



7-9 September 2015, Sheffield, UK

# Carbon Dioxide Utilisation Faraday Discussion

 #CO2

## Book of Abstracts



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## Introduction

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**Carbon Dioxide Utilisation: Faraday Discussion** is organised by the Faraday Division of the Royal Society of Chemistry.

This book contains abstracts of the 46 posters presented at Carbon Dioxide Utilisation: Faraday Discussion. All abstracts are produced directly from typescripts supplied by authors. Copyright reserved.

### Oral presentations and discussions

All delegates at the meeting, not just speakers, have the opportunity to make comments, ask questions, or present complementary or contradictory measurements and calculations during the discussion. If it is relevant to the topic, you may give a 5 minute presentation of your own work during the discussion. These remarks are published alongside the papers in the final volume and are fully citable. If you would like to present slides during the discussion please let the session chair know and load them onto the computer in the break before the start of the session.

### Posters

Posters have been numbered consecutively: P01-P46.

There will be 2 formal poster viewing sessions: 17.15 on Monday 7 September and 17.30 on Tuesday 8 September 2015.

### Poster prize

The Faraday Discussions Poster Prize, sponsored by Cogent, will be awarded to the best student poster as judged by the committee.

### Faraday discussion volume

Copies of the Discussion Volume will be distributed approximately 6 months after the meeting. To expedite this, it is essential that summaries of contributions to the discussion are received no later than Wednesday 16 September for questions and comments and Wednesday 30 September for responses. In order to keep the students fees low the Discussion Volume is NOT included in the student conference fees. A copy of the publication may be purchased at a reduced price, only for orders placed at the meeting; an application form is available from the information desk at the meeting.

### Sponsors

We would like to thank the following company for their sponsorship of Carbon Dioxide Utilisation: Faraday Discussion Poster Prize.

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## Scientific committee and speaker list

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### Scientific committee

Peter Styring  
*University of Sheffield, UK*

Katy Armstrong  
*University of Sheffield, UK*

Adam Lee  
*Aston University, UK*

Peter Licence  
*University of Nottingham, UK*

Geoffrey Maitland  
*University of Sheffield, UK*

Michael North  
*University of York, UK*

Alessandra Quadrelli  
*CEP Lyon, France*

### Invited speakers

Martyn Poliakoff  
*University of Nottingham, UK*

Walter Leitner  
*RWTH Aachen University, Germany*

Michele Aresta  
*IMM Chair, ChBE-NUS, Singapore and CIRCC-IT, Italy*

Gabriele Centi  
*University of Messina, Italy*

Peter Edwards  
*University of Oxford, UK*

Richard Heyn  
*SINTEF, Norway*

Michael Priestnall  
*Cambridge Carbon Capture, UK*

Charlotte Williams  
*Imperial College London, UK*

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## Meeting information

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All lectures will take place in **High Tor 2** on the first floor of the Edge building on the University of Sheffield Campus.

The 2 poster sessions will take place on Monday 7 September and Tuesday 8 September after the main lectures and will be in High Tor 5 which is located to the side of the main lecture room on the same floor.

Catering during the daytime will take place in High Tor 5 along with the posters.

	Mid-morning	Afternoon
Monday 7 September		15:30
Tuesday 8 September	11:00	15:30
Wednesday 9 September	10:30	

A buffet lunch on all 3 days will be served in High Tor 5. Lunch is provided for all delegates.

### Monday evening

There will be dinner on the evening of Monday 7 September; this will be served in the dining room on the ground floor of The Edge at 18.45

### Conference dinner

The Conference Dinner on the evening of Tuesday 8 September will take place in The Edge dining room from 19.00.

### Tuesday

Please note the morning will start at 9.30am

### The Edge accommodation

Your breakfast will take place in the Edge dining room.

Check in is from 14.00 and check out is by 10.00 so we recommend that you check out at breakfast. There will be a luggage store available at reception. Should you require out-of-hours assistance with your accommodation, there are details of contact numbers located at reception.

### The University of Sheffield internet access

#### Guest wireless service

Wireless internet access is obtained via a Wi-Fi code available from the registration desk upon registration. The code will also be displayed around the building.

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# Programme

## Monday 7 September

Time	Event	
11:00	Registration, tea and coffee	
12:00	Lunch	
12.45	<b>Welcome and introductions</b> Peter Styring, <i>Chair of Scientific Committee</i>	
12.55	<b>Discussion format presentation</b> Mary Macleod and Amy Hazlehurst, <i>Faraday Discussions Publishing Editors</i>	
13.00	<b>Introductory lecture</b> Martyn Poliakoff <i>University of Nottingham</i>	
<b>Session 1: Atom efficiency in small molecule and macromolecule synthesis</b> Session Chair: Peter Styring		
14.00	<b>New catalysts for carboxylation of propylene glycol to propylene carbonate via high-throughput screening</b> <u>Richard Heyn</u> , José A. Castro-Osma, James W. Comerford, Michael North and Elisabeth Tangstad <i>SINTEF Materials and Chemistry</i>	Paper 6241
14.05	<b>A MALDI-TOF MS analysis study of the binding of 4-(<i>N,N</i>-dimethylamino) pyridine to amine-bis(phenolate) chromium(III) chloride complexes: mechanistic insight into differences in catalytic activity for CO<sub>2</sub>/epoxide copolymerizations</b> <u>Christopher Kozak</u> , April M. Woods, Christina S. Bottaro, Katalin Devaine-Pressing and Kaijie Ni <i>Memorial University of Newfoundland</i>	Paper 6643
14.10	<b>Kinetic and economic analysis of reactive capture of dilute carbon dioxide with Grignard reagents</b> <u>George Dowson</u> , I. Dimitriou, R. E. Owen, D. G. Reed, R. W. K. Allen and P. Styring <i>University of Sheffield</i>	Paper 6604
14.15	Discussion	
15:30	Afternoon tea	
16.00	<b>Carbon dioxide capture and utilization: Using dinuclear catalysts to prepare polycarbonates</b> <u>Charlotte Williams</u> , N. Yi, J. Unruangsri and J. Shaw <i>Imperial College London</i>	Paper 6244
16.05	<b>Thioether-triphenolate bimetallic iron(III) complexes as robust and highly efficient catalysts for cycloaddition of carbon dioxide to epoxides</b> <u>Carmine Capacchione</u> , Antonio Buonerba, Francesco Della Monica, Assunta De Nisi, Ermanno Luciano, Stefano Milione, Alfonso Grassi and Bernhard Rieger <i>Università di Salerno</i>	Paper 6571
16.10	Discussion	
17.00	Lightning poster presentation (by invitation of the Scientific Committee)	
17:15	<b>Poster session and wine reception</b> Sponsored by Cogent	
18:45	Dinner	



**Tuesday 8 September**

Time	Event	
<b>Session 2: CO<sub>2</sub> reduction reaction</b>		
Session Chair: Mike North		
09:30	<b>Electrocatalytic conversion of CO<sub>2</sub> to produce solar fuels in electrolyte or electrolyte-less configurations of PEC cells</b> <i>Gabriele Centi, C. Ampelli, C. Genovese, B. C. Marepally, G. Papanikolaou and S. Perathoner</i> <i>University of Messina</i>	Paper 6239
09:35	<b>Improving the efficiency of electrochemical CO<sub>2</sub> reduction using immobilized manganese complexes</b> <i>Alexander Cowan, James J. Walsh, Charlotte L. Smith, Gaia Neri, George F. S. Whitehead and Craig M. Robertson</i> <i>University of Liverpool</i>	Paper 6578
09:40	<b>Discussion</b>	
10:30	<b>Morning tea</b>	
11:15	<b>Catalytic dehydrogenation of propane by carbon dioxide: A medium-temperature thermochemical process for carbon dioxide utilisation</b> <i>Peter Edwards, X. Du, B. Yao, S. Gonzalez-Cortes, V. L. Kuznetsov, Hamid AlMegren and T. Xiao</i> <i>University of Oxford</i>	Paper 6240
11:20	<b>Hydrothermal conversion of carbon dioxide into formic acid with the aid of zerovalent iron: the potential of a two-step approach</b> <i>Koen Michiels, B. Peeraer, W. van Dun, J. Spoorena and V. Meynen</i> <i>Flemish Institute for Technological Research, VITO NV</i>	Paper 6665
11:25	<b>Novel process and catalytic materials for converting of CO<sub>2</sub> and H<sub>2</sub> containing mixtures to liquid fuels and chemicals</b> <i>Moti Herskowitz, Nora Meiri, Yakov Dinburg, Meital Amoyal, Viatcheslav Koukouliev, Roxana Vidruk Nehemya and Miron V. Landau</i> <i>Ben-Guiron University of the Negev</i>	Paper 6585
11:30	<b>Discussion</b>	
12.45	<b>Lunch</b>	
<b>Session 3: CO<sub>2</sub> reduction reactions</b>		
Session Chair: Alessandra Quadrelli		
14:00	<b>Plasma-based conversion of CO<sub>2</sub>: Current status and future challenges</b> <i>Annemie Bogaerts, Tomas Kozak, Koen van Laer and Ramses Snoeckx</i> <i>University of Antwerp</i>	Paper 6608
14:05	<b>Taming microwave plasma to beat thermodynamics in CO<sub>2</sub> dissociation</b> <i>Gerard van Rooij, D. C. M. van den Bekerom, N. den Harder, T. Minea, G. Berden, W. A. Bongers, R. Engeln, M. F. Graswinckel, E. Zoethout and M. C. M. van de Sanden</i> <i>Dutch Institute for Fundamental Energy Research</i>	Paper 6676
14:10	<b>Novel windows for "solar commodities": A device for CO<sub>2</sub> reduction using plasmonic catalyst activation</b> <i>Alexander Navarrete, Sergio Muñoz, Luis M. Sanz-Moral, Juergen J. Brandner, Peter Pfeifer, Ángel Martín, Roland Dittmeyer and María J. Cocero</i> <i>University of Valladolid, Department of Chemical Engineering and Environmental Technology, High Pressure Processes Group</i>	Paper 6674
14:15	<b>Discussion</b>	
15:30	<b>Afternoon tea</b>	



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**Tuesday 8 September continued**

Time	Event	
<b>Session 4: Wider impacts</b> Session Chair: Katy Armstrong		
16:00	<b>Environmental potential of carbon dioxide utilization in the polyurethane supply chain</b> <i>André Bardow</i> , Niklas von der Assen, André Sternberg and Arne Kätelhön <i>RWTH Aachen University</i>	Paper 6663
16:05	<b>A framework for the analysis of the security of supply of utilising carbon dioxide as a chemical feedstock</b> <i>Eric Fraga</i> and Melvin Ng <i>University College London</i>	Paper 6641
16:10	<b>Investigating public perceptions of carbon dioxide utilisation (CDU) technology: A mixed methods study</b> <i>Christopher Jones</i> , D. Kaklamanou, W. M. Stuttard, R. L. Radford and J. Burley <i>University of Sheffield</i>	Paper 6656
16:15	<b>Discussion</b>	
17:30	<b>Poster session and wine reception</b> Sponsored by Cogent	
19:00	<b>Conference dinner</b>	

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**Wednesday 9 September**

Time	Event	
<b>Session 5: Capture agents and conversion mechanisms</b>		
Session Chair: Geoffrey Maitland		
09:00	<b>Extraction of Mg(OH)<sub>2</sub> from Mg silicate minerals with NaOH assisted with H<sub>2</sub>O: Implications for CO<sub>2</sub> capture from exhaust flue gas</b> <u>Michael Priestnall</u> , Silvia Madeddu, Erik Godoy, R. Vasant Kumar, Sugat Raymahasay, Michael Evans, Ruofan Wang, Seabelo Manenye and Hajime Kinoshita <i>Cambridge Carbon Capture</i>	Paper 6242
09:05	<b>CO<sub>2</sub> capture and electrochemical conversion using super basic [P6,6,6,14][124Triz]</b> Christopher Hardacre, <u>Nathan Hollingsworth</u> , S. F. Rebecca Taylor, Miguel T. Galante, Johan Jacquemin, Claudia Longo, Katherine B. Holt and Nora H. de Leeuw <i>University College London</i>	Paper 6568
09:10	<b>Highly optimized CO<sub>2</sub> capture by inexpensive nanoporous covalent organic polymers and their amine composite</b> <u>Cafer Tayyar Yavuz</u> and Hasmukh A. Patel <i>Korea Advanced Institute of Technology and Science</i>	Paper 6678
09:15	<b>Discussion</b>	
10:30	<b>Morning tea</b>	
<b>Session 6: Biotransformations and biomimetics</b>		
Session Chair: Michele Aresta		
11:00	<b>Solar energy utilization in the direct photocarboxylation of 2,3-dihydrofuran using CO<sub>2</sub></b> <u>Michele Aresta</u> , Angela Dibenedetto, Tomasz Baran, Szymon Wojtyład and Wojciech Macykd <i>ChBE-NUS, Singapore and CIRCC-IT</i>	Paper 6238
11:05	<b>CO<sub>2</sub> capture systems based on saccharides and organic superbases</b> <u>Gonçalo Carrera</u> , N. Jordão, L. C. Branco and M. Nunes da Ponte <i>LAQV, REQUIMTE, Universidade Nova de Lisboa</i>	Paper 6670
11:10	<b>An enriched electroactive homoacetogenic biocathode improves the microbial electrosynthesis of acetate through carbon dioxide reduction</b> <u>Deepak Pant</u> , Gunda Mohanakrishna, Jai Sankar Seelam and Karolien Vanbroekhoven <i>VITO, Flemish Institute for Technological Research</i>	Paper 6246
11:15	<b>Discussion</b>	
12:30	<b>Concluding remarks lecture</b> Walter Leitner <i>RWTH Aachen University</i>	
13:15	<b>Acknowledgements</b>	
13:20	<b>Close of meeting and lunch</b>	

Presenting authors are indicated in the programme by an underline. The affiliation is for the presenting author.



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## Poster presentations

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- P01 A dual-electrolyte microfluidic reactor for electro-reduction of CO<sub>2</sub>**  
Xuan, Jin; Lu, Xu; Leung, Dennis Y.C; Wang, Huizhi  
*Heriot-Watt University, UK*
- P02 Electrochemical conversion of carbon dioxide to methanol at Cu<sub>2</sub>O/ZnO gas diffusion electrodes**  
Albo, Jonathan; Castaño, Pedro; Irabien, Angel  
*University of Basque Country (UPV/EHU), Spain*
- P03 Atmospheric CO<sub>2</sub> fixation by a new type of complexes of first row metals and bis(amine)-bis(phenolate) ligands: Mechanism and conversion into value derivatives**  
Rodríguez-Silva, Laura; Carballido, Rocío; González-Riopedre, Gustavo; Maneiro, Marcelino  
*Universidade de Santiago de Compostela, Spain*
- P04 Recent advances in using CO<sub>2</sub> to manufacture fuel and chemicals**  
Wang, Hui; Wang, Liang; Kong, Lingzhao; Wei, Wei; Sun, Yuhan  
*Shanghai Advanced Research Institute, China*
- P05 The role of CO<sub>2</sub> utilisation in climate change mitigation**  
Mac Dowell, Niall; Fennell, Paul S.; Shah, Nilay; Maitland, Geoffrey C.  
*Imperial College, UK*
- P06 One-pot procedure for the synthesis of cyclic carbonate monomers from 1,3-diols and low CO<sub>2</sub> pressure: a novel, mild and safe phosgene alternative**  
Gregory, Georgina  
*University of Bath, UK*
- P07 Photocatalytic conversion of CO<sub>2</sub> into value-added chemicals by using heterostructure-based nanocatalysts**  
He, Tao  
*National Center for Nanoscience and Technology, China*
- P08 Probing the electrode/electrolyte interfacial structure of CO<sub>2</sub> electrochemical reduction to CH<sub>3</sub>OH catalyzed by the Pt-pyridine system**  
Chen, Xue-Jiao; Yu, Song; Wu, De-Yin; Tian, Zhong-Qun  
*Xiamen University, China*
- P09 Observation of guanidine-carbon dioxide complexation in solution and its role in the reaction of carbon dioxide and propargyl amines**  
Nicholls, Rachel; Kaufhold, Simon; Nguyen, Bao  
*University of Leeds, UK*
- P10 Design of experiments as a valuable tool for rational catalyst development in methanation of syngas containing hydrocarbons**  
Krebs, Florian; Baik, Joon Hyun; Simeonov, Kalin; Palkovits, Regina  
*RWTH Aachen University, Germany*
- P11 Process conditions study via design of experiments for dry reforming of methane**  
Pegios, Nikolaos; Baik, Joon Hyun; Park, Joo-Hyoung; Simeonov, Kalin; Palkovits, Regina  
*RWTH Aachen University, Germany*
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- P12 Carbon dioxide reforming of methane**  
Churina, Dina; Dossumov, Kusman; Yergazieva, Gaukhar  
*AL-Farabi Kazakh National University, Kazakhstan*
- P13 Structure-dependent electroreduction of CO<sub>2</sub> at Au-Pd core-shell nanostructures**  
Humphrey, Jo; Plana, Daniela; Celorrio, Veronica; Sadasivan, Sajanikumari; Rodríguez, Paramaconi; Tooze, Robert; Fermin, David  
*University of Bristol, UK*
- P14 Methyl esters as efficient and green water suppressors in the synthesis of dimethyl carbonate from CO<sub>2</sub>**  
Marciniak, Aryane; Mota, Claudio  
*Universidade Federal do Rio de Janeiro, Brazil*
- P15 Production of methanol and dimethyl ether from CO<sub>2</sub> hydrogenation over bifunctional catalysts**  
Silva, Renata; Mota, Claudio  
*Universidade Federal do Rio de Janeiro, Brazil*
- P16 Processing of methane to synthesis gas over the fiberglass catalysts**  
Dossumov, Kusman; Mironenko, Anatoly; Kazieva, Asel; Mansurov, Zulkhair; Kudyarova, Janar  
*Institute of Combustion Problems, Kazakhstan*
- P17 Carbon dioxide conversion of methane over the polyoxide catalysts**  
Dossumov, Kusman; Mansurov, Zulkhair; Mironenko, Anatoly; Yergazyieva, Gaukhar; Churina, Dina; Kazieva, Asel  
*Institute of Combustion Problems, Kazakhstan*
- P18 Carbon dioxide reforming of methane**  
Dossumov, Kusman; Dossumov, Kusman; Yergazieva, Gaukhar; Suynbayev, Ualikhan  
*Institute of Combustion Problems, Kazakhstan*
- P19 The direct carbonation of glycerol with CO<sub>2</sub> using heterogeneous catalysts**  
Ozorio, Leonardo; Mota, Claudio  
*Universidade Federal do Rio de Janeiro, Brazil*
- P20 High pressure CO<sub>2</sub> reduction: in operando heterogeneous catalyst characterisation setup**  
Reymond, Helena; Lauper, Andreas; Rudolf von Rohr, Philipp  
*ETH Zürich, Switzerland*
- P21 Polymers derived from biomass and incorporating carbon dioxide as replacements for petroleum based plastics**  
Ingram, Ian; McElroy, C. Rob; Dodson, Jennifer; Farmer, Thomas; North, Michael; Clark, James  
*University of York, UK*
- P22 Synthesis of cyclic carbonates from diols and carbon dioxide**  
Comerford, James; Castro-Osma, Jose; North, Michael  
*University of York, UK*
- P23 Conversion of CO<sub>2</sub> via the utilisation of atmospheric pressure plasmas**  
Foote, Alexander; North, Michael; Gans, Timo  
*University of York, UK*
- P24 Ionic liquids as catalysts for CO<sub>2</sub> transformation in dimethyl carbonate**  
Einloft, Sandra; Vieira, Michele; Bernard, Franciele; Grillo, Igor; Seferin, Marcus  
*Pontifical Catholic University of Rio Grande do Sul, Brazil*
-



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- P25 **Electrochemically driven carbon dioxide mineralisation**  
Lamb, Katie; North, Michael; Parkin, Alison  
*University of York, UK*
- P26 **Cycloaddition of epoxide and CO<sub>2</sub> to cyclic carbonate catalyzed by vanadium complexes of amine-bis(phenolate) ligands**  
Elkurtehi, Ali; M. Kerton, Francesca  
*Memorial University of Newfoundland, Canada*
- P27 **Hydrothermal conversion of CO<sub>2</sub> into higher hydrocarbons and oxygenates**  
Quintana Gomez, Laura; McGregor, James  
*The University of Sheffield, UK*
- P28 **Fresh water generation by oxidising methane with carbon dioxide to combat the effects of global warming; Potential uses of the graphite by-product**  
Coogan, Anthony  
*Retired, Ireland*
- P29 **Effect of NaNO<sub>3</sub> promoter on desorption of CO<sub>2</sub> of MgO absorbent**  
Jo, Seung-Ik; Kim, Kang-Yeong; Kwak, Jin-Su; An, Young-In; Kwon, Young-Uk  
*Sungkyunkwan University, Republic of Korea*
- P30 **Effect of alkaline-earth metal carbonate salts on CO<sub>2</sub> absorption on NaNO<sub>3</sub>-MgO absorbent**  
Kim, Kangyeong; Jo, Seung-Ik; Kwak, Jin-Su; Ahn, Young-In; Kwon, Young Uk  
*Sungkyunkwan University, Republic of Korea*
- P31 **Photoelectrochemical conversion of CO<sub>2</sub> to useful fuels: Opportunities and challenges**  
Janaky, Csaba; Hursan, Dorottya; Kormanyos, Attila; Rajeshwar, Krishnan  
*MTA TKI, Hungary*
- P32 **Waste CO<sub>2</sub> and biomass-based chemical synthesis for the green economy**  
Dodson, Jennifer; Vega Barbero, Jose; Topi, Corrado; Mota, Claudio; North, Michael  
*University of York, UK*
- P33 **CO<sub>2</sub> capture and separation from simulated flue gas using low cost solid sorbents and a pressure swing process**  
Reed, Daniel; Dowson, George; Styring, Peter  
*The University of Sheffield, UK*
- P34 **Modelling of CO<sub>2</sub> reduction by pulsed corona discharge**  
Moss, Matthew; Yanallah, Khelifa  
*The University of Sheffield, UK*
- P35 **A hybrid QM/MM embedded cluster approach to modelling the reactivity of carbon dioxide over metal oxide surfaces**  
Farrow, Matthew; Downing, Christopher A.; Dutta, Gargi; Keal, Thomas W.; Sherwood, Paul; Sokol, Alexey A.; Catlow, C. Richard A.  
*University College London, UK*
- P36 **Influence of the ionic liquid cation on the electrochemical reduction of CO<sub>2</sub>**  
Michez, Roman; Christophe, Jennifer; Doneux, Thomas; Buess-Herman, Claudine  
*Université Libre de Bruxelles, Belgium*
- P37 **Multivariate models for ionic liquids catalytic systems in CO<sub>2</sub> cycloaddition to propylene oxide**  
Seferin, Marcus; Grillo, Igor; Vieira, Michele; Bernard, Franciele; Einloft, Sandra  
*Pontifical Catholic University of Rio Grande do Sul, Brazil*
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- P38 Direct synthesis of cyclic carbonate from alkenes**  
Alsaari, Raiedhah; Nowicka, Ewa; Miedziak, Peter; Kondrat, Simon; Edwards, Jennifer; Hutchings, Graham  
*Cardiff University, UK*
- P39 Synthesis of cyclic carbonates catalysed by aluminium heteroscorpionate complexes**  
Castro-Osma, José A.; Martínez, Javier; Alonso-Moreno, Carlos; Lara-Sánchez, Agustín; North, Michael; Otero, Antonio  
*University of Castilla-La Mancha, Spain*
- P40 Understanding the potential of carbon dioxide utilization**  
Armstrong, Katy; Styring, Peter; Zaragoza, Ana Villa; Wilson, I.D. Grant  
*The University of Sheffield, UK*
- P41 Improved solid oxide electrolysis for CO<sub>2</sub> conversion, using microchanneled cathode supports.**  
Parkinson, Gordon; Xu, Shanshan; Shao, Xin; Dong, Dehua; Hucker, Leigh; Marin, Justin; Pham, Thang  
*Curtin University, Australia*
- P42 Carbon dioxide utilisation for methanol fuel production: Life cycle analysis**  
Villa, Ana  
*The University of Sheffield, UK*
- P43 Challenges for solar fuel production via photocatalysis**  
Bay, Elizabeth; Ola, Oluwafunmilola; Bos, Jan-Willem; Maroto-Valer, Mercedes  
*Heriot Watt University, UK*
- P44 Photoautotrophic carbon uptake by microalgae for biotransformations**  
Vaidyanathan, Seetharaman; Kapoore, Rahul; Pandey, Deeptanshu  
*The University of Sheffield, UK*
- P45 CO<sub>2</sub> biorefinery model: A Sustainable biosequestration strategy with simultaneous energy and value addition**  
Modestra, J. Annie; Butti, Sai Kishore; Velvizhi, G; Amulya, Hari Prasad, K. R.; Chiranjeevi, P; Rohith, M. V.; Shikha, D  
*CSIR-IICT, India*
- P46 Size controlled formation of PdZn nanoparticulate for CO<sub>2</sub> hydrogenation**  
Bahruji, H.; Bowker, M; Dimitratos, N; Hutchings, G. J.; Golunski, S  
*Cardiff University, UK*

Underline denotes presenting author to whom affiliation applies

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# A dual-electrolyte microfluidic reactor for electro-reduction of CO<sub>2</sub>

Xu Lu,<sup>[a]</sup> Dennis Y.C. Leung,<sup>[a]</sup> Huizhi Wang,<sup>[a,b]</sup> and Jin Xuan<sup>[a,b]</sup>

<sup>a</sup>Department of Mechanical Engineering, The University of Hong Kong, Hong Kong

<sup>b</sup>School of Engineering and Physical Sciences, Heriot-Watt University, UK

Electrochemical process, with its nature of efficient and controllable operation in mild condition, provides a sustainable prospect towards the reduction of CO<sub>2</sub> into usable fuels. In this study, we introduce a dual-electrolyte configuration for CO<sub>2</sub> electro-reduction system. The thermodynamically determined cell potential could be lowered by pairing cathode with acidic electrolyte and anode with alkaline medium. Lowered pH on cathode side would favour the reaction kinetics and improve the selectivity of the catalyst. It is also experimentally corroborated that alkaline anolyte ensures the oxygen formation at low equilibrium potential<sup>1</sup>.

However, a membrane has been found to be necessary as a separator to maintain distinctive conditions on each electrode sides<sup>1</sup> and avoid anode poisoning by the products generated at the cathode<sup>2</sup>. For these reasons, most of current researches have been conducted on membrane-based electrolytic reactor<sup>1,2</sup>, whose restrictions include high membrane cost, low interphase contact, crossover etc. To tackle these bottlenecks, microfluidic technique<sup>3</sup> is implemented. Microfluidics refers to the phenomenon that two laminar fluids flowing in a micro-scale channel would intrinsically form a controllable layer that functions the same as traditional membrane. This virtual separating layer (Figure 1) frees a dual-electrolyte reactor from limitations of membrane and offers a high heat & mass transfer rate to achieve efficient electro-reduction of CO<sub>2</sub>.

With the cutting-edge membrane-less architecture and dual-electrolyte configuration, the reactor design proposed in this paper would not only help to address the most pressing hindrances of conventional membrane electrolytic cell, but also benefit the reduction of thermodynamic barrier and enhancement of reactivity.

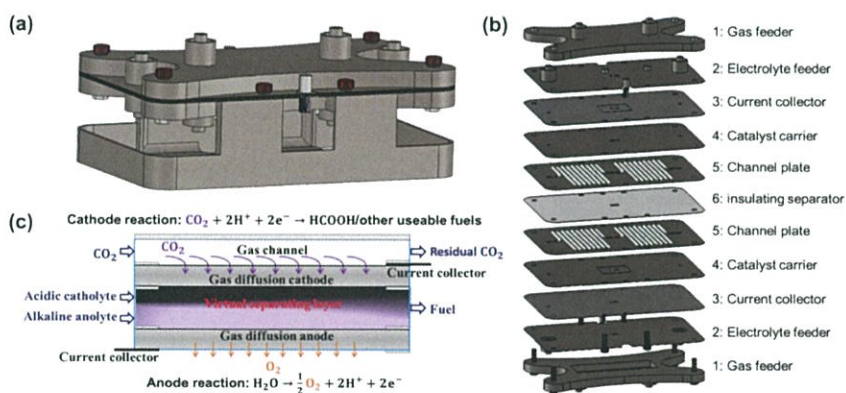


Figure 1. Demonstration of the microfluidic reactor. (a) Assembly drawing; (b) Component configuration; and (c) Schematic diagram of the dual-electrolyte microfluidic reactor for CO<sub>2</sub> electro-reduction (N.B. the virtual separating layer is identified by fluorescein microscopy).

## Acknowledgment

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# Electrochemical conversion of carbon dioxide to methanol at $\text{Cu}_2\text{O}/\text{ZnO}$ gas diffusion electrodes

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## Introduction

In the last century with the intensification of human industrial activities, the balance between the  $\text{CO}_2$  produced and consumed on earth has gradually been disrupted, leading to a higher concentration of  $\text{CO}_2$  in the atmosphere and making global warming a pressing issue. The recycling of  $\text{CO}_2$  by electrochemical reduction uses energy to transform  $\text{CO}_2$  into its reduced forms and it has attracted worldwide interest due to its potential environmental and economic benefits.<sup>1</sup> This technology, coupled to a renewable energy source, such as wind or solar, could generate carbon neutral fuels or industrial chemicals that are conventionally derived from petroleum. Among the possible reduction products from this process, the  $\text{CO}_2$  conversion to methanol, with relatively high energy density and stable storage properties, is regarded as a feasible approach that is entering the stage of gradual implementation.<sup>2</sup> Among the studied materials to reduce  $\text{CO}_2$  electrochemically, copper oxides (e.g.  $\text{Cu}_2\text{O}$ ) are considered unique with both intermediate hydrogen overpotentials and CO adsorption allowing higher methanol yields.<sup>3</sup> Besides, Zn is able to stabilize  $\text{Cu}^+$  atoms and remove impurities that can deactivate the catalyst for methanol production in the long run.<sup>4</sup>

## Aim

The present study aims to evaluate the performance of a filter-press type electrochemical cell for the continuous electro-reduction of  $\text{CO}_2$  to methanol under ambient conditions when  $\text{Cu}_2\text{O}/\text{ZnO}$  mixtures are used as electrocatalysts in gas diffusion electrodes (GDE). The electrodes are prepared by spray-coating of the metal particles in carbon supports. The filter press-cell consists of two compartments divided by an ion exchange membrane. A Pt plate is selected as the anode, along with an Ag/AgCl saturated with KCl as a reference electrode. Particular emphasis is placed on evaluating and comparing the methanol production and Faradaic efficiencies at different loads of  $\text{Cu}_2\text{O}-\text{ZnO}$  particles and current density levels. The results are compared to current state of the art for  $\text{CO}_2$  electro-reduction to methanol.

## Acknowledgement

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# Atmospheric CO<sub>2</sub> fixation by a new type of complexes of first row metals and bis(amine)-bis(phenolate) ligands: Mechanism and conversion into value derivatives

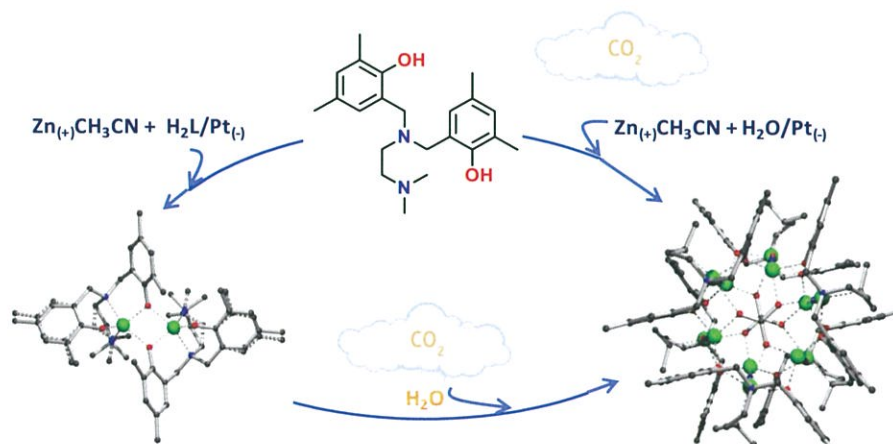
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The utilization of carbon dioxide as a raw material for chemical syntheses is an attractive strategy to valorize this product. According to this vision, CO<sub>2</sub> is no longer seen as a waste product with dangerous for the environment. The use of CO<sub>2</sub> as a chemical feedstock will almost certainly not reduce its atmospheric concentration significantly; however, it may provide access to high-value products from a low-cost resource.<sup>1</sup> Indeed, significant efforts have been attracted to convert the thermodynamically stable and comparatively unreactive CO<sub>2</sub> molecule into value-added compounds in an efficient manner. To date, metal complexes for CO<sub>2</sub> fixation has also contributed to our understanding of C–C and C–H bond formation reactions as well as C–O bond cleavage reactions involved in the catalytic processes for converting CO<sub>2</sub> into high-value products.<sup>2</sup>

Herein, we report a new type of complexes of inexpensive first-row metals, using bis(amine)-bis(phenolate) ligands (H<sub>2</sub>L), that are able to fix atmospheric carbon dioxide. Dinuclear zinc and cobalt complexes and a trinuclear nickel complex with these ligands were afforded by electrochemical oxidation in non-aqueous conditions. These products, characterized by different spectroscopic techniques and X-ray diffraction studies, react in presence of water and atmospheric carbon dioxide. The chemistry involved in these efficient and selective reactions allows proposing the mechanism through water activation for fixation of carbon dioxide and its conversion into carbonate by this type of complexes. Zinc and cobalt carbonate complexes were isolated and their structures solved by X-ray crystallography. Progress on the obtention of chemical value derivatives from these CO<sub>2</sub> fixation processes will be also discussed.



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## Recent advances in using CO<sub>2</sub> to manufacture fuel and chemicals

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Carbon dioxide (CO<sub>2</sub>) emission has become a global issue due to the significant and continuous rise of atmospheric CO<sub>2</sub> concentration due to the recent accelerated growth in consumption of the petrified carbon-based energy worldwide. Thus, effective strategies and technologies are required to reduce the CO<sub>2</sub> emission. In principle, there are at least three routes of reducing the CO<sub>2</sub> content in the atmosphere, such as curbing its emission, CO<sub>2</sub> capture and storage (CCS), and CO<sub>2</sub> utilization. Among them, effective strategies in using CO<sub>2</sub> to manufacture fuel and chemicals in terms of ecologic CO<sub>2</sub> capture & recycle may play a key role in minimizing CO<sub>2</sub> emission.

Our research activities focus on use of CO<sub>2</sub> for the chemical industry and to grow microalgae combined with further conversion processing. We not only converted CO<sub>2</sub> to methanol, syngas, linear and cyclic carbonates, but conducted large-scale cultivation of microalgae with selective conversion of microalgae into value-added chemicals and biocrude oil.

In the case of microalgae using CO<sub>2</sub>-enriched air, the productivity reached approximated 1.0 g/L/day with substantial composition of carbohydrate, which can serve as the substrate for commodity chemicals. For such purposes, new catalyst system is being developed to convert microalgae into chemicals and biocrude oil directly. Because the process uses green feedstock and free of organic solvent, such catalytic utilization of microalgae for chemicals should provide a potential renewable route for the production of valuable chemicals from microalgae. Furthermore, those microalgae containing proteins can also be used for biofertilizer for the reduction of CO<sub>2</sub> and N<sub>2</sub>O emission.



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# The role of CO<sub>2</sub> utilisation in climate change mitigation

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Despite a prolonged global economic recession and acknowledgment of the unequivocal connection between anthropogenic CO<sub>2</sub> emissions and climate change, the magnitude and rate of anthropogenic CO<sub>2</sub> emissions appears to be inexorably increasing<sup>1</sup>. However, a readily deployable solution is at hand: CO<sub>2</sub> capture and sequestration (CCS)<sup>2</sup>. Based on mature technologies such as gas scrubbing and cryogenic air separation, CCS is a promising solution to this important problem. Unfortunately, despite an understanding of the underlying relationship between CO<sub>2</sub> and climate change stretching back over a century<sup>3</sup>, we have yet to actually do very much about it. Typically the challenge given to the deployment is one of cost; “CCS is too expensive” or “CCS is not profitable”, which is may be true, if one compares CCS to unabated fossil fuels or to the heavily subsidised renewable energy sector. It is in this context which CO<sub>2</sub> capture and utilisation (CCU) is typically mentioned, and given that the market prices of several relevant compounds have been steadily increasing over recent years, this appears increasingly attractive. Similarly, under certain economic conditions, CO<sub>2</sub>-EOR can provide an economically attractive option. Indeed, in recent years, CO<sub>2</sub> EOR has been acting as a “demand pull” for the capture and transport of anthropogenic CO<sub>2</sub> in the US<sup>4</sup>.

This contribution addresses the chemical engineering and economic issues that will influence the eventual commercial viability of CCU technologies, such as those presented at this Discussion. We consider the technoeconomics of process scale-up from the lab to industrial scale of some leading CCU options, and also the spatial distribution of CO<sub>2</sub> sources and regions in Europe where a CO<sub>2</sub> utilisation industry might be important. We present the results of an engineering analysis of leading CO<sub>2</sub> conversion options and place this in a generalised European context. Importantly this work provides some preliminary information on the likely economics of these processes. We identify key technical bottlenecks in the scale-up of these processes in addition to key knowledge gaps in the open literature which hamper the robust evaluation of these processes. We also give consideration to the role which CO<sub>2</sub>-EOR can play on a global scale, given its position as one of the most technically mature options for large-scale CO<sub>2</sub> utilisation. We take this analysis further to consider how rapidly these new technologies might be deployed across the globe, extending this analysis for the period to 2050. We finally give some thoughts on policy and regulatory incentives which might be required to assist in the deployment of the various CO<sub>2</sub> conversion and utilisation options.

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# One-pot procedure for the synthesis of cyclic carbonate monomers from 1,3-diols and low CO<sub>2</sub> pressure: a novel, mild and safe phosgene alternative

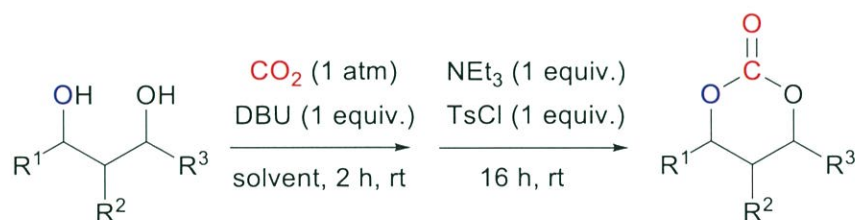
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Aliphatic Polycarbonate (APCs) are attractive polymers for biomedical applications because of their low toxicity and biodegradability.<sup>1</sup> Traditional synthesis by polycondensation of diols with dialkyl carbonates is often limited by poor control of the polymer molecular weight. Subsequently, the copolymerisation of epoxides with CO<sub>2</sub> as an abundant, renewable and safe resource has been extensively studied as a promising greener alternative though can be limited by the substrate scope. Hence the controlled ring-opening polymerisation (ROP) of typically 6-membered cyclic carbonates has emerged as an attractive choice for APC synthesis with potential to access a wide range of well-defined and functional degradable polymers.

Ideally, cyclic carbonate monomers can be prepared by the direct coupling of CO<sub>2</sub> and 1,3-diols with water as the sole by-product and allowing for both CO<sub>2</sub> utilisation and the sustainable sourcing of diols from biomass such as sugars. Nevertheless, thermodynamic and kinetic limitations often mean that phosgene is used in place of CO<sub>2</sub>, a particularly toxic reagent synthesised from CO and Cl<sub>2</sub> in an energy intensive process. Safer derivatives such as 1,1'-carbonyldiimidazole often lead to unwanted side reactions, low reactivity and difficult work-ups. Thus, we present a simple, safe and efficient novel procedure for the synthesis of 6-membered cyclic carbonates from 1,3-diols using CO<sub>2</sub> as the carbonating agent at room temperature and 1 atm pressure.<sup>2</sup> Using readily available starting materials, DBU facilitated CO<sub>2</sub> insertion is followed by cyclisation via an *in situ* tosylation step.



Retention of stereochemistry when optically active diols were used suggests a nucleophilic addition-elimination mechanism rather than an S<sub>N</sub><sub>2</sub> pathway. This is supported by DFT calculations, which reveal the lower energy barrier for tosylation of the carbonate compared to the free alcohol group as key in determining the mechanistic outcome. On-going work looking to exploit a mechanism switch for the synthesis of challenging cyclic carbonates from sugars as well as our latest progress towards the development of a catalytic method for this coupling, will also be presented.

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# Photocatalytic conversion of CO<sub>2</sub> into value-added chemicals by using heterostructure-based nanocatalysts

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Overtyping your abstract text here. Ensure you read the following guidelines carefully: The photocatalytic reduction of CO<sub>2</sub> into value-added chemicals (such as CH<sub>4</sub> and CH<sub>3</sub>OH) is an attractive approach for capturing greenhouse gas and, meanwhile, solving the problem of shortage of sustainable energy. However, the photoreduction efficiency is very low hitherto, especially for the utilization of visible light. Fabrication of the heterostructure-based nanocatalysts may afford a feasible way to solve this issue. On the one hand, the presence of a heterojunction at the interface is in favour of the separation of photogenerated charge carriers. The suppression of these charge carriers can thus be enhanced greatly and, thereby, the photocatalytic efficiency. On the other hand, the utilization of narrow-bandgap semiconductor in the fabrication of heterostructure-based nanocatalysts can efficiently use the visible light. In addition, the photostability of the nanocatalysts can also be improved. Here the wide-bandgap semiconductor (such as TiO<sub>2</sub>, CeO<sub>2</sub>, SrTiO<sub>3</sub> and ZnO) is combined respectively with the narrow-bandgap semiconductor (such as Cu<sub>2</sub>O, Bi<sub>2</sub>S<sub>3</sub>, CdS and ZnTe). The resultant heterostructure-based nanocatalysts exhibit an improved visible-light ( $\geq 420$  nm) photocatalytic activity when compared with the counterpart nanocatalysts based on the corresponding single semiconductor. 1-5 The CH<sub>4</sub> and CH<sub>3</sub>OH are found to be the major products of CO<sub>2</sub> photoreduction. The related mechanism has been studied too. We envision that this may afford a viable approach to facilitate the R&D of high-efficient photocatalysts for the photoreduction of CO<sub>2</sub>.

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# Probing the electrode/electrolyte interfacial structure of CO<sub>2</sub> electrochemical reduction to CH<sub>3</sub>OH catalyzed by the Pt-pyridine system

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According to recent researches the presence of specific small aromatic organics, e.g. the pyridium ion, greatly alters the (photo)electrochemical reduction mechanism of the CO<sub>2</sub> conversion on the surface of some transition metals/semiconductors in the acidic electrolyte solutions.<sup>[1]</sup> The most pronounced results include a Faraday efficiency of 22% CH<sub>3</sub>OH and 11% HCOOH reduced from CO<sub>2</sub> in the aqueous electrolyte on the Pt surface observed by Prof. Bocarsly's group.<sup>[1c]</sup> The result is so inspiring considering that Pt is almost completely inert to CO<sub>2</sub> reduction at ambient conditions. Interestingly, the distribution of the reduction products is strikingly surface-dependent, indicating the significance of the electrode/electrolyte interface, which unfortunately is far from clear to support any of the proposed mechanisms.<sup>[1c, 2]</sup>

With the application of the ultra-thin shell (ca. 1 nm), pinhole-free Au@Pt (core@shell) nanoparticles, the surface-enhanced Raman spectroscopy (SERS) method can be utilized at the Pt surface to obtain a highly sensitive vibrational band information of the electrode/electrolyte interface during the electrochemical reduction process. According to our preliminary result, the reduction of the pyridium ion in the absence of CO<sub>2</sub> leads to the reactive H<sub>ads</sub> formation, which co-adsorbs with the deprotonated pyridine with the interfacial structure tuning by the electrode potential and the pH of the electrolyte. The introduction of CO<sub>2</sub> consumes the H<sub>ads</sub>, leading to the synchronous development of the Pt-CO and CO band at the same potential region. The reduction intermediate CO<sub>ads</sub>, which can only be eliminated at oxidative potentials (>+0.5 V), adsorb on Pt very strongly with both linear and bridged adsorption configuration. To the best of our knowledge, this is the first time the 2e<sup>-</sup> reduced product CO was detected on the Pt surface in the Pt-Py electrocatalytic system toward the CO<sub>2</sub> reduction. The evidence of the methanol and formic acid product is still lacking and requires more careful analysis considering the dispute in the literature.

## Acknowledgement

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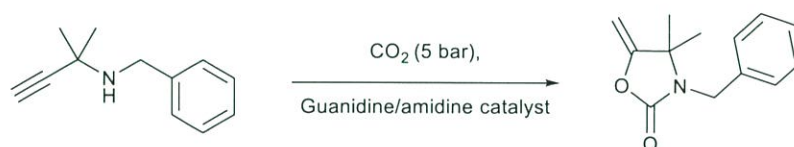
# Observation of guanidine-carbon dioxide complexation in solution and its role in the reaction of carbon dioxide and propargyl amines

Rachel Nicholls<sup>a</sup>, Simon Kaufhold<sup>b</sup> and Bao N. Nguyen<sup>a</sup>

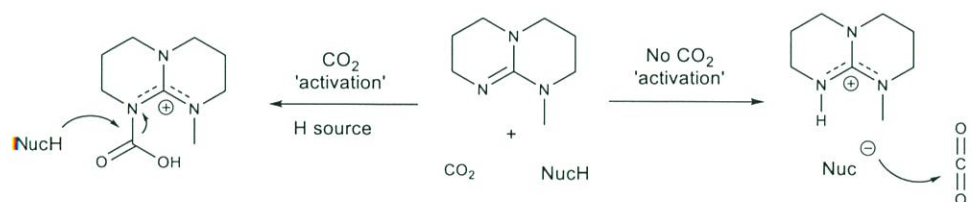
<sup>a</sup>School of Chemistry, University of Leeds, Leeds, West Yorkshire, LS2 9JT, UK

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The origin of catalytic activity in the synthesis of cyclic carbonates from propargylamines and CO<sub>2</sub><sup>1,2</sup> can be difficult to delineate due to the ability of the guanidine or amidine catalyst to act as both a superbases and as a strong nucleophile (Scheme 1).<sup>3</sup> There are therefore two equally probable mechanisms of action. Either the substrate is deprotonated by the superbases, or complexation of the guanidine/amidine with CO<sub>2</sub> enables transcarboxylation to the substrate, (Scheme 2).



Scheme 1: Synthesis of cyclic carbonates from propargylamines and CO<sub>2</sub> as reported by Costa<sup>1</sup>



Scheme 2: Two proposed mechanisms of action when MTBD is used as the catalyst

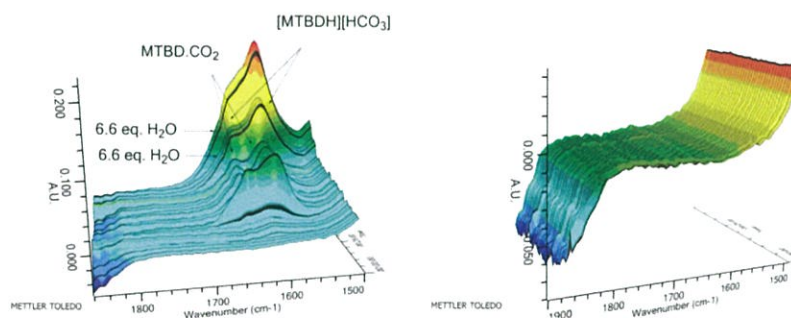


Fig. 1: ATR-FTIR spectra of reaction between CO<sub>2</sub> with a) MTBD and b) TMG

ATR-FTIR spectroscopy was used to study potential guanidine-CO<sub>2</sub> complexes in solution to represent the reaction conditions. It was found that the cyclic guanidines, TBD and MTBD, form stable complexes with CO<sub>2</sub>, whereas other active guanidine and amine catalysts did not (Fig. 1). Through comparison of the observed complexation with catalytic activity and the effect of solvent, it is proposed that the catalytic activity is due to the ability of the catalyst to deprotonate the substrate, as opposed to the formation of complexes with CO<sub>2</sub>.<sup>4</sup>

## References

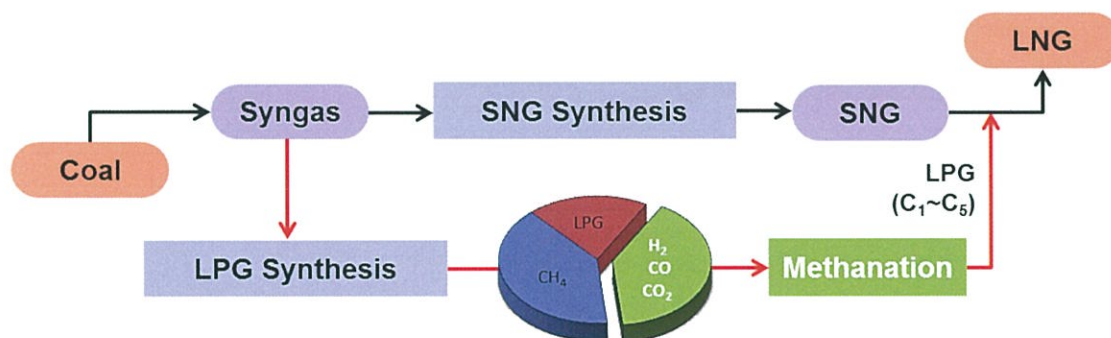
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# Design of experiments as a valuable tool for rational catalyst development in methanation of syngas containing hydrocarbons

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Particularly in liquefied petroleum gas (LPG) synthesis residual syngas remains after the reaction. Removing CO and CO<sub>2</sub> by methanation is economically competitive compared to gas separation. Direct conversion would enable the industry to meet the demands for feeding an SNG/LPG blend into the liquefied natural gas (LNG) pipeline network without further purification.

Therefore, a PlackettBurman design<sup>1</sup>, as an efficient screening method was used to identify a catalyst lead as a selective methanation catalyst in the presence of LPG components. Seven factors, each with two levels, high and low (Table 1), were evaluated for the main effects, and consecutively ranked according to their impact on the respective catalyst performance. The eight resulting catalysts were prepared in duplication (sixteen in total), and were fully characterized via N<sub>2</sub>-physisorption, XRD, ICP-OES, TPR, and TEM before and after reaction. Their catalytic performance was determined in an in-house-build reactor setup using on-line gas chromatography.<sup>2</sup>

**Table 1: Summary of factors and levels for the screening according to Plackett-Burman.**

#	Factor	Lower level (-)	Upper level (+)
1	Molar ratio Fe/Ni	Fe/Ni = 0/1	Fe/Ni = 1/1
2	Metal loading with respect to the support	5 wt%	15 wt%
3	Type of support	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
4	MgO as supporting promotor to the support	0 wt%	10 wt%
5	Potassium as promotor to the final catalyst	0 wt%	5 wt%
6	Dilution of catalyst with quartz	Quartz/Cat. = 0/1	Quartz/Cat. = 1/1
7	Preparation method	Impregnation	Precipitation

Most of the observed trends are in agreement with literature. Finally, we obtained a set of factors which are relevant to control the catalytic behaviour. The design of experiments approach proved to be an efficient method in rational catalyst development by testing multiple factors at the same time with highly reduced experimental expense.

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