



Design, implementation and production upscaling of novel, high-performance, cluster-based catalysts for CO₂ hydrogenation

Deliverable D7.6

First papers



Grant Agreement No:	955650
Project start date:	01.11.2020
Duration of the project:	48 months
Deliverable number	7.7
Deliverable leader	KU Leuven
Due date:	30/11/2022 (M24)
Actual submission date:	14/03/2024 (M40)
Dissemination level:	RE-Public
Author(s):	Ewald Janssens (KU Leuven)

Preamble

In the initial time schedule of the project, the plan was to submit a deliverable **reporting on the publication/acceptance of the first peer-reviewed papers** of each ESR in November 2022. It became clear in the first two years of the project that this timing was not feasible for two main reasons: i) most ESRs were recruited later than initially foreseen, and ii) many of the individual project required an important amount of instrumental development, implying a slower trajectory towards publication.

At the board meeting of June 2023, it was decided that quality of publication should prevail over a fast track towards publication and that the publication progress would become an agenda item on every supervisory board meeting. These decisions are in line with the recommendation by the expert evaluator of the interim project review *“The agenda for the expected scientific publications for each of the ESRs is to be updated. It is recommended that the Supervisory Board evaluate the progress on peer-reviewed articles to see that those are on schedule. Important progress was reported on each sub-topic, but given the time constrains, it is recommended to perhaps keep the focus on high impact publications.”*

At the board meeting of January 17, 2024, it was determined that not all ESRs have a first paper accepted but all are on a trajectory towards publication. It was decided to report on the status of publications as it is now and to explain possible reasons for delay.

Overview of the publications by the Catchy network

The list below contains the publications that resulted from the Catchy project. The names of ESRs are underlined. First and joint first authors are indicated with an asterisk.

1. *Screening of transition metal doped copper clusters for CO₂ activation*, Máté Szalay, Dániel Buzsáki, Júlia Barabás, Endre Faragó, Ewald Janssens, László Nyulászi, Tibor Höltzl, *Physical Chemistry Chemical Physics* **23**, 21738-21747 (2021).
<https://pubs.rsc.org/en/content/articlelanding/2021/cp/d1cp02220b>
2. *IR spectroscopic characterization of the co-adsorption of CO₂ and H₂ onto cationic Cu_n⁺ clusters*, Olga V. Lushchikova, Máté Szalay, Hossein Tahmasbi, Ludo B. F. Juurlink, Jörg Meyer, Tibor Höltzl, Joost M. Bakker, *Physical Chemistry Chemical Physics* **23**, 26661-26673 (2021).
<https://pubs.rsc.org/en/content/articlelanding/2021/cp/d1cp03119h>
3. *C₂ product formation in the CO₂ electroreduction on boron-doped graphene anchored copper clusters*, Tibor Höltzl, Ewald Janssens, Balázs Barhács, *Physical Chemistry Chemical Physics* **24**, 21417-21426 (2022).
<https://pubs.rsc.org/en/content/articlelanding/2022/cp/d2cp01316a>
4. *Unveiling the role of C₆₀-supported vanadium single atoms for catalytic overall water splitting*, Mengyang Li, Tao Yang, Joost M. Bakker, Ewald Janssens, Gao-Lei Hou, *Cell Reports Physical Science* **3** (6), 100910 (2022).
<https://www.sciencedirect.com/science/article/pii/S2666386422001886>
5. *Water splitting by C₆₀-supported vanadium single atoms*, Gao-Lei Hou, Tao Yang, Mengyang Li, Jan Vanbuel, Olga V. Lushchikova, Piero Ferrari, Joost M. Bakker, Ewald Janssens, *Angewandte Chemie - International Edition* **60** (52), 27095-27101 (2022).
<https://onlinelibrary.wiley.com/doi/abs/10.1002/anie.202112398>
6. *Tuning the degree of CO₂ activation by carbon doping Cu_n⁻ (n = 3–10) clusters: an IR spectroscopic study*, Olga V. Lushchikova, Máté Szalay, Tibor Höltzl, Joost M. Bakker, *Faraday Discussions* **242**, 252-268 (2023).
<https://pubs.rsc.org/en/content/articlelanding/2023/fd/d2fd00128d>
7. *Gas phase deposition of well-defined bimetallic gold-silver clusters for photocatalytic applications*, Vana Chinnappa Chinnabathini, Fons Dingenen, Rituraj Borah, Imran Abbas, Johan van der Tol, Zviadi Zarkua, Francesco D'Acapito, Thi Hong Trang Nguyen, Peter Lievens, Didier Grandjean, Sammy W. Verbruggen, Ewald Janssens, *Nanoscale* **15**, 6696-6708 (2023).
<https://pubs.rsc.org/en/content/articlelanding/2023/nr/d2nr07287d>
8. *Multistep CO₂ activation and dissociation mechanisms on Pd_xPt_{4-x} clusters in the gas phase*, Renata Sechi, Tibor Höltzl, *Journal of Physical Chemistry A*, **127** (21), 4596–4608 (2023).
<https://pubs.acs.org/doi/10.1021/acs.jpca.2c08333>
9. *Co_{3-x}Fe_xO₄ inverse opals with tunable catalytic activity for high-performance overall water splitting*, Thi Hong Trang Nguyen, Zviadi Zarkua, Chinnabathini Vana Chinnappa, Wenjian Hu, Sreeprasanth Pulinthanathu Sree, Didier Grandjean, Deepak Pant, Ewald Janssens, *Nanoscale* **15**,

10306-10318 (2023).

<https://pubs.rsc.org/en/content/articlelanding/2023/nr/d2nr07300e>

- 10 *Recent advances in copper chalcogenides for CO₂ electroreduction*, Wenjian Hu, Didier Grandjean, Jan Vaes, Deepak Pant, Ewald Janssens, *Physical Chemistry Chemical Physics* **25**, 30785-30799 (2023).
<https://pubs.rsc.org/en/content/articlelanding/2023/cp/d3cp04170k>
- 11 *CO₂ and H₂ activation on zinc-doped copper clusters*, Bárbara Zamora, László Nyulászi, Tibor Höltzl, *ChemPhysChem* **25** (1), e202300409 (2024).
<https://chemistry-europe.onlinelibrary.wiley.com/doi/full/10.1002/cphc.202300409>
- 12 *Gold nanoparticles for CO₂ electroreduction: An optimum defined by size and shape*, Esperanza Sedano Varo, Rikke Egeberg Tankard, Joakim Kryger-Baggesen, Joerg Jinschek, Stig Helveg, Ib Chorkendorff, Christian Danvad Damsgaard, Jakob Kibsgaard, *Journal of the American Chemical Society* **146** (30), 2015-2023 (2024).
<https://pubs.acs.org/doi/10.1021/jacs.3c10610>
- 13 *Stable mass-selected AuTiO_x nanoparticles for CO oxidation*, Rikke Egeberg Tankard[‡], Filippo Romeglio[‡], Stefan Kei Akazawa, Alexander Krabbe, Olivia Fjord Sloth, Niklas Mørch Secher, Sofie Colding-Fagerholt, Stig Helveg, Richard Palmer, Christian Danvad Damsgaard, Jakob Kibsgaard, Ib Chorkendorff, *Physical Chemistry Chemical Physics*, Accepted (2024),
<https://pubs.rsc.org/en/content/articlehtml/2024/cp/d4cp00211c>

Status towards first publication for each ESR

- **ESR1: Imran Abbas**
 - Coauthor of **article 7**
 - A microreactor was built for testing minute quantities of cluster-based catalysts at 40 bar pressure. Delivery times of some parts of the setup were longer than foreseen, in particular the mass flow controllers suffered from post-covid chip supply chain issues. After the completion of this instrument development, there were more delays due to a failure of the original o-rings employed in the microreactor. In the meantime, all technical problems have been fixed and data has been generated successfully using the new microreactor setup. A manuscript describing the performance of the reaction for CO₂ hydrogenation on cluster-based catalysts is being written and is expected to be ready in April.
- **ESR2: Joao Coroa**

The first publication of Joao will deal with the effect of the magnetic field on cluster growth in a magnetron source with inert gas aggregation. Unbalancing the magnetic field has proven to be highly effective in increasing the cluster flux/growth. The most likely explanation is the electron energy/density interaction with specimens in plasma (ions and neutrals). The publication is delayed because of difficult experiment design (to measure negative, neutral, and positive clusters separately) and challenges with the OES technique (hard to observe ions since they mostly exist in the UV region). One final experiment needs to be done that confirms the ion/neutral ratio and thus the ionization rate depending on the magnetic field. A final draft is expected end of May 24; paper submission end of June 24/ beginning of July 24.
- **ESR3: Pavol Mikolay**

Pavol is preparing a first publication about the activation of CO₂ on copper oxide clusters in the gas phase. The paper is delayed due to the time-consuming theoretical search for cluster structures that can explain the experimental infrared spectra. The first manuscript is prepared together with ESR 6 (BME) and submission is expected in May 2024.
- **ESR4: Deepak Pradeep**

Deepak's first paper has a working title "IR spectroscopic characterization of the CO₂ adsorption on cationic V-doped Co clusters (VCo_n⁺)". The delay in finalizing the manuscript is partially caused by experimental problems in commissioning our new source for bimetallic clusters, and partially due to some crucial theoretical calculations that are still underway. Submission of the manuscript is expected in May 2024
- **ESR5: Renata Sechi (until Dec. 2022)**
 - First author of **article 8**
Bao-Ngan Nguyen-Ha (as of Jan. 2024)
 - Too soon for a publication related to her work for the Catchy project
- **ESR6: Bárbara Zamora**
 - First author of **article 11**

- **ESR7: Waqas Pervez**

- position was terminated in May before finalization of a publication

- **ESR8: Dimitra Papamichail**

Dimitra's first paper will report on a systematic study of electrochemistry for CO₂ electroreduction using as catalysts oxidized Cu and Cu₉₀Pd₁₀ alloy clusters on various carbon substrates (glassy carbon, carbon paper and carbon paper with a microporous layer). While the electrochemistry results have been obtained, more detailed structural analysis of both pristine and reacted systems is currently underway. SEM imaging is planned, as is the characterization of the substrates using Raman Spectroscopy and Atomic Force Microscopy. Furthermore, insight into the mechanisms will be gained by model system investigations using Density Functional Theory studies. Discussions on experiment vs. theory are planned during her secondment in Budapest in May 2024 (Nguyễn Hà Bảo Ngân, Tibor Höltzl). The expected timeline for completing the manuscript is August 2024. With respect to the initial planning of this project, delays occurred as time was spent to assure reproducibility of the various electrodes after obtaining first promising results. Moreover, modifications of the testing conditions with higher sensitivity were needed to evaluate these low-loaded samples.

- **ESR9: Sumant Phadke**

Sumant is preparing a publication with as title: "High-pressure cell for in situ grazing incidence XAS characterization of model catalysts on planar supports. A version of the manuscript has been circulated to all co-authors. It will be finalized by the end of March, after implementing characterization of the samples using SEM and optical microscopy. The delay in submission of the publication originated from multiple revisions by the student and the need for the supplementary characterization.

- **ESR10: Deema Balalta**

The preliminary title of Deema's first publication is: "Design and Fabrication of 3D Printed Holder and Mask for MEMS-based Chips for In Situ Electron Microscopy". The chip holder was designed and fabricated at U Antwerp and successful deposition of clusters was done at KU Leuven on a gas-heating chip. However, the liquid-biasing chips require a more selective deposition due to the smaller area available for the viewing window. Moreover, the small distance between the electrodes ~ 20 μm requires a mask that exposes the working electrode only and covers the other ones. The delay in finalizing the publication has been primarily due to the intricate mask-making process. This process requires precise measurements that were previously unattainable. However, the consortium has recently acquired a specialized laser-cutting machine, which significantly expedites the mask production process. As a result, Deema anticipate that the remaining tasks, required to finish the paper, including data analysis and manuscript preparation, will be completed by the end of July 2024.

- **ESR11: Filippo Romeggio**

- Joint first author of **article 13**

- **ESR12: Esperanza Sedano Varo**
- First author of **article 12**
- **ESR13: Wenjian Hu**
- First author of **article 10**
- **ESR14: Maximilian Winzely**
- Maximilian prepared a first publication about the design of a spectro-electrochemical cell with which grazing incidence XAS can be performed. The article is currently under revision by the co-authors and is expected to be submitted in the month April.