale the experiment levels and provide efficient tool to analyse the CO₂ reduction by corona discharge. The spatial distribution of the species generated in a wire-cylinder negative corona discharge in carbon dioxide has been computed using a plasma chemistry model. The model includes the most significant reactions between electrons, ions, atoms and molecules. Continuity equations for all species present in the corona plasma are applied, which are coupled with Poisson's equation for electric field calculations. The numerical model is able to reproduce the basic structure of the corona discharge, and highlights the importance of reactor parameters on the CO₂ reduction.

Key words

Corona discharge, CO₂ reduction, Modelling, Plasma chemistry.