

# Aiming for More Sustainable Cross-Coupling Chemistry by Employing Single-Atom Catalysis on Scale

Dario Poier<sup>ab</sup>, Sharon Mitchell<sup>b</sup>, Victor Tulus<sup>b</sup>, Gonzalo Guillén-Gosálbez<sup>b</sup>, Javier Pérez-Ramírez<sup>b</sup>, and Roger Marti<sup>\*a</sup>

**Abstract:** Scaling up syntheses from mg to kg quantities is a complex endeavor. Besides adapting laboratory protocols to industrial processes and equipment and thorough safety assessments, much attention is paid to the reduction of the process' environmental impact. For processes including transition metal catalyzed steps, e.g., cross-coupling chemistry, this impact strongly depends on the identity of the metal used. As such, a key approach is the replacement of single-use with reusable heterogeneous catalysts. Transition metal single-atom heterogeneous catalysts (SAC), a novel class of catalytic materials, might exhibit all the necessary properties to step up to this task. This article shall discuss current applications of SAC in cross-coupling chemistry from the point of a process chemist and shed light on the NCCR Catalysis contribution to the field. Investigations of the stability–activity–selectivity relationship of SACs in combination with early-stage life-cycle assessments (LCA) of potential processes lay the foundation for large-scale application tailored catalyst synthesis. Ultimately, prevailing challenges are highlighted, which need to be addressed in future research.

**Keywords:** Cross-coupling reactions · Life-cycle assessment · Process chemistry · Single-atom catalysis · Sustainability



**Dario Poier** is pursuing his PhD as a NCCR Catalysis fellow, supervised by Roger Marti (HEIA-FR) and Javier Pérez-Ramírez (ETHZ). His research aims to reveal the opportunities and challenges of applying single-atom heterogeneous catalysts in organic chemistry.



**Gonzalo Guillén-Gosálbez** holds the Chair of Chemical Systems Engineering at ETH Zurich. His research focuses on the evaluation and optimization of sustainable industrial systems using life cycle assessment and mathematical modeling. He currently leads the sustainability work package of the NCCR Catalysis.



**Sharon Mitchell** is a lecturer in the Advanced Catalysis Engineering group at ETH Zurich. Her research focuses on the precision design of catalytic materials, including those based on low-nuclearity species, towards sustainable technologies. She acts as Program Advisor for NCCR Catalysis.



**Javier Pérez-Ramírez** holds the Chair of Catalysis Engineering at ETH Zurich. His research pursues the discovery and understanding of catalytic materials and process concepts, leading to technologies for the carbon-neutral manufacture of chemicals and energy carriers. He serves as Director of NCCR Catalysis.



**Victor Tulus** is a post-doctoral researcher in the Sustainable Process Systems Engineering Lab at ETH Zurich. His research focuses on developing and applying novel methodologies integrating life cycle assessment and mathematical programming tools to identify sustainable alternatives for diverse process systems.



**Roger Marti** is Full Professor UAS of Organic Chemistry & Process Chemistry at the Institute ChemTech at HEIA Fribourg. His research focuses on catalysis, synthetic organic chemistry & sustainable process chemistry. Within the NCCR Catalysis he is involved in upscaling and implementation of catalytical processes.

\*Correspondence: Prof. R. Marti<sup>a</sup>, E-mail: roger.marti@hefr.ch

<sup>a</sup>Institute of Chemical Technology, Haute école d'Ingénierie et d'Architecture Fribourg, HES-SO University of Applied Sciences and Arts Western Switzerland, Boulevard de Pérolles 80, CH-1700 Fribourg, Switzerland; <sup>b</sup>Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, CH-8093 Zurich, Switzerland.

## 1. Introduction

Identifying a compound of interest – be it in academia or industry – is generally followed by a comprehensive study of chemical and physical properties, making accessibility to the compound an important factor. Relying on the output of inefficient small-scale synthesis routes might be feasible for laboratory screenings, but at the latest when thinking about commercialization or clinical trials, the availability of large product quantities needs to be ensured. However, scaling up a synthesis from mg to g or even kg quantities is not a straightforward task. Synthesis protocols can rarely be transferred from the lab to an industrial plant without adaptations. Additionally, with increasing scale the ‘how’ of a reaction becomes as important as the final result, as the chemical industry’s environmental impact is an ever-growing topic of concern. This imposes limitations on the process chemist regarding the choice of reagents and synthetic approaches. Thus, an important part of process chemistry is the modification of reactions and process parameters to balance efficiency and sustainability.

Two key concepts in this regard are the implementation of catalytic transformations and the utilization of continuous flow processing. In 2018, the ACS Green Chemistry Institute Pharmaceutical Roundtable made two noteworthy additions to their list of ‘Key Green Chemistry Research Areas’,<sup>[1]</sup> i) the development of effective and versatile methodology utilizing cheap and sustainable metals, and ii) catalyst immobilization without significant loss in kinetics. Both concerns are directly linked to the progressing depletion of precious metal deposits and the awareness about the environmental impact of their extraction.<sup>[2]</sup> A new class of heterogeneous metal catalysts that could address both concerns simultaneously are single atom heterogeneous catalysts (SACs, see Fig. 1).<sup>[3–5]</sup>

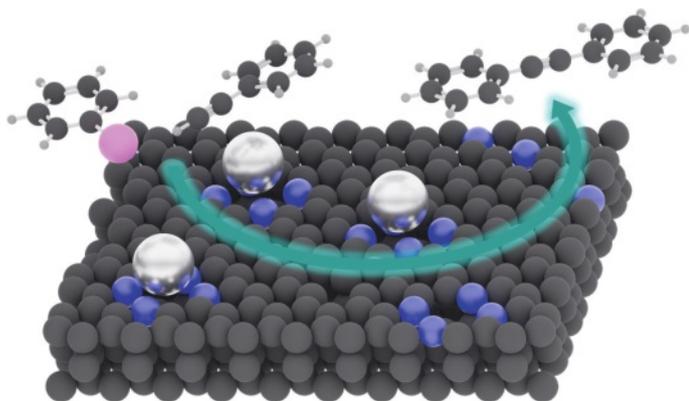


Fig. 1. Palladium single-atoms supported on nitrogen doped carbon utilized for the Sonogashira cross-coupling of iodobenzene and phenylacetylene.

## 2. Process Chemistry and SAC

Scaling up a synthesis from (milli-)gram to kilogram quantities towards a safe, robust, and sustainable process is a complex endeavor and generally involves multiple steps (see Fig. 2).<sup>[6]</sup> The work is often preceded by route finding and scouting to find alternative, shorter, and ideally convergent syntheses to the target molecule. Nowadays, this work is supported by new and sometimes open-access Computer-aided Synthesis Planning (CASP) tools. Still, it requires a lot of chemical knowledge and experience in evaluating and selecting promising synthesis routes. An important aspect of *Process Chemistry & Development* – besides the scale increase and sustainability – is the safety of a process and the underlying chemistry. A thermal process safety assessment comprising of *e.g.*, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) or reaction calorimetry are key

technologies in this regard. Identification of decomposition events and knowledge about heat release and transfer within the reaction mixture build the necessary foundation for determining a safe operation space.<sup>[7]</sup> Furthermore, the chemical processes (including the reaction but also pre- and post-reaction treatment of substrates and waste) are developed and optimized with industrial equipment and safety standards in mind, which can both significantly differ from a laboratory environment. This includes optimization of reaction parameters (*e.g.*, reaction temperature, solvent use, stoichiometry of reagents) but also replacing complex and expensive process steps such as flash chromatography with ‘simple’ crystallizations or distillations. Now, what is the current state of science and what can we expect regarding the development of new industrial processes using SAC? Where does the SAC constitute an added value? Based on experience and discussions with researchers from industry, three opportunities for industrial applications come to mind:

- Route finding and scouting – pre-selection of routes by CASP tools feasible for SAC
- Synthesis enabling & optimization – development and use of SAC as novel catalytic systems
- Process development – catalyst recycling and application of continuous flow chemistry

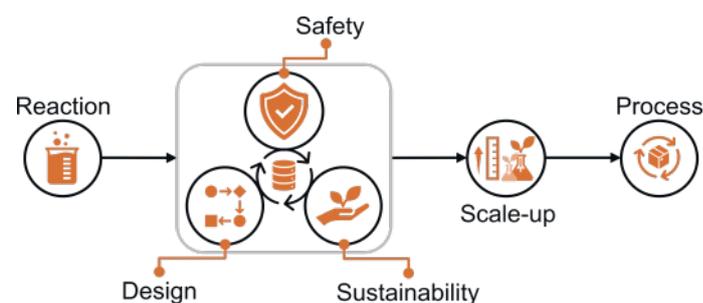


Fig. 2. Schematic overview for developing a reaction from research stage to an industrial viable process.

### 2.1 SACs in Cross-coupling Reactions

Classical cross-coupling chemistry is traditionally dominated by highly specialized homogeneous organopalladium systems.<sup>[8]</sup> However, the demand for more sustainable processes and the awareness of resource depletion led to an increasing effort to replace precious metal based organometallic catalysts with earth-abundant and solid-supported (heterogeneous) alternatives. Nonetheless, the replacement of Pd with cheap and sustainable metals is far from trivial. SACs are a young member within the heterogeneous catalyst family. They consist of catalytically active centers which are atomically distributed on the surface of a solid carrier.<sup>[9]</sup> The systematic synthesis of transition metal SACs has been made possible only through advances in atomic-resolution characterization, such as scanning transmission electron microscopy, which allows distinction between metal atoms and clusters on a solid support.<sup>[10]</sup> The ability to tailor the coordination environment of the active center through the carrier synthesis and choice of deposition method creates opportunities to reach selective activity similar to that of homogeneous catalysts. Additionally, the spatial isolation of the centers on solid surfaces theoretically enables a maximum atom utilization, although affected by active site accessibility. Published work on this topic only emerged in the last 5 years (Table 1), illustrating the incredibly early state of research in this field. Owing to the ease of procedure, most studies utilized the Suzuki reactions as an application example, with a rather limited metal scope compared to the efforts that were

Table 1. Overview of SAC catalyzed cross-coupling reactions

Suzuki-Miyaura Reaction						
Entry	Metal	Carrier	Aryl-X	Reagent	Additive	Solvent
1	Pt <sup>[11]</sup>	Sulfur-doped carbon	Br, I	Cs <sub>2</sub> CO <sub>3</sub>		THF
2	Pd <sup>[12]</sup>	Graphitic carbon nitride	Br, I	K <sub>2</sub> CO <sub>3</sub>	PPh <sub>3</sub>	DME/H <sub>2</sub> O 1:1
3	Pd <sup>[13]</sup>	ZnO-ZrO <sub>2</sub>	Br, I	K <sub>2</sub> CO <sub>3</sub>		EtOH/H <sub>2</sub> O 3:2
4	Pd <sup>[14]</sup>	CeO <sub>2</sub>	Br, I	K <sub>2</sub> CO <sub>3</sub>		EtOH/H <sub>2</sub> O 2:1
5	Pd <sup>[15]</sup>	Carbon nitride/reduced graphene oxide	I	aq. NaOH		THF
6	Pd <sup>[16]</sup>	Ti <sub>0.87</sub> O <sub>2</sub>	Br, I	K <sub>2</sub> CO <sub>3</sub>		DMF/H <sub>2</sub> O 1:1
7	Pd <sup>[17]</sup>	Nitrogen-doped carbon	I	K <sub>2</sub> CO <sub>3</sub>		DME
8	Ni <sup>[17]</sup>	Nitrogen-doped carbon	I	K <sub>2</sub> CO <sub>3</sub>		THF
9	Pd <sup>[18]</sup>	Zr-MOP-BPY	Br	Na <sub>2</sub> CO <sub>3</sub>		MeOH/H <sub>2</sub> O 1:1
10	Pd <sup>[19]</sup>	Nitrogen-doped carbon	Cl, Br, I	NaOH	TBACl	H <sub>2</sub> O
11	Pd <sup>[20]</sup>	FeO <sub>x</sub>	Br	K <sub>2</sub> CO <sub>3</sub>		EtOH/H <sub>2</sub> O 2:1
12	Pd <sup>[21]</sup>	Phosphomolybdic acid/ZrO <sub>2</sub>	I	K <sub>2</sub> CO <sub>3</sub>		EtOH/H <sub>2</sub> O 2:1
13	Pd <sup>[22]</sup>	UiO-66-NH <sub>2</sub> (MOF)	Br, I	K <sub>2</sub> CO <sub>3</sub>		iPrOH/H <sub>2</sub> O 1:3
Sonogashira-Hagihara Reaction						
14	Pd <sup>[23]</sup>	TiO <sub>2</sub>	I	K <sub>2</sub> CO <sub>3</sub>		EtOH
15	Pd <sup>[24]</sup>	Nitrogen-doped carbon	I	NEt <sub>3</sub>	PPh <sub>3</sub> , CuI	MeCN
Mizoroki-Heck Reaction						
16	Pd <sup>[25]</sup>	Carbon-doped boron nitride	Cl			
Ullmann Reaction						
17	Pd <sup>[26]</sup>	Gold alloy	Cl, Br, I	NaOH		H <sub>2</sub> O
18	Cu, Fe, Cu/Fe <sup>[27]</sup>	Graphitic carbon nitride	I	Cs <sub>2</sub> CO <sub>3</sub>	CuI	DMF
19	Cu <sup>[28]</sup>	Nitrogen-doped graphene	I	K <sub>3</sub> PO <sub>4</sub>		EtOH
20	Ni <sup>[29]</sup>	Triazine/pyridine covalent organic frameworks	Br	DABCO		DMA
21	Ni <sup>[30]</sup>	Carbon nitride	Br, I, Cl	Quinuclidine		DMA
Glaser Hay Reaction						
22	Cu <sup>[31]</sup>	Nitrogen-doped carbon	-			MeCN/H <sub>2</sub> O 1:1

made for homogeneous catalysis so far.<sup>[32,33]</sup> There are only a few examples of other cross-coupling reactions, e.g. two recent studies of the Sonogashira-Hagihara reaction or Sun *et al.* with computational work on the Mizoroki-Heck coupling.

The carrier materials for the single-atoms were either carbon-based (e.g., nitrogen-doped mesoporous carbon, Entry 10, or exfoliated graphitic carbon nitride, Entry 2), metal oxides (e.g., ZnO-ZrO<sub>2</sub>, Entry 3, or FeO<sub>x</sub>, Entry 11), metal-organic frameworks (MOFs, Entry 13) or metal-organic polyhedral materials (MOPs, Entry 9). Looking at the experimental procedures of the catalytic activity evaluation, with a few exceptions, in most cases aryl iodide or bromides are used and converted in presence of a carbonate base.

Compared to the accumulated work on homogeneously catalyzed cross-couplings, an immense knowledge void concerning the application potential of SAC in organic chemistry has yet to be filled.<sup>[34,35]</sup> Pioneering efforts demonstrated the importance of multidisciplinary to gain a mechanistic understanding on the atomic scale through a combined approach of in-depth catalyst characterization, detailed investigation of the materials' catalytic activity and density-functional theory (DFT) derived system modeling.<sup>[12]</sup>

## 2.2 Application of SACs in Flow Chemistry

Recently, the application of continuous flow chemistry in process development and production has become very popular. Although the pharmaceutical industry still largely relies on multipurpose batch or semi-batch reactors, it is evident that interest is arising toward continuous flow manufacturing of organic molecules, including heterogeneous catalysis using SACs.<sup>[36]</sup> Among the examples of cross-coupling reactions in Table 1, there are just two evaluating SACs in fixed bed flow reactors. A continuous test

of multiple hours on-stream in the Suzuki reaction evidenced constant activity, verifying the absence of leaching.<sup>[12]</sup> Fu *et al.* used a Pd1/C3N4/rGO catalyst in form of a fixed bed in a flow reactor and observed for the SAC catalyst the same reactivity for the Suzuki reaction as in batch operation and 10 h on-stream without loss of catalytic activity.<sup>[15]</sup>

## 2.3 Catalyst Stability

An important aspect in the process development of catalytic processes using heterogeneous transition metal catalysts is metal leaching into the reaction solution. Not only does this negatively affect the performance of the catalyst in subsequent reactions, but it also raises the question about the origin of catalytic activity as the leached metal species could act as an *in situ* generated homogeneous catalyst. The dissolved Pd atoms can also partially re-deposit on the carrier material, either in form of nanoparticles or single-atom species.<sup>[37]</sup> The fact that solid-supported and leached metal species experience different coordination environments will inevitably decrease the system's selectivity. Understanding if, how, and in what quantities leaching occurs is essential to develop robust and scalable processes. This makes a thorough empirical investigation of the SAC stability in varying chemical environments necessary. The resulting data will build the foundation for future identification of structure related descriptors to predict the catalysts' stability-activity-selectivity profile.

## 3. Sustainability

Solvents often make up the largest part of a reaction mixture, so it is very important to use sustainable and non-toxic solvents, so-called 'green solvents'. Looking at the list of solvents used in SAC-catalyzed cross-coupling reactions so far (Table 1), a trend

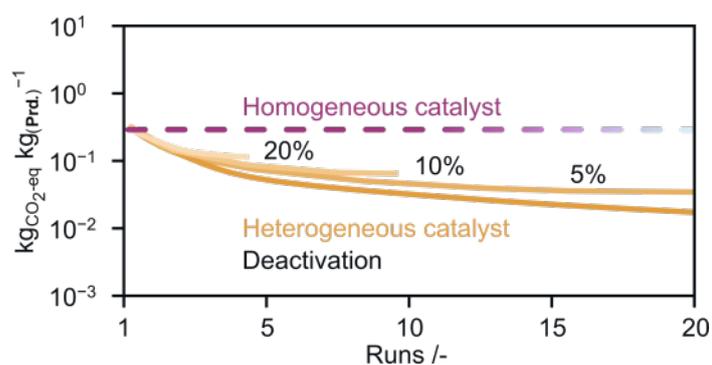


Fig. 3. LCA comparison of the homogeneously (purple) and heterogeneously (yellow) catalyzed Sonogashira reaction. Assumed deactivation of the heterogeneous catalyst as inset percentages (black).

towards aqueous alcohol mixtures seems dominant. Nonetheless, classic polar protic solvents like DMF, DMA, THF as well as DME are still utilized although considered ‘critical’ solvents with major environmental issues. There is a plethora of literature and tools (e.g. from ACS Green Chemistry Institute<sup>[38]</sup>) available to guide scientists in the choice of solvents, such as suggesting the substitution of e.g. THF with alternatives like 2-methyl-THF.<sup>[39,40]</sup> As a process chemist, it is also worthwhile to determine established metrics such as PMI<sup>[41]</sup> for the research on SAC-catalyzed reactions. This enables a fast and simple assessment of the conditions not only regarding the quality but also the quantity of chemicals used. A detailed evaluation of the reaction and its environmental impact if applied on a larger scale requires a detailed LCA, however. Of the SAC studies summarized in Table 1, only one assessed the environmental benefits within different metrics, including the global warming potential (GWP). A comprehensive cradle-to-gate life cycle analysis (LCA) of the homogeneous vs. heterogeneous Sonogashira reaction revealed that as little as two recycles were sufficient to reduce the GWP score 4 to 60 times for the SAC catalyst in comparison to the homogeneous catalyst (see Fig. 3). This is assuming negligible leaching of palladium into the reaction solution.

#### 4. Conclusions

Within the frame of NCCR Catalysis, our work focuses on studying the opportunities and challenges of applying SAC in organic synthesis including detailed mechanistic investigation and sustainability assessment. SACs have emerged as well-suited alternatives to organometallic complexes for cross-coupling reactions. The nano-structuring of their surface can unlock unprecedented activities, letting a heterogeneous catalyst outperform classical homogeneous catalysts such as the widely used Pd(PPh<sub>3</sub>)<sub>4</sub>. However, due to the early stage of this field, many questions are yet to be answered. Identifying structural descriptors to predict its stability for varying chemical environments will be key for its use in applied chemistry. At the same time, knowledge about the stability will enable detailed studies regarding the selective activity of the material, and eventually, yield structure–performance descriptors. Looking further toward potential applications, a matter that needs to be addressed is substrate transfer limitations. Considering the use in mid- to late-stage transformations of multi-step synthetic routes relevant for the pharmaceutical or fine chemical industry, will require the target functionality of the compound to reach the active center on the catalyst. As such, only a limited number of the present centers might be able to be catalytically active. Here, empirical research will lay the foundation to unravel the SACs stability-activity-selectivity relationships and guide toward the development of novel robust tailor-made carrier materials. With such new SACs in hand, stability under varying chemical conditions and in flow chemistry can be challenged for complex applications.<sup>[42]</sup>

LCA will take on an important role in pinpointing early on where the SACs will be able to make difference, and to reveal sustainability weak spots in potential implementations. However, if we talk about sustainability, we must also apply appropriate and standardized ways to calculate metrics, otherwise their comparison becomes meaningless.<sup>[43]</sup>

A wealth of opportunity and open questions that can only be addressed through an interdisciplinary approach, combining catalyst design and optimization, sophisticated analytics and characterization of catalyst materials, synthesis and implementation on larger scale, and sustainability assessment – competencies well represented in NCCR Catalysis.

#### Acknowledgements

This publication was created as part of NCCR Catalysis (grant number 180544), a National Centre of Competence in Research funded by the Swiss National Science Foundation. The authors want to thank the NCCR Catalysis Project Office comprising Dr. Marie Francine Lagadec, Lauren Gamp and Annabelle Kin for their work and support.

Received: December 6, 2022

- M. C. Bryan, P. J. Dunn, D. Entwistle, F. Gallou, S. G. Koenig, J. D. Hayler, M. R. Hickey, S. Hughes, M. E. Kopach, G. Moine, P. Richardson, F. Roschangar, A. Steven, F. J. Weiberth, *Green Chem.* **2018**, *20*, 5082, <https://doi.org/10.1039/C8GC01276H>.
- A. J. Hunt, A. S. Matharu, A. H. King, J. H. Clark, *Green Chem.* **2015**, *17*, 1949, <https://doi.org/10.1039/C5GC90019K>.
- Y. Hu, H. Li, Z. Li, B. Li, S. Wang, Y. Yao, C. Yu, *Green Chem.* **2021**, *23*, 8754, <https://doi.org/10.1039/D1GC02331D>.
- G. Giannakakis, S. Mitchell, J. Pérez-Ramírez, *Trends Chem.* **2022**, *4*, 264, <https://doi.org/10.1016/j.trechm.2022.01.008>.
- S. Mitchell, E. Vorobyeva, J. Pérez-Ramírez, *Angew. Chem.* **2018**, *130*, 15538, <https://doi.org/10.1002/ange.201806936>.
- N. G. Anderson, ‘Practical Process Research and Development - A guide for Organic Chemists’, Academic Press, Oxford, **2012**.
- F. Stoessel, ‘Thermal Safety of Chemical Processes: Risk Assessment and Process Design (Second Edition)’, Wiley VCH, **2020**.
- J. Magano, J. R. Dunetz, *Chem. Rev.* **2011**, *111*, 2177, <https://doi.org/10.1021/cr100346g>.
- S. K. Kaiser, Z. Chen, D. Faust Akl, S. Mitchell, J. Pérez-Ramírez, *Chem. Rev.* **2020**, *120*, 11703, <https://doi.org/10.1021/acs.chemrev.0c00576>.
- M. Kottwitz, Y. Li, H. Wang, A. I. Frenkel, R. G. Nuzzo, *Chem. Methods* **2021**, *1*, 278, <https://doi.org/10.1002/cmtd.202100020>.
- E.-K. Lee, S.-A. Park, H. Woo, K. Hyun Park, D. W. Kang, H. Lim, Y.-T. Kim, *J. Catal.* **2017**, *352*, 388, <https://doi.org/10.1016/j.jcat.2017.05.005>.
- Z. Chen, E. Vorobyeva, S. Mitchell, E. Fako, M. A. Ortuño, N. López, S. M. Collins, P. A. Midgley, S. Richard, G. Vilé, J. Pérez-Ramírez, *Nat. Nanotechnol.* **2018**, *13*, 702, <https://doi.org/10.1038/s41565-018-0167-2>.
- G. Ding, L. Hao, H. Xu, L. Wang, J. Chen, T. Li, X. Tu, Q. Zhang, *Commun. Chem.* **2020**, *3*, 43, <https://doi.org/10.1038/s42004-020-0289-y>.
- X. Tao, R. Long, D. Wu, Y. Hu, G. Qiu, Z. Qi, B. Li, R. Jiang, Y. Xiong, *Small* **2020**, *16*, 2001782, <https://doi.org/10.1002/smlf.202001782>.
- N. Fu, X. Liang, Z. Li, W. Chen, Y. Wang, L. Zheng, Q. Zhang, C. Chen, D. Wang, Q. Peng, L. Gu, Y. Li, *Nano Res.* **2020**, *13*, 947, <https://doi.org/10.1007/s12274-020-2720-1>.
- Y. Jin, F. Lu, D. Yi, J. Li, F. Zhang, T. Sheng, F. Zhan, Y. Duan, G. Huang, J. Dong, B. Zhou, X. Wang, J. Yao, *CCS Chem.* **2021**, *3*, 1453, <https://doi.org/10.31635/ccschem.020.202000388>.
- J. Liu, Z. Chen, C. Liu, B. Zhang, Y. Du, C.-F. Liu, L. Ma, S. Xi, R. Li, X. Zhao, J. Song, X. Z. Sui, W. Yu, L. Miao, J. Jiang, M. J. Koh, K. P. Loh, *J. Mater. Chem. A* **2021**, *9*, 11427, <https://doi.org/10.1039/D1TA00012H>.
- S. Kim, S. Jee, K. M. Choi, D.-S. Shin, *Nano Res.* **2021**, *14*, 486, <https://doi.org/10.1007/s12274-020-2885-7>.
- H. Wei, X. Li, B. Deng, J. Lang, Y. Huang, X. Hua, Y. Qiao, B. Ge, J. Ge, H. Wu, *Chin. J. Catal.* **2022**, *43*, 1058, [https://doi.org/10.1016/S1872-2067\(21\)63968-2](https://doi.org/10.1016/S1872-2067(21)63968-2).
- X. He, H. Zhang, X. Zhang, Y. Zhang, Q. He, H. Chen, Y. Cheng, M. Peng, X. Qin, H. Ji, D. Ma, *Nat. Commun.* **2022**, *13*, 5721, <https://doi.org/10.1038/s41467-022-33442-2>.
- J. R. Patel, A. U. Patel, *Nanoscale Adv.* **2022**, *4*, 4321, <https://doi.org/10.1039/D2NA00559J>.
- S. Ji, X. Lu, M. Zhang, L. Leng, H. Liu, K. Yin, C. Xu, C. He, J. H. Horton, J. Zhang, Z. Li, *Chem. Eng. J.* **2023**, *452*, 139205, <https://doi.org/10.1016/j.cej.2022.139205>.

- [23] X. Zhang, Z. Sun, B. Wang, Y. Tang, L. Nguyen, Y. Li, F. F. Tao, *J. Am. Chem. Soc.* **2018**, *140*, 954, <https://doi.org/10.1021/jacs.7b09314>.
- [24] D. Faust Akl, D. Poier, S. C. D' Angelo, T. P. Araújo, V. Tulus, O. V. Safonova, S. Mitchell, R. Marti, G. Guillén-Gosálbez, J. Pérez-Ramírez, *Green Chem.* **2022**, *24*, 6879, <https://doi.org/10.1039/D2GC01853E>.
- [25] N. Cao, N. Wang, M. Ran, C. Chen, C. Jiang, W. Sun, *ACS Appl. Nano Mater.* **2020**, *3*, 10905, <https://doi.org/10.1021/acsanm.0c02165>.
- [26] L. Zhang, A. Wang, J. T. Miller, X. Liu, X. Yang, W. Wang, L. Li, Y. Huang, C.-Y. Mou, T. Zhang, *ACS Catal.* **2014**, *4*, 1546, <https://doi.org/10.1021/cs500071c>.
- [27] E. Vorobyeva, V. C. Gerken, S. Mitchell, A. Sabadell-Rendón, R. Hauert, S. Xi, A. Borgna, D. Klose, S. M. Collins, P. A. Midgley, D. M. Kepaptsoglou, Q. M. Ramasse, A. Ruiz-Ferrando, E. Fako, M. A. Ortuño, N. López, E. M. Carreira, J. Pérez-Ramírez, *ACS Catal.* **2020**, *10*, 11069, <https://doi.org/10.1021/acscatal.0c03164>.
- [28] Y. Zhang, S. Ye, M. Gao, Y. Li, X. Huang, J. Song, H. Cai, Q. Zhang, J. Zhang, *ACS Nano* **2022**, *16*, 1142, <https://doi.org/10.1021/acsnano.1c08898>.
- [29] Z. Li, S. Qiu, Y. Song, S. Huang, J. Gao, L. Sun, J. Hou, *Sci. Bull.* **2022**, *67*, 1971, <https://doi.org/10.1016/j.scib.2022.09.010>.
- [30] M. Kwak, J. Bok, B.-H. Lee, J. Kim, Y. Seo, S. Kim, H. Choi, W. Ko, W. Hooch Antink, C. W. Lee, G. H. Yim, H. Seung, C. Park, K.-S. Lee, D.-H. Kim, T. Hyeon, D. Yoo, *Chem. Sci.* **2022**, *13*, 8536, <https://doi.org/10.1039/D2SC02174A>.
- [31] P. Ren, Q. Li, T. Song, Y. Yang, *ACS Appl. Mater. Interfaces* **2020**, *12*, 27210, <https://doi.org/10.1021/acsmi.0c05100>.
- [32] I. P. Beletskaya, F. Alonso, V. Tyurin, *Coord. Chem. Rev.* **2019**, *385*, 137, <https://doi.org/10.1016/j.ccr.2019.01.012>.
- [33] A. Biffis, P. Centomo, A. Del Zotto, M. Zecca, *Chem. Rev.* **2018**, *118*, 2249, <https://doi.org/10.1021/acs.chemrev.7b00443>.
- [34] Z. Chen, J. Liu, M. J. Koh, K. P. Loh, *Adv. Mater.* **2022**, *34*, 2103882, <https://doi.org/10.1002/adma.202103882>.
- [35] W.-H. Li, J. Yang, D. Wang, Y. Li, *Chem* **2022**, *8*, 119, <https://doi.org/10.1016/j.chempr.2021.10.030>.
- [36] M. Pagliaro, C. Della Pina, R. Ciriminna, *ChemCatChem* **2022**, *14*, e202200768, <https://doi.org/10.1002/cctc.202200768>.
- [37] M. Genelot, V. Dufaud, L. Djakovitch, *Adv. Synth. Catal.* **2013**, *355*, 2604, <https://doi.org/10.1002/adsc.201300357>.
- [38] Green Chemistry, <https://www.acs.org/content/acs/en/greenchemistry.html>, accessed November 30, 2022.
- [39] P. Dutta, A. McGranaghan, I. Keller, Y. Patil, N. Mulholland, V. Murudi, H. Prescher, A. Smith, N. Carson, C. Martin, P. Cox, D. Stierli, M. Bousseghoune, F. Barreateau, J. Cassayre, E. Godineau, *Green Chem.* **2022**, *24*, 3943, <https://doi.org/10.1039/D2GC00698G>.
- [40] J. Sherwood, J. H. Clark, I. J. S. Fairlamb, J. M. Slattery, *Green Chem.* **2019**, *21*, 2164, <https://doi.org/10.1039/C9GC00617F>.
- [41] E. R. Monteith, P. Mampuy, L. Summerton, J. H. Clark, B. U. W. Maes, C. R. McElroy, *Green Chem.* **2020**, *22*, 123, <https://doi.org/10.1039/C9GC01537J>.
- [42] B. C. Gates, M. Flytzani-Stephanopoulos, D. A. Dixon, A. Katz, *Catal. Sci. Technol.* **2017**, *7*, 4259, <https://doi.org/10.1039/C7CY00881C>.
- [43] J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev.* **2018**, *118*, 434, <https://doi.org/10.1021/acs.chemrev.7b00435>.

#### License and Terms



This is an Open Access article under the terms of the Creative Commons Attribution License CC BY 4.0. The material may not be used for commercial purposes.

The license is subject to the CHIMIA terms and conditions: (<https://chimia.ch/chimia/about>).

The definitive version of this article is the electronic one that can be found at <https://doi.org/10.2533/chimia.2023.127>