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Surface Organo-Iron Chemistry Towards Efficient Reverse Water-Gas Shift Catalysis

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Abstract: The low-temperature reverse water-gas shift (LT-RWGS) is a critical and energy effective technology for syngas production and the mitigation of anthropogenic carbon emissions. Developing efficient and well-defined catalysts for the LT-RWGS, from which structure-activity relationships can be drawn, is a significant challenge. Herein we describe how the identification of the grafting properties of tetramesityldiiron (Fe_2Mes_4) helps with designing tailored and highly efficient catalysts of $PtFe@SiO_2$ composition. To that end, a molecular analogue, $Fe_2Mes_3OSi(O^tBu)_3$, was synthesized and characterized by X-ray diffraction, ^{57}Fe-Mössbauer and ^{1}H-NMR spectroscopy. The results confirmed that tetramesityldiiron grafts onto silica *via* selective displacement of a single mesityl ligand, forming $Fe_2Mes_3@SiO_2$, while steric hindrance likely prevents secondary interactions with surface siloxide bridges. This work highlights the potential of tetramesityldiiron as a versatile precursor for synthesizing bimetallic $MFe@SiO_2$ systems, enabling the rational development of highly efficient LT-RWGS and CO_2 hydrogenation catalysts.

Keywords: Bimetallic nanoparticles · CO_2 conversion · ^{57}Fe Mössbauer spectroscopy · Heterogeneous catalysis · Surface organometallic chemistry

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Prof. Dr. Christophe Copéret graduated from CPE Lyon in 1992 (Lyon, France) and obtained a PhD in chemistry in 1996 from Purdue University (West Lafayette, USA) under the guidance of Prof. E. Negishi. He then conducted a postdoctoral stay at the Scribbs Research Institute (La Jolla, USA) in the group of Prof. K. B. Sharpless before joining CNRS in 1998, where he was promoted to the position of CNRS research director in 2008. Since 2010 he has been a professor in the Department of Chemistry and Applied Biosciences at ETH Zürich focusing on designing functional materials with applications in catalysis, molecular recognition, imaging, and microelectronics using molecular-, material- and surface-chemistry approaches.

1. Introduction

The reverse water-gas shift (RWGS) and its reverse reaction (WGS) are critical technologies in the chemical industry and are central to CO_2 conversion and syngas production – key strategies for mitigating carbon emissions.[1–4] The RWGS enables CO_2 to be converted into syngas (CO / H_2), which can be further processed into valuable chemicals through Fischer-Tropsch, or methanol synthesis.[5–8] RWGS is endothermic ($\Delta H°$ = +42.1 kJ/mol), and therefore favored at high temperatures (500–700 °C). However, the harsh conditions lead to catalyst deactivation and high energy cost. Consequently, ongoing research aims at developing catalysts for moderate temperature operation (300–500 °C) to enhance the catalyst productivity. Supported Pt-based catalysts have emerged as promising candidates for the low-temperature RWGS (LT-RWGS) when doped with appropriate promoters.[9–13]

Iron promotion has garnered particular interest because of the natural abundance and low cost of iron, but its promotional role in RWGS remains poorly understood.[14] Two mechanisms are typically proposed for CO_2 activation:[1,9,15,16] i) hydrogen-mediated activation (CO_2 forms hydroxycarbonyl intermediates then decomposes to CO), and ii) redox-mechanisms (the reduced promoter directly activates CO_2, producing CO, followed by re-reduction of the promoter by H_2).[14] To better understand the role of iron as a promoter in RWGS, it is essential to design catalytic materials with precisely defined nanoparticle-support interfaces and compositions, such as Pt-Fe alloys.

However, industrially conventional preparation methods, like precipitation or impregnation in water, often result in complex, poorly defined materials, which complicate efforts to establish structure-reactivity relationships.[17,18]

To address these challenges, we have recently utilized Surface Organometallic Chemistry (SOMC) to prepare tailored, silica-supported Pt-Fe bimetallic catalysts by a sequential grafting approach (Fig. 1a),[19] which show outstanding activity and selectivity in LT-RWGS.

In fact, bimetallic $PtFe@SiO_2$ catalysts drastically outperform the monometallic reference materials ($Pt@SiO_2$ and $Fe@SiO_2$)

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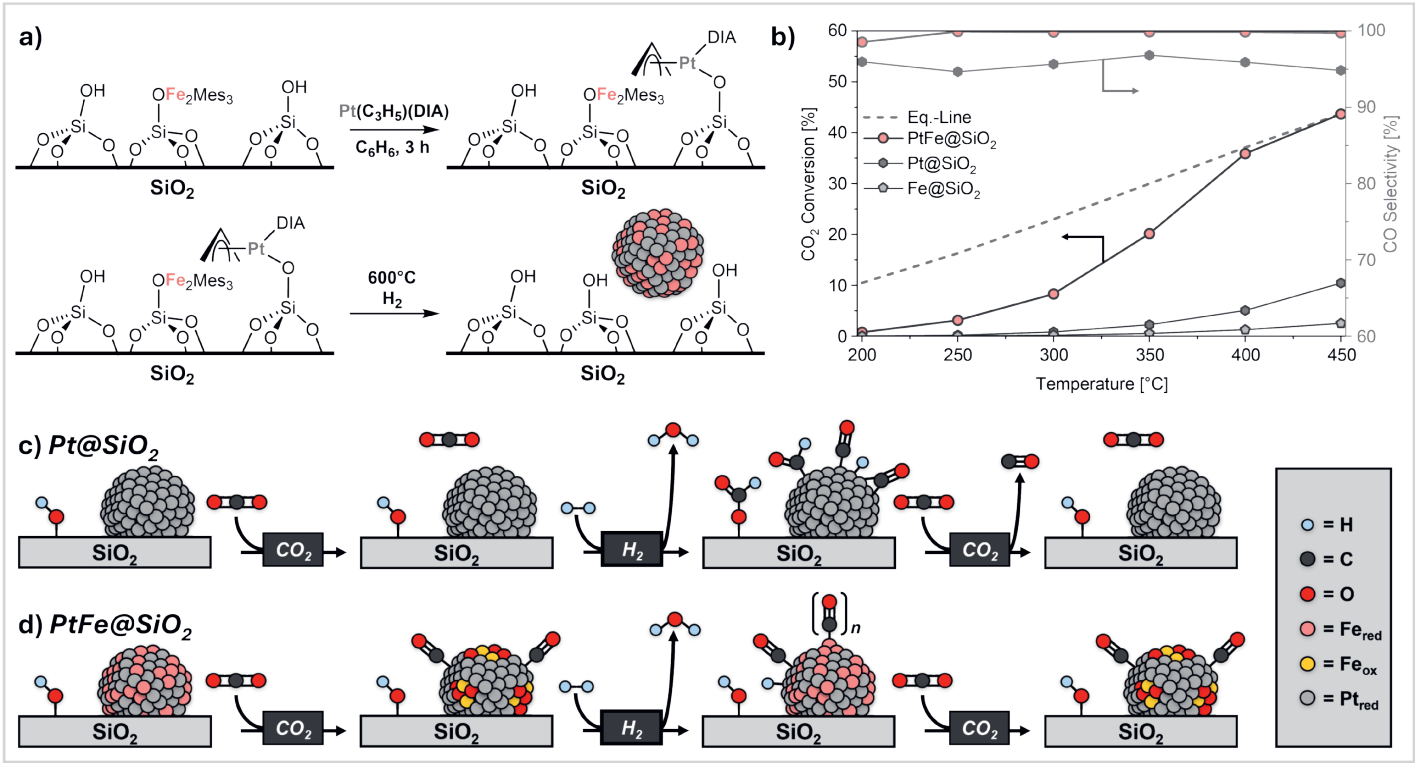

Fig. 1. (a) Synthesis of $PtFe@SiO_2$ by sequential grafting (starting from $Fe_2Mes_3@SiO_2$); (b) CO_2 conversion [left] and CO selectivity [right] at various temperatures for the monometallic ($Pt@SiO_2$ and $Fe@SiO_2$) and bimetallic ($PtFe@SiO_2$) systems (Conditions: 20 mL min^{-1} (1:3:1 $CO_2/H_2/Ar$) at 1 bar and 200-450 °C), Catalyst amount: 20 mg diluted in 2 g SiC; (c-d) Schematic representation of distinct mechanistic pathways for $Pt@SiO_2$ and $PtFe@SiO_2$ under LT-RWGS conditions: (c) Hydrogen mediated CO_2 activation over monometallic $Pt@SiO_2$; (d) CO_2 activation by Fe^0-Fe^{n+} redox couple and H_2 activation by Pt in $PtFe@SiO_2$.

in terms of CO_2 conversion, as well as CO selectivity. Notably, the bimetallic system achieves thermodynamic equilibrium conversion at a remarkably low temperature of 400 °C (*ca.* 37% conversion), while upholding high CO selectivity >99.5%, highlighting the improved energy efficiency of the process (Fig. 1b). A suite of analyses revealed the formation of bulk Pt-Fe alloys and provided insights into the chemical state of the catalysts during the reaction. *In situ* diffuse reflectance FT-IR spectroscopy (DRIFTS), combined with CO_2/H_2 gas-switching experiments, captured dynamic changes in the surface chemistry of Pt and Fe. The results highlighted an alloying-dealloying process consistent with a redox mechanism for CO_2 conversion to CO in the presence of Fe (Fig. 1d), while monometallic $Pt@SiO_2$ achieves CO formation by a hydrogen-mediated mechanism under the involvement of carbon-containing intermediates, such as hydroxycarbonyls, carbonates or formates, (Fig. 1c) for further details, see the original publication.[19] We have therefore established a clearer understanding of the promotional effects of iron and its critical role in facilitating LT-RWGS.

However, the surface organometallic chemistry of iron (II) remains underdeveloped and an understanding of the structure of surface intermediates during the catalyst preparation remains elusive. In that context, while tetramesityldiiron (Fe_2Mes_4) has emerged as a promising precursor for the SOMC of iron,[20] the grafting mechanism and surface structure of immobilized Fe_2Mes_4 remains a topic of debate.[21] In our work we were able to further elucidate the grafting behavior of the iron mesityl precursor by ^{57}Fe-Mössbauer spectroscopy and X-ray diffraction using a molecular analogue.

2. Surface Organometallic Chemistry

Over the past decades, SOMC has emerged as a powerful tool for the development of well-defined catalytic systems supported on metal-oxides. From single-site catalysts (commonly employed in olefin metathesis)[22] to the formation of nanoparticles on the surface (usually for small molecule conversion),[23] the variety of potential material compositions and structures is vast and enables in depth catalyst design.[22–26] The synthesis of a material by SOMC requires surface -OH (hydroxyl-) groups that can react with tailored organometallic precursors in protonolysis type reactions, in a process termed grafting. Upon immobilization of the molecular precursor, the material can be subjected to various post-treatments (synthetic air, hydrogen) to form single-site catalysts or supported nanoparticles, respectively.

A large variety of molecular precursors for most transition metals and certain group 13/14 elements have been identified.[26,27] However, the mechanisms, by which they anchor to the surface of the metal oxide, and the nature of surface species remains elusive in certain cases. While iron-siloxide or iron-amide complexes have previously been used for the generation of Fe(II) single-site catalysts,[28–30] organoiron complexes, such as Fe_2Mes_4, have been envisioned as promising precursors for the formation of metallic iron-particles.

2.1 *Surface Chemistry of Tetramesityldiiron*

Iron mesityl is a dark red, homoleptic iron complex with a dimeric structure, containing bridging and terminal mesitylene ligands.[20] In the context of SOMC, the debate has centered on the nature of the tetramesityldiiron structure after grafting. Indeed, this molecular precursor can graft to the surface by displacing the terminal or bridging mesityl-ligand yielding mesitylene (MesH) as a coproduct (Fig. 2). Furthermore, in view of the dimeric nature of the complex, it is possible that it can also react through multiple anchoring sites simultaneously, which would influence the grafting stoichiometry.

A solution of tetramesityldiiron in benzene readily reacts with silica dehydroxylated at 700 °C (SiO_{2-700}) to form MesH

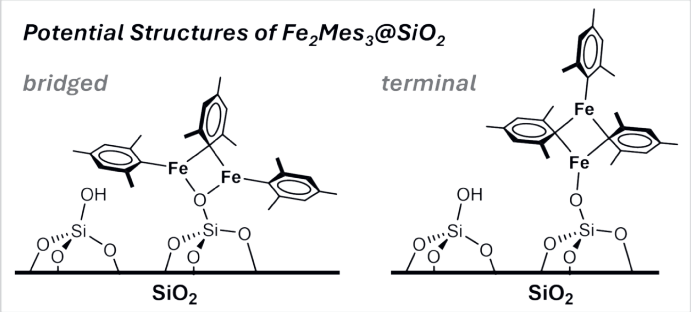

Fig. 2. Potential structures of $Fe_2Mes_3@SiO_2$ (bridging *vs.* terminal) debated in literature.

and a deep-red material, accompanied by the complete loss of color in the reaction solution. The high efficiency of the grafting, together with the formation of MesH as the by-product, allows for the quantitative analysis of this process by ^{1}H-qNMR. The experimental data shows the formation of one equivalent of MesH per grafted molecule of Fe_2Mes_4. This indicates that the molecular precursor grafts by displacement of only one mesityl ligand to form $Fe_2Mes_3@SiO_2$ (Fig. 3c). Upon treating this material under a dynamic atmosphere of H_2 at 600 °C the Fe(II) ion is reduced to its metallic state under the formation of small nanoparticles with a narrow size distribution (1.5 ± 0.2 nm), evidencing the reducibility of the precursor.[19] While for practical purposes, this information is sufficient, the elucidation of a fundamental grafting mechanism requires additional attention.

In an attempt to produce a model system that bears structural resemblance to $Fe_2Mes_3@SiO_2$, tetramesityldiiron was reacted with tris-*tert*-butoxysilanol ($HOSi(O^tBu)_3$), which has previously been used as a molecular mimic for the surface of highly dehydroxylated silica.[31] The reaction yields a monosubstituted complex, where one of the bridging mesityl ligands is exchanged by one siloxy ligand, as evidenced by solution ^{1}H-NMR and single crystal X-ray diffraction (XRD, CCDC Dep. Nr. 2415333) (Fig. 3d). Notably, the use of multiple equivalents of $HOSi(O^tBu)_3$ does not change the outcome of the reaction, indicating the preferential reaction with only one silanol for this complex and the formation of a very stable species. XRD measurements also reveal a secondary interaction between one of the Fe(II) centers and a lone pair of electrons of an oxygen atom on the $OSi(O^tBu)_3$ ligand, evidenced by a short d(Fe-O) of 2.315(2) Å, leading to two inequivalent Fe centers. This dissymmetry was further investigated by ^{57}Fe-Mössbauer spectroscopy of the unlabeled crystalline materials. The Mössbauer spectrum for Fe_2Mes_4 at 100K (Fig. 3a) shows a single doublet of Lorentzian lines with an isomer shift $\delta = 0.380(1)$ mm s^{-1} and a quadrupole splitting $\Delta E_Q = 1.618(2)$ mm s^{-1}, indicating the presence of two equivalent Fe centers in this compound. At 250 K the spectrum shows an additional spectroscopic signature of an impurity (details upon request) which can be attributed to ferric decomposition products of Fe_2Mes_4.[21] On the other hand, the spectrum of $Fe_2Mes_3OSi(O^tBu)_3$ at 100 K (Fig. 3b) shows two doublets of Lorentzian lines ($\delta_1 = 0.362(2)$ mm s^{-1}, $\Delta E_{Q,1} = 1.603(4)$ mm s^{-1} and $\delta_2 = 0.588(2)$ mm s^{-1}, $\Delta E_{Q,2} = 0.601(4)$ mm s^{-1}) with similar intensity and line width, confirming that the two Fe sites in $Fe_2Mes_3OSi(O^tBu)_3$ are indeed inequivalent.

At low temperature, the relative signal intensities of the two sub-spectra are close to the expected 1:1 ratio, while at elevated temperatures a slight deviation from this distribution is observed (details upon request), indicating (also small) differences in the Debye temperature for both Fe sites in this material. While one Fe site shows similar δ and ΔE_Q values to those in Fe_2Mes_4 (suggesting a similar coordination and binding situation), the second species shows a significantly increased isomer shift (and smaller ΔE_Q value), indicating an increased *d*-orbital occupancy, which can be attributed to a stronger *p*- or *s*-donation to Fe, likely originating from the secondary Fe-O interaction observed in the crystal structure.

The molecular species reported herein is mostly consistent with an early proposal for the grafted species, that claims the presence of a bridging siloxy ligand.[21] Furthermore it highlights the presence of a possible secondary interaction between one of the Fe centers and the surface, yielding two inequivalent Fe centers, explaining the difficulty in capturing high quality spectra for surface species. Nevertheless, the reported Mössbauer

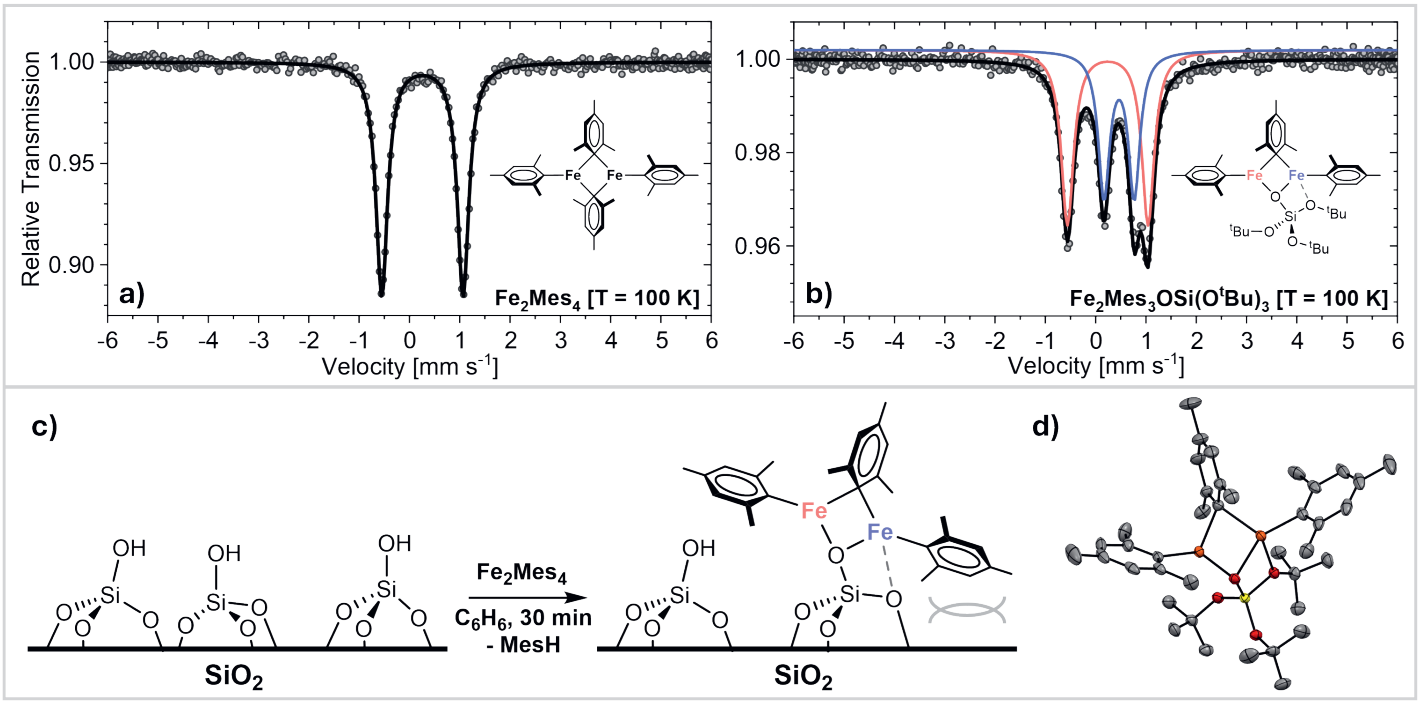

Fig. 3. a) ^{57}Fe Mössbauer spectrum for Fe_2Mes_4 at T= 100K with experimental data (grey) and a fit with a doublet of Lorentzian lines (black). b) ^{57}Fe Mössbauer spectrum for $Fe_2Mes_3OSi(O^tBu)_3$ at T= 100K with experimental data (grey) and a fit with two doublets of Lorentzian lines (red, blue). c) Proposed grafting mechanism of Fe_2Mes_4. d) Single-crystal XRD structure of $Fe_2Mes_3OSi(O^tBu)_3$ as a molecular analogue.

spectrum of $Fe_2Mes_3@SiO_2$ shows different spectral features:[21] it indicates the presence of one single Fe site, probably because of geometrical constraints on the support (no κ^2-coordination of the surface siloxy ligand) or the presence of residual dynamics that would make the two Fe centers equivalent.

3. Conclusions

As discussed above, tetramesityldiiron is a typical molecular precursor for SOMC and the synthesis of mono- and multimetallic Fe-containing nanoparticles that were developed in the context of CO_2 hydrogenation. Here, we have shown that the reaction of tetramesityldiiron with a molecular analogue of an isolated -OH group, $HOSi(O^tBu)_3$, yields a well-defined compound, ($Fe_2Mes_3OSi(O^tBu)_3$) that was characterized by ^{1}H-NMR, XRD and ^{57}Fe-Mössbauer spectroscopy. This compound is unreactive towards additional $HOSi(O^tBu)_3$, clearly indicating the stability of this dimer – a structure reminiscent of $Fe_2(OSi(O^tBu)_3)_4$. This confirms the preferred formation of a dimeric Fe compound with a bridging siloxy ligand, further supporting earlier surface chemistry studies, but also highlighting the possible presence of additional secondary interactions between one of the Fe centers and a κ^2-coordination of a siloxy ligand. This additional interaction makes the two iron atoms inequivalent as shown by both XRD and Mössbauer spectroscopy, which complexifies spectroscopic investigations of surface species, and showcases the complexity of grafting di-nuclear species.

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Author Contributions

C.H. and C.C. conceptualized the project. C. H. performed synthetic and catalytic experiments and wrote the manuscript. M. W. and D. B. performed Mössbauer spectroscopy measurements.

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[1] M. González-Castaño, B. Dorneanu, H. Arellano-García, *React. Chem. Eng*. **2021**, *6*, 954, https://doi.org/10.1039/d0re00478b.
[2] M. Zhu, Q. Ge, X. Zhu, *Trans. Tianjin Univ*. **2020**, *26*, 172, https://doi.org/10.1007/s12209-020-00246-8.
[3] X. Su, X. Yang, B. Zhao, Y. Huang, *J. Energy Chem*. **2017**, *26*, 854, https://doi.org/10.1016/j.jechem.2017.07.006.
[4] W. Zhang, J. Sun, H. Wang, X. Cui, *Chem. -Asian J.* **2024**, *19*, e202300971, https://doi.org/10.1002/asia.202300971.
[5] W. Zhou, K. Cheng, J. Kang, C. Zhou, V. Subramanian, Q. Zhang, Y. Wang, *Chem. Soc. Rev*. **2019**, *48*, 3193, https://doi.org/10.1039/C8CS00502H.
[6] X. Pan, F. Jiao, D. Miao, X. Bao, *Chem. Rev*. **2021**, *121*, 6588, https://doi.org/10.1021/acs.chemrev.0c01012.
[7] R. Zhang, Y. Wang, P. Gaspard, N. Kruse, *Science* **2023**, *382*, 99, https://doi.org/10.1126/science.adh8463.
[8] H. M. Torres Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A. I. Dugulan, K. P. de Jong, *Science* **2012**, *335*, 835, https://doi.org/10.1126/science.1215614.
[9] X. Chen, Y. Chen, C. Song, P. Ji, N. Wang, W. Wang, L. Cui, *Front. Chem.* **2020**, *8*, 709, https://doi.org/10.3389/fchem.2020.00709.
[10] H. Wang, M. S. Bootharaju, J. H. Kim, Y. Wang, K. Wang, M. Zhao, R. Zhang, J. Xu, T. Hyeon, X. Wang, S. Song, H. Zhang, *J. Am. Chem. Soc*. **2023**, *145*, 2264, https://doi.org/10.1021/jacs.2c10435.
[11] Z. Zhao, M. Wang, P. Ma, Y. Zheng, J. Chen, H. Li, X. Zhang, K. Zheng, Q. Kuang, Z.-X. Xie, *Appl. Catal., B* **2021**, *291*, 120101, https://doi.org/10.1016/j.apcatb.2021.120101.
[12] Y. He, D. Huang, *Molecules* **2023**, *28*, 6630, https://doi.org/10.3390/molecules28186630.
[13] S. Mine, T. Yamaguchi, K. W. Ting, Z. Maeno, S. M. A. H. Siddiki, K. Oshima, S. Satokawa, K.-i. Shimizu, T. Toyao, *Catal. Sci. Technol*. **2021**, *11*, 4172, https://doi.org/10.1039/D1CY00289A.
[14] A. Ruiz Puigdollers, P. Schlexer, S. Tosoni, G. Pacchioni, *ACS Catal*. **2017**, *7*, 6493, https://doi.org/10.1021/acscatal.7b01913.
[15] B. Yan, B. Zhao, S. Kattel, Q. Wu, S. Yao, D. Su, J. G. Chen, *J. Catal*. **2019**, *374*, 60, https://doi.org/10.1016/j.jcat.2019.04.036.
[16] L. Chen, I. A. W. Filot, E. J. M. Hensen, *J. Phys. Chem. C* **2023**, *127*, 20314, https://doi.org/10.1021/acs.jpcc.3c03983.
[17] J. R. A. Sietsma, A. Jos van Dillen, P. E. de Jongh, K. P. de Jong, in 'Scientific Bases for the Preparation of Heterogeneous Catalysts', **2006**, p. 95, https://doi.org/10.1016/s0167-2991(06)80895-5.
[18] P. Munnik, P. E. de Jongh, K. P. de Jong, *Chem. Rev.* **2015**, *115*, 6687, https://doi.org/10.1021/cr500486u.
[19] C. Hansen, W. Zhou, E. Brack, Y. Wang, C. Wang, J. Paterson, J. Southouse, C. Coperet, *J. Am. Chem. Soc*. **2024**, *146*, 27555, https://doi.org/10.1021/jacs.4c08517.
[20] H. Müller, W. Seidel, H. Görls, *J. Organomet. Chem*. **1993**, *445*, 133, https://doi.org/10.1016/0022-328X(93)80198-K.
[21] R. R. Langeslay, H. Sohn, B. Hu, J. S. Mohar, M. Ferrandon, C. Liu, H. Kim, A. Jeremy Kropf, C. Yang, J. Niklas, O. G. Poluektov, E. Ercan Alp, P. Ignacio-de Leon, A. P. Sattelberger, A. S. Hock, M. Delferro, *Dalton Trans*. **2018**, *47*, 10842, https://doi.org/10.1039/C8DT02720J.
[22] C. Coperet, Z. J. Berkson, K. W. Chan, J. de Jesus Silva, C. P. Gordon, M. Pucino, P. A. Zhizhko, *Chem. Sci*. **2021**, *12*, 3092, https://doi.org/10.1039/d0sc06880b.
[23] S. R. Docherty, C. Coperet, *J. Am. Chem. Soc*. **2021**, *143*, 6767, https://doi.org/10.1021/jacs.1c02555.
[24] C. Coperet, *Chem. Rev*. **2010**, *110*, 656, https://doi.org/10.1021/cr900122p.
[25] C. Coperet, *Acc. Chem. Res*. **2019**, *52*, 1697, https://doi.org/10.1021/acs.accounts.9b00138.
[26] C. Copéret, A. Comas-Vives, M. P. Conley, D. P. Estes, A. Fedorov, V. Mougel, H. Nagae, F. Núñez-Zarur, P. A. Zhizhko, *Chem. Rev*. **2016**, *116*, 323, https://doi.org/10.1021/acs.chemrev.5b00373.
[27] C. Ehinger, X. Zhou, M. Candrian, S. R. Docherty, S. Pollitt, C. Coperet, *JACS Au* **2023**, *3*, 2314, https://doi.org/10.1021/jacsau.3c00334.
[28] C. Nozaki, C. G. Lugmair, A. T. Bell, T. D. Tilley, *J. Am. Chem. Soc*. **2002**, *124*, 13194, https://doi.org/10.1021/ja020388t.
[29] A. W. Holland, G. Li, A. M. Shahin, G. J. Long, A. T. Bell, T. D. Tilley, *J. Catal*. **2005**, *235*, 150, https://doi.org/10.1016/j.jcat.2005.07.003.
[30] P. Sot, Doctoral Thesis, ETH Zurich 26291, Zurich, **2019**, https://doi.org/10.3929/ethz-b-000374827.
[31] S. R. Docherty, D. P. Estes, C. Copéret, *Helv. Chim. Acta* **2018**, 101, e1700298, https://doi.org/10.1002/hlca.201700298.