

## EuropaCat 2019

### Catalysis without borders

#### Reviewed by Andrew Richardson\*, Katie Smart

Johnson Matthey, PO Box 1, Chilton Office,  
Belasis Avenue, Billingham, TS23 1LB, UK

\*Email: [andrew.richardson@matthey.com](mailto:andrew.richardson@matthey.com)

#### 1. Introduction

The 14th European Congress on Catalysis (EuropaCat 2019), themed 'Catalysis without Borders', was held on the 18th–23rd August 2019 at the Eurogress conference centre in Aachen, Germany. The conference hosted over 1500 participants from academia and industry across the world, with around 400 lectures and 800 posters presented throughout the week. There were six parallel sessions; this review is a small selection of the talks attended by the reviewers.

#### 2. Plenary Lectures

Plenary lectures of an hour were intended to showcase the significant breadth and depth of scientific knowledge acquired by established academics over the course of their careers. Summaries of key themes presented in the lectures are provided below.

Two plenary lectures were delivered on the subject of using molecular oxygen as a reagent, one by Professor Karen Goldberg of the University of Pennsylvania, USA and another by Professor Shannon Stahl from the University of Wisconsin-Madison, USA. Professor Goldberg opened by highlighting how molecular O<sub>2</sub> represents the ideal oxidant for chemical transformations, with the 'jackpot' being to achieve benign and facile routes to chemicals with atmospheric O<sub>2</sub>, avoiding O<sub>2</sub> separation from air. Professor Stahl provided

examples of work studying the control of molecular O<sub>2</sub> reactivity including maximising the energy efficiency of O<sub>2</sub> reduction to water in fuel cells and achieving selective oxidation of organic molecules without overoxidation to carbon dioxide or other undesirable byproducts (1–3).

A high-impact plenary was presented by Professor Ib Chorkendorff from the Technical University of Denmark. The talk started with a few headline data to emphasise that sectors such as aviation, long haul transport and the chemical industry will always have to rely on the same chemical building blocks we use today rather than full electrification. The speaker predicted that the chemical demands of the future should be met by 'solar' fuels in the form of photovoltaics providing the energy for electrochemistry. Several areas of focus within the research team were summarised including a collaboration with Haldor Topsøe, Denmark, in electrified steam reforming (4), green hydrogen generation (5) and electrochemical hydrogenation of CO<sub>2</sub> (6).

Professor Valentin Parmon of the Boreskov Institute of Catalysis SB RAS in Novosibirsk, Russia, presented an overview of some non-traditional approaches to achieve various endothermic thermocatalytic transformations. An example was the application of nuclear radiation to supply heat for steam reforming in an integrated chemical-nuclear reactor. A steam reforming catalyst was developed for the system; a porous uranium oxide support with nickel on the surface and titanium dioxide to protect against nucleotides (7). Solar energy was also considered to provide heating for steam reforming, temperatures >1000 K can be achieved by concentrating solar radiation (8). More recent work in the Parmon group focused on the use of microwaves to supply energy to reactions such as H<sub>2</sub> evolution from alkanes though the cost

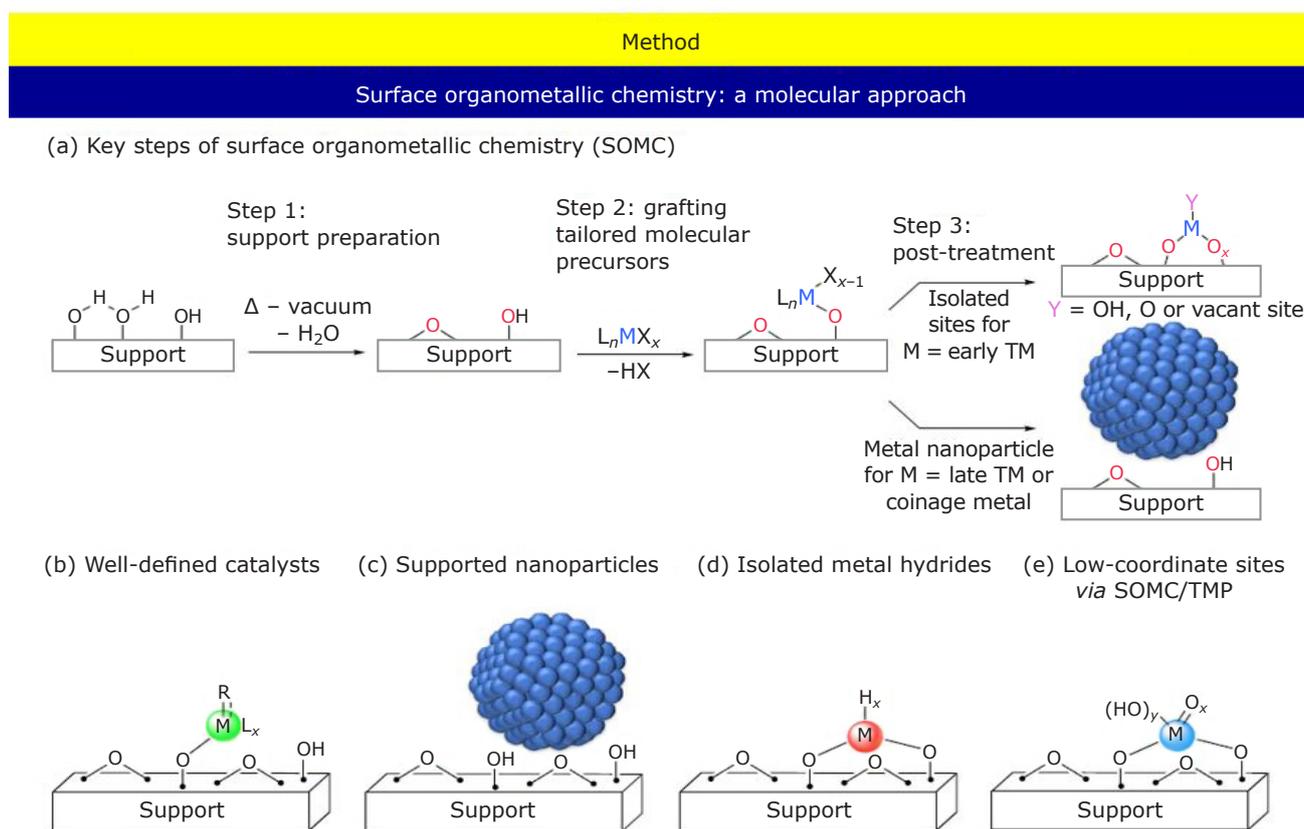


Fig. 1. Molecular processes investigated by the Copéret group reproduced with kind permission from Professor Copéret (12, 13)

of the electrical energy required is prohibitive for large scale application (9).

A range of fundamental structure-activity relationships were described in the lecture of Professor Christophe Copéret from ETH Zürich, Switzerland. Work in the group is focused on the understanding and control of chemistry on surfaces, with the ultimate goal to generate isolated metal sites with defined chemical environment to elucidate structure-activity relationships. The approach in the team has led to highly active and selective single-site catalysts that out-performed their homogeneous counterparts, but that also provided useful information to understand industrial catalysts. Several examples were provided in the lecture including details of research into chromium polymerisation catalysts to generate a Cr(II) species directly rather than the need to reduce Cr(VI) *in situ* (10). An example was also provided for copper-particle catalysed methanol synthesis from methane, investigating the effect of the support; copper on alumina displayed higher activity than copper on silica (11). **Figure 1** summarises work undertaken in the Copéret team

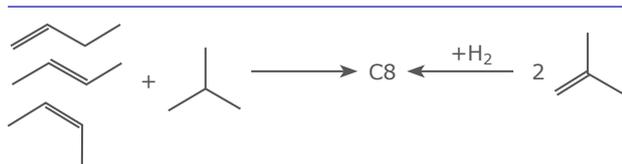
and acknowledges the 'pioneering' work of Denis Ballard, Imperial Chemical Industries (ICI), UK.

### 3. Industrial Forum

The industrial forum sessions of the conference are to present work undertaken by industrial corporations or of direct industrial application. Over the course of the conference there were 21 talks in the industrial forum by both academics and speakers from commercial organisations.

#### 3.1 Growth of Chemicals

Joe Scheper from ExxonMobil Chemical Europe Inc, Belgium, opened the industrial forum with a talk focussed on the projected growth in global chemical demand, set to outpace gross domestic product (GDP) growth. Attention was drawn to <15% of a barrel of oil being converted to chemicals pre-1990, *versus* 25–40% at present, and projected to be 40–80% post 2020. Specific examples were given of technology to enable this growth, including the ExxonMobil EMTAM<sup>SM</sup> process for selective *para*-xylene production from toluene and methanol.



Scheme I

*Para*-xylene is smaller than the *meta*- or *ortho*-variants, so can be targeted for selective transport through specifically sized zeolite pores. Avoiding reaction on the outer surfaces of zeolites minimises byproduct formation and catalyst attrition resistance was highlighted as critical for this fluid bed regenerative process. Some future developments required to sustain the necessary global growth in chemicals were presented. Processes to take plastic waste and turn this into a chemical feedstock as well as algae-based routes to biofuels with 50,000 barrels (bbl) of petroleum products being projected to be produced from algae in the not too distant future.

Andrei Parvulescu from BASF SE, Germany, then went on to discuss growing demand for highly branched C7 and C8 alkanes owing to their superior fuel burning efficiency. C4 alkene dimerisation or alkylation of isobutane with propene or butenes were presented as routes (Scheme I).

Solid acid catalysts have been proposed for both of these processes but suffer from relatively poor stability and selectivity. One successfully evaluated catalyst for alkylation was a zeolite beta made *via* seed-assisted synthesis without organic structure directing agent, providing a high density of acid sites and easy ability to be modified by dealumination. The catalyst was shown to have superior activity and selectivity compared to conventional zeolite beta and control of product mix was demonstrated through manipulation of reaction temperature and olefin concentration (14).

Jean-Paul Lange from Shell Global Solutions International BV, The Netherlands, continued the theme of growth in chemicals, discussing how as populations become wealthier demand for petrochemicals will rise. Fossil fuels would be able to meet this increase in demand, as they are still abundant and will have lower demand in future as the automotive sector decarbonises. Shell analysis predicts that the petrochemical industry will be affected by limited carrying capacity of the earth and societal calls for a more circular economy. Therefore, focus must be placed on transforming the linear petrochemicals industry into a circular one built on recycled plastics. There was also agreement between Shell and the earlier discussions led by ExxonMobil, with Shell predicting that as transport

electrifies, oil capacity will be liberated for use in chemicals and a 4% annual growth in chemicals could be expected. Some data was also shared looking at CO<sub>2</sub> cost *versus* product value, with formaldehyde and monoethylene glycol coming out as the most expensive (i.e. relatively cheap chemical product made with high CO<sub>2</sub> emissions).

### 3.2 European Federation of Catalysis Societies Applied Catalysis Award

The European Federation of Catalysis Societies (EFCATS) award for 2019 was awarded to Professor Glenn Sunley of BP Plc, UK, and was accompanied by a talk titled 'Adventures in C1 Chemistry'. Glenn talked through some of his career highlights, including work done on the BP Cativa™ process for acetic acid production and the elucidation of the reaction mechanism in collaboration with the University of Sheffield, UK (15). Work was also presented about a collaboration with University of California, Berkeley, USA and the California Institute of Technology, USA, investigating the conversion and mechanistic features of methanol homologation to triptane over an indium iodide catalyst (16, 17). Special mention was also given to some recent Fischer-Tropsch technology development as a result of the long-term collaboration between BP and Johnson Matthey, UK, described as 'stunning engineering'. The first license for this technology has already been sold and will enable Fulcrum BioEnergy Inc, USA, to convert 175,000 tonnes of household rubbish into 11 million gallons of jet fuel each year (18, 19).

### 3.3 SunCarbon – Creating a New Value Chain from Forest to Refineries

Christian Hulteberg from SunCarbon (both a process and Swedish based company) described their newly launched process for the transformation of lignin into vehicle fuel. This process is dual-function, removing lignin from a typical pulp mill cycle allowing debottlenecking of the pulp mill evaporator and also providing the mill with an additional value stream. Lignin is extracted by membrane filtration and then homogenised in a homogeneously catalysed process. The resultant product is then purified and mixed with vacuum gas oil to make it liquid and pumpable, before being shipped to a refinery. The adjacent pulp mill is capable to take care of any and all waste products of the SunCarbon process. Once at the refinery,

the material undergoes standard hydrotreatment and is transformed into vehicle fuel. The feedstock was reported to contain up to 20% O, which would place significant additional H<sub>2</sub> demand on the refinery hydrotreater.

#### 4. Carbon Dioxide Utilisation

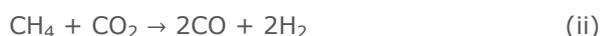
An ongoing theme of EuropaCat 2019 was the focus of many research groups on utilisation of CO<sub>2</sub>. Many talks were presented on addressing various aspects of the Sabatier reaction for CO<sub>2</sub> hydrogenation, on the dry reforming of methane (DRM) for H<sub>2</sub> production or for the direct synthesis of methanol from CO<sub>2</sub>.

Matteo Monai from Utrecht University, The Netherlands, presented a short talk on work done tuning metal-support interactions on supported Ni catalysts for the Sabatier reaction hydrogenating CO<sub>2</sub> to CH<sub>4</sub> (Equation (i)):



Both a reaction mechanism with carbide and formate intermediates are observed on Ni catalysts and both mechanisms were reported to be sensitive to particle size and local structure. Using strong metal-support interactions and a reducible support, it was possible to 'embed' Ni particles into the support material and suppress sintering. Enhanced C–C coupling was also observed on these materials when utilising the embedded metal particles, the mechanism for which was still subject to investigation (20).

An experimental programme investigating the mechanism for carbon formation over rhodium on alumina catalysts in the DRM was shared by Gianluca Moroni from the Politecnico di Milano, Italy (Equation (ii)):



A variety of CH<sub>4</sub>:CO<sub>2</sub> ratios were flowed over the catalyst at temperatures from 300–700°C in an *operando*-Raman annular reactor with gas analysis by Micro GC Natural Gas Analyzer (Agilent, USA). An adverse dependence between CH<sub>4</sub> concentration and activity was observed and a presented microkinetic model was said to predict experimentally observed activity with catalyst surface area as an input. Catalyst activity was also observed to reduce with increased carbon monoxide levels, and C deposition was said to begin on the Rh sites before migration and deposition on adjacent sites on the support (21).

Shohei Tada from The University of Tokyo, Japan, gave a talk on work done investigating catalysts for the conversion of CO<sub>2</sub> to methanol. Zirconia supported Cu catalysts were discussed and work was presented showing Cu species being metallic during reaction and methanol synthesis being performed at Cu-ZrO<sub>2</sub> interface sites (22). Tada went on to discuss the importance of finding a good support material to suppress methanol decomposition to CO, with the methanol-support interaction being said to be key. Methanol weakly adsorbs on an amorphous surface (a-ZrO<sub>2</sub>) and strongly adsorbs on a monoclinic surface (m-ZrO<sub>2</sub>), with the stronger interaction yielding more unfavourable decomposition of methanol to CO (23, 24).

#### 5. Conclusions

EuropaCat 2019 was a large conference with wide-ranging themes delivered in multiple sessions over six days. It has not been possible to summarise the conference in its entirety. Major topics included: alternative energy inputs (plasma, electrochemistry, light); ammonia synthesis; biomass valorisation; CO<sub>2</sub> to chemicals; dry reforming; Fischer-Tropsch catalysis; industrial forum; mechanistic insights; nitrogen oxides (NO<sub>x</sub>) reduction; organometallic catalysis; and zeolite catalysis. More information can be found on the conference website.

#### References

1. J. M. Keith, R. P. Muller, R. A. Kemp, K. I. Goldberg, W. A. Goddard and J. Oxgaard, *Inorg. Chem.*, 2006, **45**, (24), 9631
2. J. L. Look, D. D. Wick, J. M. Mayer and K. I. Goldberg, *Inorg. Chem.*, 2009, **48**, (4), 1356
3. M. C. Denney, N. A. Smythe, K. L. Cetto, R. A. Kemp and K. I. Goldberg, *J. Am. Chem. Soc.*, 2006, **128**, (8), 2508
4. S. T. Wismann, J. S. Engbæk, S. B. Vendelbo, F. B. Bendixen, W. L. Eriksen, K. Aasberg-Petersen, C. Frandsen, I. Chorkendorff and P. M. Mortensen, *Science*, 2019, **364**, (6442), 756
5. J. Kibsgaard and I. Chorkendorff, *Nature Energy*, 2019, **4**, (6), 430
6. S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Nørskov, T. F. Jaramillo and I. Chorkendorff, *Chem. Rev.*, 2019, **119**, (12), 7610

7. Y. I. Aristov, Y. Y. Tanashev, S. I. Prokopiev, L. G. Gordeeva and V. N. Parmon, *Int. J. Hydrogen Energy*, 1993, **18**, (1), 45
8. Y. I. Aristov, V. I. Fedoseev and V. N. Parmon, *Int. J. Hydrogen Energy*, 1997, **22**, (9), 869
9. S. Horikoshi, M. Kamata, T. Sumi and N. Serpone, *Int. J. Hydrogen Energy*, 2016, **41**, (28), 12029
10. M. P. Conley, M. F. Delley, G. Siddiqi, G. Lapadula, S. Norsic, V. Monteil, O. V. Safonova and C. Copéret, *Angew. Chemie Int. Ed.*, 2014, **53**, (7), 1872
11. J. Meyet, K. Searles, M. A. Newton, M. Wörle, A. P. van Bavel, A. D. Horton, J. A. van Bokhoven and C. Copéret, *Angew. Chemie Int. Ed.*, 2019, **58**, (29), 9841
12. C. Copéret, A. Comas-Vives, M. P. Conley, Deven P. Estes, A. Fedorov, V. Mougél, H. Nagae, F. Núñez-Zarur and Pavel A. Zhizhko, *Chem. Rev.*, 2016, **116**, (2), 323
13. C. Copéret, *Acc. Chem. Res.*, 2019, **52**, (6), 1697
14. B. Yilmaz, U. Müller, M. Feyen, S. Maurer, H. Zhang, X. Meng, F.-S. Xiao, X. Bao, W. Zhang, H. Imai, T. Yokoi, T. Tatsumi, H. Gies, T. De Baerdemaeker and D. De Vos, *Catal. Sci. Technol.*, 2013, **3**, (10), 2580
15. A. Haynes, P. M. Maitlis, G. E. Morris, G. J. Sunley, H. Adams, P. W. Badger, C. M. Bowers, D. B. Cook, P. I. P. Elliott, T. Ghaffar, H. Green, T. R. Griffin, M. Payne, J. M. Pearson, M. J. Taylor, P. W. Vickers and R. J. Watt, *J. Am. Chem. Soc.*, 2004, **126**, (9), 2847
16. J. E. Bercaw, P. L. Diaconescu, R. H. Grubbs, N. Hazari, R. D. Kay, J. A. Labinger, P. Mehrkhodavandi, G. E. Morris, G. J. Sunley and P. Vagner, *Inorg. Chem.*, 2007, **46**, (26), 11371
17. J. H. Ahn, B. Temel and E. Iglesia, *Angew. Chemie Int. Ed.*, 2009, **48**, (21), 3814
18. 'JM and BP License Waste-to-Fuels Technology to Fulcrum BioEnergy', Johnson Matthey, London, UK, 25th September, 2018
19. A. Coe and J. Paterson, *Chem. Eng.*, 2019, (937/938), 33
20. C. Hernández Mejía, C. Vogt, B. M. Weckhuysen and K. P. de Jong, *Catal. Today*, 2020, **343**, 56
21. A. Maghsoumi, A. Ravanelli, F. Consonni, F. Nanni, A. Lucotti, M. Tommasini, A. Donazzi and M. Maestri, *React. Chem. Eng.*, 2017, **2**, (6), 908
22. K. Larmier, S. Tada, A. Comas-Vives and C. Copéret, *J. Phys. Chem. Lett.*, 2016, **7**, (16), 3259
23. S. Tada, A. Katagiri, K. Kiyota, T. Honma, H. Kamei, A. Nariyuki, S. Uchida and S. Satokawa, *J. Phys. Chem. C*, 2018, **122**, (10), 5430
24. S. Tada, S. Kayamori, T. Honma, H. Kamei, A. Nariyuki, K. Kon, T. Toyao, K. Shimizu and S. Satokawa, *ACS Catal.*, 2018, **8**, (9), 7809

## The Reviewers



Andrew Richardson graduated from the University of Newcastle Upon Tyne, UK with an MChem in Chemistry. Andrew joined Johnson Matthey in 2012 and has worked across a number of catalysis and absorbent research areas. He is currently a Principal Researcher at Johnson Matthey's Chilton site in Billingham, UK.



Katie Smart has a PhD in Chemistry from the University of Paul Sabatier, France, where she studied at the Laboratoire de Chimie de Coordination in Toulouse. Katie has worked at Johnson Matthey since 2013 and is currently Technical Development Manager for the high-temperature shift research and development team at the Chilton site in Billingham.