Symposium
Catalysis Science – Quo Vadis?

TUM Catalysis Resarch Center (CRC)
Japan Science and Technology Agency (JST)

Online Webinar
July 27 and 28, 2020

Dear Colleagues,

We wish to thank you for participating to a cutting-edge, distinguished International Symposium *Catalysis Science – Quo Vadis?*, which is aiming to connect emerging leaders in Catalysis Science from Japan with a matching selection of early and mid-career scientists from Europe.

Since 2015 Japan Science and Technology Agency (JST) has started a research program in the framework of JST-PRESTO and JST-CREST, entitled *Science and Creation of Innovative Catalysts*, aiming at cultivating frontier researches of catalysts and developing a novel way for efficient conversion of natural carbon resources to useful chemicals or energy. To address this challenging topic, JST selected promising scientists and supports researches on design of novel catalyst materials, theoretical modelling of catalytic materials and processes, and development of advanced measurement methods.

As you all know, and for obvious reasons, we are very sad that we cannot meet in a real, physical meeting, as we intented it to take place in Garching at the TUM Catalysis Research Center. Nevertheless, in the past four months, we have all learned to deal with this situation on many levels and to find unconventional ways to communicate with each other. With this being said, the natural alternative for us was not to cancel the meeting, but to make this symposium happen online.

The Symposium will take place on two days – July 27 and 28, 2020 – as an online webinar of two hours on each day. Being aware of the pitfalls of such events, we have thought of an innovative and tongue-in-cheek way to provide you with a chance to get to meet each other. For this, the core idea of the Symposium is to form teams of two from each Japan and Europe and to cross-present each other’s research in a flash talk in a total of 7-8 minutes. You will find the team composition on the following two pages. We encourage you to contact your team partners and to exchange and discuss with them a nice way to highlight each other’s work and scientific contributions.

Instructions on how to log in to the online meeting via a link to a Microsoft Teams session are provided separately via e-mail. It is not necessary to download any apps for this.

We hope that the Symposium will provide opportunities not only to discuss recent research topics in the field and hopefully, but also to stimulate future collaborations among young researchers at an international level, with the hope that in 2021, we can still accomplish to have a classic meeting in person, hosted by TUM CRC.

We wish you fruitful and entertaining two days of *Catalysis Science – Quo Vadis*!

Yours,

Hiroshi KITAGAWA & Roland A. FISCHER

Time Table of the Symposium – Day 1

Monday, July 27th	
16:00 pm JST 9:00 am CET	*Introduction to the Symposium & Keynote Talk* Hiroshi KITAGAWA and Roland A. FISCHER
16:10 9:10	*Tandem Presenation 1* Yutaka HITOMI and Ulf-Peter APFEL
16:20 9:20	*Tandem Presenation 2* Corinna R. HESS and Takuya KURAHASHI
16:30 9:30	*Tandem Presenation 3* Koji OOHORA and Stephan C. HAMMER
16:40 9:40	*Tandem Presenation 4* Rosa ARRIGO and Takanori KOITAYA
16:50 9:50	*Tandem Presenation 5* Kazuhiro TAKANABE and Aliaksandr S. BANDARENKA
17:00 10:00	*Tandem Presenation 6* Jennifer STRUNK and Keisuke TAKAHASHI
17:10 10:10	*Tandem Presenation 7* Sandra LUBER and Takahiro MATSUMOTO
17:20 10:20	*Tandem Presenation 8* Jun TAKAYA and Harun TÜYSÜZ
17:30 10:30	*Tandem Presenation 9* Juliane SIMMCHEN and Hiroaki KOTANI
17:40 10:40	*Tandem Presenation 10* Maricruz SANCHEZ-SANCHEZ and Shuhei OGO

Time Table of the Symposium – Day 2

Tuesday, July 28th

16:00 pm JST 9:00 am CET	*Tandem Presenation 11* Emma K. GIBSON and Søren KEGNÆS and Ken MOTOKURA
16:15 9:15	*Tandem Presenation 12* Yasuyuki YAMADA and Andrew J. LOGSDAIL
16:25 9:25	*Tandem Presenation 13* Ayako HASHIMOTO and Thomas LUNKENBEIN
16:35 9:35	*Tandem Presenation 14* Yuji KIKUKAWA and Markus ROSE
16:45 9:45	*Tandem Presenation 15* Clotilde S. CUCINOTTA and Atsushi ISHIKAWA
17:00 10:00	*Tandem Presenation 16* Ryo NOUCHI and Christopher S. KLEY
17:10 10:10	*Tandem Presenation 17* Lauren N. TAKAHASHI and Florian MEIRER
17:20 10:20	*Tandem Presenation 18* Barbara A. J. LECHNER and Masazumi TAMURA
17:30 10:30	*Tandem Presenation 19* Dana D. MEDINA and Atushi URAKAWA
17:40 10:40	*Closing Remarks* Hiroshi KITAGAWA and Roland A. FISCHER

Hiroshi KITAGAWA, Prof. Dr., was born in December 1961 in Osaka. He finished his Ph.D. at Kyoto University in 1991 under the supervision of of Prof. Gunji Saito. After working as an Assistant Professor at the Institute for Molecular Science (IMS) and Japan Advanced Institute of Science and Technology (JAIST), he was appointed as an Associate Professor at the University of Tsukuba in 2000. He became a Professor of Chemistry at Kyushu University in 2003 and moved to Kyoto University as a Professor in 2009. He is now Vice Provost and Deputy Executive-Vice President for Research at Kyoto University. He is also engaged at JST as a Research Director of ACCEL and is a Director of the network-type research institution Science and Creation of Innovative Catalysts, PRESTO. He is interested in cooperative quantum properties that protons and electrons show in solid materials, such as ferromagnetism and superconductivity, as well as hydrogen storage, super-protonic conductivity and the photolysis of water. This focus covers a wide range of materials, from organic to inorganic matter, such as transition metal complexes, metal nanoparticles, coordination polymers and mixed-valence compounds. He has published more than 350 original research papers dealing with solid-state chemistry, coordination chemistry, nanoscience, low-dimensional electron systems, and molecular-based conductors.

Webpage of the Kitagawa research team

Roland A. Fischer, Prof. Dr., Dr. h.c., holds the Chair of Inorganic and Metal-Organic Chemistry at the Technical University Munich (TUM) and is Director of the TUM Catalysis Research Center (CRC). Previously he was Professor of Inorganic Chemistry at Ruhr-University Bochum (1997-2015) and Heidelberg University (1996-1997). He has been elected Vice President of the Deutsche Forschungsgemeinschaft (DFG) in 2016 and member of the Governing Board of Science Europe. He is member of the Award Selection Committee of the Alexander von Humboldt Foundation, member of the Scientific Advisory Board of the German Chemical Industry Fund and is elected member of the European Academy of Sciences. His research interest focuses on functional molecular materials for advanced applications in energy conversion, catalysis, gas storage and separation, chemical sensing, photonics and microelectronics. Currently, he is steering the DFG Priority Program 1928 “Coordination Networks: Building Blocks for Functional Systems”. Recent accomplishments are highlighted at TUM press releases, such as: “Superatoms as Catalysts”, “The Gods of Small Things” and “Activity of fuel cell catalysts doubled

Webpage of the Fischer research team

Participants from Japan: CVs and Abstracts

Participants from Europe: CVs and Abstracts

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Short Biography. Ayako Hashimoto studies at In-situ Characterization Technique Development Group, National Institute for Materials Science as a senior researcher and conducts some students as an associate professor of University of Tsukuba. She recived Birks Award from Microbeam Analysis Society in 2010, Best Paper Award in Kenbikyo from the Japanese Society of Microscopy in 2010 for development of scanning confocal electron microscopy as a new three dimentional imaging.
Her recent research interest is on development of new observation techniques and systems for transmission electron microscopy (TEM). These days, she focuses on in-situ TEM observation of energy and environmental materials such as solar cells, fuel cells and catalytic materials. She developed some specimen holder systems to observe these materials under light irradiation, high temperature in gas phase. The goal is to contribute to elucidate the structures of the materials under their actual working conditions and the mechanisms of their reaction and degradation.

Five Selected Publications of Relevance to Catalysis Science.

- Topologically Immobilized Catalysis Centre for Long-term Stable Carbon Dioxide Reforming of Methane, S. Shoji, X. Peng, T. Imai, P. S. M. Kumar, K. Higuchi, Y. Yamamoto, T. Tokunaga, S. Arai, S. Ueda, A. Hashimoto, N. Tsubaki, M. Miyauchi, T. Fujita, H. Abe, *Chem. Sci.* **2019**, *10*, 3701–3705.
- Two-Dimensional CuO Inside the Supportive Bilayer Graphene Matrix, D. Kvashnin, A. Kvashnin, E. Kano, A. Hashimoto, M. Takeguchi, H. Naramoto, S. Sakai, S. Pavel, *J. Phys. Chem. C*, **2019**, *123*, 17459–17465.
- Mesoporous Rh Emerging from Nanophase-Separated Rh-Y Alloy, A. S. B. M. Najib, X. Peng, A. Hashimoto, S. Shoji, T. Iida, Y. Bai, H. Abe, *Chem. Asian J.* **2019**, *14*, 2802–2805.
- Reversible Low-Temperature Redox Activity and Selective Oxidation Catalysis Derived from the Concerted Activation of Multiple Metal Species on Cr and Rh-incorporated Ceria Catalysts, S. Ikemoto, X. Huang, S. Muratsugu, S. Nagase, T. Koitaya, H. Matsui, G. Yokota, T. Sudoh, A. Hashimoto, Y. Tan, S. Yamamoto, J. Tang, I. Matsuda, J. Yoshinobu, T. Yokoyama, S. Kusaka, R. Matsuda, M. Tada, *Phys. Chem. Chem. Phys.* **2019**, *21*, 20868–20877.
- Development of Gas Environmental Heating Specimen Holder System, A. Hashimoto, H. Akimoto, M. Takeguchi, *Advanced Microscopy and Theoretical Calculation Letters*, **2019**, *6*, 108–109.

Recent Press Releases

“Topologically immobilized catalysis for methane conversion”.

DEVELOPMENT OF GAS ENVIRONMENTAL HEATING SPECIMEN HOLDER SYSTEM FOR IN-SITU OBSERVATION OF CATALYTIC MATERIALS

Ayako Hashimoto,[1,2,3] Xiaobo Peng,[1] Hideki Abe[1,4]

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Transmission electron microscopy (TEM) is a usuful method to observe and analyze materials with atomic scale. However, TEM observation is generaly performed in vacuum, which is very different from actual uses of materials. Therefore, in-situ TEM obseravtions under actual conditions have been designed and developed for long time. For example, catalytic nanomaterials were recentry observed in gas phases at high temperature by various in-situ TEM techiniques. We recentry developed a gas environmental heating specimen holder system for in-situ TEM observation of catalytic materials.[1] In this study, we observed Ni-based catalysts for dry reforming reaction by using the holder system to study its actual structures under the reaction condition.

Figure 1 shows the holder system installed to an aberration-corrected TEM (JEM-ARM200F, JEOL, Japan). The specimen holder contains a gas nozzle, pressure gauge, heater chip and electrical wires. A specimen is mounted on the heater chip (E-chip, Protochips, USA) and sandwiched between two orifice plates. Gas is introduced from a gas tank to the specimen space and evaluated thrugh the orificces by microscope pumps. The presure of the speciman space can be kept at about 1 Pa due to differential pumping effect. We observed nanophase-separated Ni#YOx catalyist in a mixed gas of CH$_4$ and CO$_2$ at different temperature, whcih was recentry fabricated from NiY alloy to improve its efficency of dry reforming reaction.[2] We found nanophase-separated region was stable even under the reaction condition, while Ni nanoparticles moved on the catalyst. Furthermore, we analyzed the elements and chemical bonding states of the catalyst by electron energy loss spectroscopy. We could detect change in oxidation states of Ni phases in Ni#YOx and Ni nanoparticles during reaction.

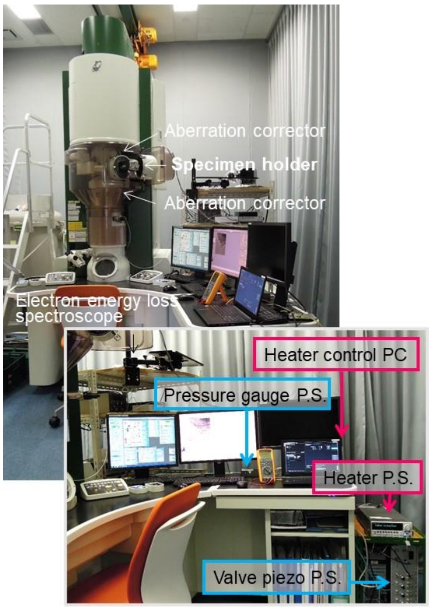

Figure 1. Gas environmental heating specimen holder system installed to a microscope.

Acknowledgements. This work was partially supported by PREST(No.17939123) and CREST(No.JPMJCR15P1), JST, KAKENHI, JSPS(No. 25390035) and Nanotechnology Platform project, MEXT.

References

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[2] Shoji, S.; Peng, X.; Imai, T.; Kumar, P. S. M.; Higuchi, K.; Yamamoto, Y.; Tokunaga, T.; Arai, S.; Ueda, S.; Hashimoto, A.; Tsubaki, N.; Miyauchi, M.; Fujita, T.; Abe, H., *Chem. Sci.* **2019**, *10*, 3701–3705.

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Short Biography. Yutaka Hitomi studied synthetic organic chemistry and coordination chemistry at Kyoto University (Ph.D. 1999) in the labs of late Prof. Yoshihiko Itoh, Prof. Hisanobu Ogoshi and later Prof. Susumu Kitagawa. Then, He spent two years as a postdoctoral fellow with Prof. Thomas V. O'Halloran to learn chemical biology. In 2001, he joined the catalyst lab of Prof. Takuzo Funabiki and Prof. Tsunehiro Tanaka at Kyoto University as an assistant professor. In 2008, he moved to his current university. His research interest is the development of useful oxidation catalysts and molecular tools based on bioinspired metal complexes.

Five Selected Publications of Relevance to Catalysis Science.

- Oxidative DNA Cleavage, Formation of *μ*-1,1-Hydroperoxo Species, and Cytotoxicity of Dicopper(II) Complex Supported by a *p*-Cresol-Derived Amide-Tether Ligand*,* Y. Kadoya, K. Fukui, M. Hata, R. Miyano, Y. Hitomi, S. Yanagisawa, M. Kubo, M. Kodera, *Inorg. Chem.* **2019**, *58*, 14294–14298.
- Acceleration of Hydrolytic DNA Cleavage by Dicopper(II) Complexes with *p*-Cresol-Derived Dinucleating Ligands at Slightly Acidic pH and the Mechanistic Insights*,* M. Kodera, Y. Kadoya, K. Aso, K. Fukui, A. Nomura, Y. Hitomi, H. Kitagishi, *Bull. Chem. Soc. Jpn.* **2019**, *92*, 739–747.
- Green fabrication of nanoporous $BiVO_4$ films on ITO substrates for photoelectrochemical water-oxidation*,* S. Okunaka, Y. Hitomi, H. Tokudome, *RSC Adv.* **2018**, 8, 31575–31580.
- DNA Cleavage through Reductive Dioxygen Activation by Iron-Bleomycin Mimics with Carboxamido Ligation: Correlation between DNA Cleavage Efficacy and Redox Potential, A. Nomura, Y. Iwamoto, K. Arakawa, A. Kashida, M. Kodera, Y. Hitomi, *Chem. Lett.*, **2017**, *46*, 1109–1111.
- Specific Enhancement of Catalytic Activity by a Dicopper Core: Selective Hydroxylation of Benzene to Phenol with Hydrogen Peroxide**,** T. Tsuji, A. A. Zapoutra, Y. Hitomi, K. Mieda, T. Ogura, Y. Shiota, K. Yoshizawa, H. Sato, M. Kodera, *Angew. Chem. Int. Ed.* **2017**, *56*, 7779–7782.

SELECTIVE OXIDATION CATALYSTS BASED ON BIO-INSPIRED NONHEME IRON COMPLEXES

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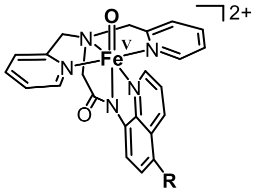
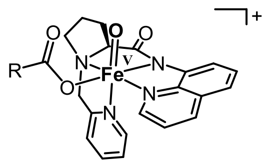
Recent technologies developed in the field of bioinorganic chemistry allow to trap and characterize metal-dioxygen adducts and even metal-oxo species of metalloenzymes that are capable of selectively functionalizing non-activated alkane sp^3 C−H bonds. What's more, the accumulated knowledge in this filed now enables researchers to develop functional model complexes that re-produce biologically relevant metal-oxo species in flasks to analyze their structure and reactivity more closely. In fact, some of functional model complexes can catalytically oxidize inert alkane sp^3 C−H bonds with hydrogen peroxide as an oxidant and with moderate to high regioselectivity. The reaction is potentially useful with synthetic purpose; however, their further application in organic synthesis is hampered by their low turnover number. As our initial contribution to this area, we recently developed an iron(III) complex supported by an anionic pentadentate carboxylamido ligand, $\mathrm{Fe^{III}dpaq^H}$ (H-$\mathrm{dpaq^H}$ = 2-[bis(pyridin-2-ylmethyl)amino]-*N*-(quinolin-8-yl)acetamide), which promotes regioselective hydroxylation with hydrogen peroxide as an oxidant, with high regioselectivity.[1] Cold-spray ionization mass measurements revealed the formation of oxoiron(V) species in the reaction between $\mathrm{Fe^{III}dpaq^H}$ and hydrogen peroxide. The carboxylamido coordination should stabilize the high valent oxoiron species. Further mechanism study revealed that the carboxylamido coordination itself is not enough to accomplish the O–O bond heterolysis, and that a proton facilitates O–O bond heterolysis in collaboration with the carboxylamido ligation. Therefore, it can be noted that the nonheme $\mathrm{Fe^{III}dpaq^H}$ can perform the heme-enzyme-type chemistry based on the so-called "push–pull" concept. Our next objective was to develop more selective and robust catalysts on the basis of this finding. To this end, we prepared FeIIIdpaq derivatives that have a series of substituent groups at the 5-position of the quinoline moiety in the parent ligand $\mathrm{dpaq^H}$ ($\mathrm{dpaq^R}$, R = OMe, H, Cl, or NO_2). The series of substituents was expected to alter the electronic structure of the iron–oxo group systematically, without changing the steric hindrance around the group.[2] We have identified a systematic ligand effect on the selectivity and TON for C–H bond hydroxylation catalyzed by mononuclear iron(III)-carboxylamido complexes; as the substituent group became more electron-withdrawing, both the selectivity and the turnover number increased. Recently we developed a new iron(III)-caroxylamido complex, which shows higher selectivity than the $\mathrm{Fe^{III}dpaq^R}$ series, and enhance its selectivity and TON in the presence of acetic acid. We currently speculate that the enhancement is in conjunction with the reversible formation of acetate(oxo)iron(V) species and acrylperoxoiron(III) species.



Fe(dpaq^R)



Fe(propaq)

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[2] Hitomi, Y.; Arakawa, K.; Kodera, M. *Chem. Eur. J.* **2013,** *19*, 14697−14701.

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Short Biography. Atsushi Ishikawa received my Ph.D. at Department of Molecular Engineering of Kyoto University in 2011, under the supervision of Prof. Shigeyoshi Sakaki. After that, He worked as post-doc researcher at Quantum Chemistry Research Institute (2011-2013, Prof. Hiroshi Nakatsuji), Waseda University (2013-2017, Prof. Hiromi Nakai), and NIMS (2017, Dr. Yoshitaka Tateyama). In 2017, He joined the current PRESTO project as the JST PRESTO researcher. Since 2019 he is working as a senior researcher at NIMS.

His research interest is theoretical simulation of homogeneous and heterogeneous catalytic reactions. His main target is that multi-scale simulation technique for catalyst; sequential combination of (i) atomic/molecular level calculations such as quantum chemistry or first-principle, (ii) microkinetic simulations for predicting the reaction rate, and (iii) chemical engineering simulation for the chemical reactor. He is also interested in combination of the machine-learning technique and atomic/molecular level simulations, and have reported some application on catalyst/battery system.

Five Selected Publications of Relevance to Catalysis Science.

- What is the active site for the oxidative coupling of methane catalyzed by MgO? A metadynamics-biased ab initio molecular dynamics study, A. Ishikawa, Y. Tateyama, *J. Phys. Chem. C* **2020**, *124*, 6054−6062.
- Machine learning prediction of coordination energies for alkali group elements in battery electrolyte solvents, A. Ishikawa, K. Sodeyama, Y. Igarashi, T. Nakayama, Y. Tateyama, M. Okada, *Phys. Chem. Chem. Phys.* **2019**, *21*, 26399−26405.
- Reaction energy benchmarks of hydrocarbon combustion by gaussian basis and plane wave basis approaches, A. Ishikawa and Y. Tateyama, *J. Comp. Chem.* **2019**, *40*, 1866−1873.
- First-principles microkinetic analysis of NO + CO reactions on Rh(111) surface toward understanding NOx reduction pathways, A. Ishikawa and Y. Tateyama, *J. Phys. Chem. C* **2018**, *122*, 17378−17388.
- Catalytic performance of Ru, Os, and Rh nanoparticles for ammonia synthesis: A density functional theory analysis, A. Ishikawa, T. Doi, H. Nakai, *J. Catal.* **2018**, *357*, 213−222.

DENSITY FUNCTIONAL THEORY-BASED MICROKINETIC ANALYSIS OF THE OXIDATIVE COUPLING OF METHANE

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The oxidative coupling of methane (OCM) is a major catalytic reaction in natural gas utilization. MgO or Li-doped MgO has long been examined as a representative heterogeneous OCM catalysis,[1-2] and in this research we investigated this system with first-principle density functional theory (DFT) combined with microkinetic and reactor simulations. First of all, we performed the metadynamics-biased *ab initio* molecular dynamics (AIMD) to identify the active site for the C-H dissociation on the pristine and Li-doped MgO surfaces.[3] The calculated free energy surfaces reveal that the C-H dissociation favorablly occurs on Li-doped surface, MgO(110), and stepped MgO but not on the pristine MgO(100) (Figure 1). Then, we performed the DFT-based microkinetic study. Here, 164 elementary reactions including gas-phase and surface reactions were considered, and their thermodynamic and kinetic parameters were determined by DFT calculations. The stepped site at MgO was considered as the active site, based on the AIMD study. Our calculated CH_4 conversion and C_2 selectivity was consistent with experimental results, thus showing these can be calculated from atomic simulations without using any kinetic experimental parameters.

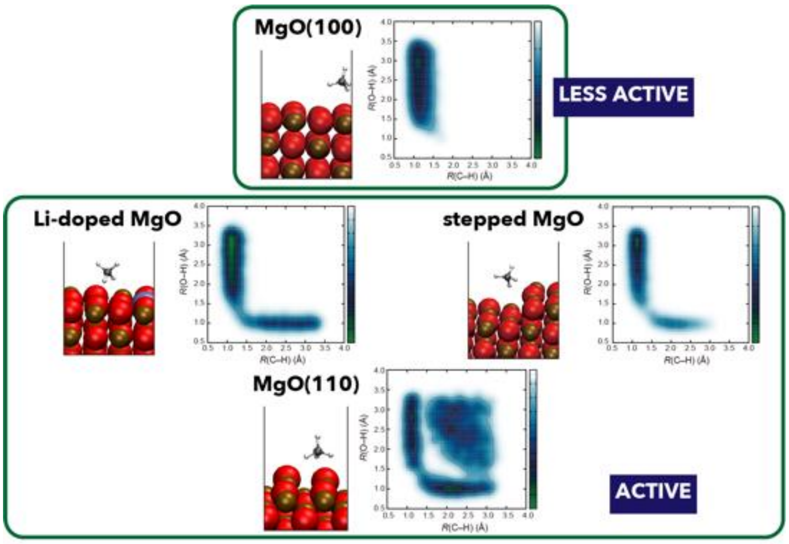

Figure 1. The snapshopt surface structure and the free energy surfaces calculated with the metadynamics-biased AIMD simulations. The free energy surface shows the C-H dissociation is hardly occurs on the pristine MgO(100) surface but promoted on the Li-doped MgO, stepped MgO, and MgO(110) surfaces.

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Short Biography. Yuji Kikukawa is the associated professor at Kanazawa University. I received my M.S. (2008) and Ph.D. (2011) degrees from the University of Tokyo under the direction of Prof. Noritaka Mizuno. I continuously worked at Mizuno's lab as a postdoctoral research fellow. I moved to Kanazawa University as an assistant professor in 2014, and then was promoted to a associat professor in 2018. He received The Young Scientists' Priz of The Commendation for Science and Technology by the MEXT (2019). His research interests include synthesis and development of functional metal-oxide cluster molecules, called polyoxometalates (POMs), for advanced applications in molecular container, anion receptor, gas storage, and catalyst. Tungsten-based POMs possess the rigid structures to be utilized as inorganic ligands. By insertion of metal or metal-oxide cores into POM structures, highly functionalized catalytic or optical materials were obtained. Vanadium-based POMs show relatively flexible structures. By controlling the molecular structure, he developed the utility of POMs. Recently, he focused on the bowl-type POM with 4.4 Å cavity entrance, which prefers to stabilize anionic moiety at the centre of the structure, even if the POM possesses large anion charge. Vanadium oxide is known well as efficient oxidation catalysts. Currently, he is developing the oxidation catalyst of the vanadium-based POMs with H_2O_2 and O_2 as an oxidant.

Five Selected Publications of Relevance to Catalysis Science.

- Induced-Fitting and Polarization of Bromine Molecule in an Electrophilic Inorganic Molecular Cavity and Its Bromination Reactivity, Y. Kikukawa, K. Seto, D. Watanabe, H. Kitajima, M. Katayama, S. Yamashita, Y. Inada, Y. Hayashi, *Angew. Chem. Int. Ed. under revision.*
- Redox active mixed-valence hexamanganese double-cubane complexes supported by tetravanadates, T. Maruyama, A. Namekata, H. Sakiyama, Y. Kikukawa, Y. Hayashi, *New J. Chem*. **2019**, *43*, 17703–17710.
- Evaluation of Chemo- and Shape-Selective Association of a Bowl-Type Dodecavanadate Cage with an Electron-Rich Group, Y. Kikukawa, H. Kitajima, Y. Hayashi, *Dalton Trans*. **2019**, *48*, 7138–7143.
- Solid State Umbrella-type Inversion of a VO_5 Square Pyramidal Unit in a Bowl-type Dodecavanadate Induced by Insertion and Elimination of a Guest Molecule, Y. Kikukawa, K. Seto, S. Uchida, S. Kuwajima, Y. Hayashi, *Angew. Chem. Int. Ed.* **2018**, *57*, 16051–16055.
- Synthesis and structural characterization of tube type tetradecavanadates, S. Kuwajima, Y. Arai, H. Kitajima, Y. Kikukawa, Y. Hayashi, *Acta Crystallogr*. *C* **2018**, *C74*, 1295–1299.

DETECTION OF POLARIZED BROMINE IN DODECAVANADATE AND ITS REACTIVITY

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The production of an appropriate reaction field is essential for the development of alkane functionalization, which is difficult albeit one of the most important reactions to achieve. The direct conversion of alkane to bromoalkane is usually carried out by free radical processes. On the other hand, polarized bromination of methane is expected to be highly selective for monobromomethane. In this work, a half-spherical molecule of vanadium-oxide was utilized to prepare polarized bromine. Dodecavanadate, $[V_{12}O_{32}]^{4-}$ (**V12**) composed of twelve VO_5 square pyramids, possesses a 4.4 Å cavity entrance, and the cavity shows unique electrophilicity.[1-3] The interior of **V12** is relatively cationic owing to high-valent and coordinatively unsaturated vanadium atoms to stabilize an electron-rich group or anion, while the cavity entrance is relatively anionic owing to the eight oxygen atoms. Due to the high polarizability, Br_2 was inserted into **V12** to form $[V_{12}O_{32}(Br_2)]^{4-}$ (**V12(Br2)**, Figure 1). The inserted Br_2 was polarized, as detected with a peak at 185 cm^{-1} by IR spectroscopy. The elongation of Br−Br distance of 2.33 Å is estimated by the extended X-ray absorption fine structure spectroscopy. The reaction of **V12(Br2)** and toluene yielded bromination of toluene at the ring, showing the electrophilicity of the inserted Br_2 molecule. Bromination of pentane with **V12(Br2)** showed high selectivity for 3-bromopentane (64%) among the monobromopentane products and preferred *threo* isomer among 2,3-dibromopenane. **V12(Br2)** was also reacted with butane and propane. The unique inorganic cavity traps Br_2 leading the polarization of the diatomic molecule. Due to its new reaction field, the trapped Br_2 shows selective functionalization of alkanes.

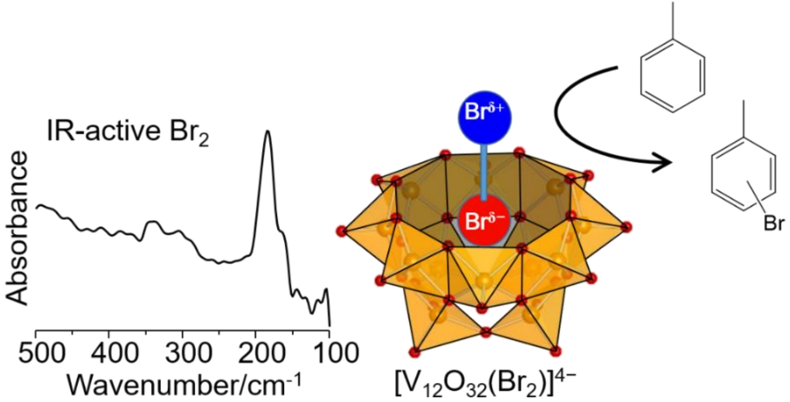

Figure 1. IR spectrum and structure of polarized Br_2 in **V12** and electrophilic bromination.

Acknowledgements. This work was supported by JST PRESTO Grant

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Short Biography. Takanori Koitaya was received his Ph. D. at The University of Tokyo (UT) in 2013. He is now an assistant professor in the research group of Professor Toshihiko Yokoyama at the Institute for Molecular Science. His research interest is in understanding reaction mechanism of heterogeneous catalysis by means of operando spectroscopic methods, such as near ambient-pressure photoelectron spectroscopy, and polarization-modulation infrared reflection absorption spectroscopy. Currently, he focuses on the reaction of inert C1 molecules, such as methane and carbon dioxide, on metallic model catalysts.

Five Selected Publications of Relevance to Catalysis Science.

- CO_2 Activation and Reaction on Zn-Deposited Cu Surfaces Studied by Ambient-Pressure X-ray Photoelectron Spectroscopy, T. Koitaya, S. Yamamoto, Y. Shiozawa, Y. Yoshikura, M. Hasegawa, J. Tang, K. Takeuchi, K. Mukai, S. Yoshimoto, I. Matsuda, J. Yoshinobu, *ACS Catal.* **2019**, *9*, 4539–4550.
- Reversible low-temperature redox activity and selective oxidation catalysis derived from the concerted activation of multiple metal species on Cr and Rh-incorporated ceria catalysts, S. Ikemoto, X. Huang, S. Muratsugu, S. Nagase, T. Koitaya, H. Matsui, G.I. Yokota, T. Sudoh, A. Hashimoto, Y. Tan, S. Yamamoto, J. Tang, I. Matsuda, J. Yoshinobu, T. Yokoyama, S. Kusaka, R. Matsuda, M. Tada, *Phys. Chem. Chem. Phys.* **2019**, *21*, 20868–20877.
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THE OXIDATIVE CONVERSION OF METHANE ON PALLADIUM SURFACES STUDIED BY SOFT X-RAY AMBIENT PRESSURE XPS

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Characterization of heterogeneous catalysts *under operation condition* is essential for understanding reaction mechanism and nature of active sites. Various *operando* methods for observation of working catalysts have been developed to investigate chemistry occurring on the surface of the catalyst. We have investigated reactions of inert molecules, such as carbon dioxide and methane, using an ambient-pressure XPS system at SPring-8 soft X-ray beam line BL07LSU [1, 2]. The XPS measurements can be currently performed in the presence of reactant gases up to 2000 Pa using synchrotron radiation or a conventional X-ray source. In the gas environment, the sample can be heated up to around 900 K to investigate thermal reaction on the surface of catalysts, and cooled to 170 K to investigate equilibrium physisorption of inert molecules under the near ambient-pressure condition.

Here, I will report our recent AP-XPS results on the methane conversion reaction on single crystal Pd surfaces. Catalytic conversion of methane molecules into more valuable chemicals is a challenging topic. In order to investigate the surface reaction of methane on the surface, the operando spectroscopic measurements in the presence of feed gases is quite important because of very small reaction probability of methane on metal surfaces. The reactivity of the methane oxidation on the Pd model catalysts depends significantly on the gas-phase composition and pressure. The reactive site does not inherently exist on Pd surface, but is created by redox processes in the presence of oxygen and methane gases. A part of methane was converted into ethane on the activated surface at about 600 K through the oxidative coupling reaction. The observed oxidative coupling of methane (OCM) proceeds at much lower temperature compared to reported OCM catalysts.

Acknowledgements. This work was financially supported by JST ACT-C (Grant No. JPMJCR12YU), JST PRESTO (No. JPMJPR17S3), and the Grant-in-Aid for Young Scientists (Nos. 16H06027 and 17K14432) from JSPS.

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Short Biography. Hiroaki Kotani received his PhD degree in Graduate School of Engineering from Osaka University in 2007 under the supervision of Professor Shunichi Fukuzumi. After working as a JSPS fellow at Tokyo Institute of Technology, he joined Fukuzumi's group as a specially appointed researcher, again. In 2011, he moved to the University of Tsukuba to join the group of Professor Takahiko Kojima as an assistant professor. His research interests include the development of functional transition-metal complexes and the clarification of their reaction mechanisms based on the kinetic analysis.

Five Selected Publications of Relevance to Catalysis Science.

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- A Mechanistic Dichotomy in Two-Electron Reduction of Dioxygen Catalyzed by *N*,*N*'-Dimethylated Porphyrin Isomers, Suzuki, W.; Kotani, H.; Ishizuka, T.; Kojima, T., *Chem. Eur. J.,* DOI: 10.1002/chem.202000942.

THERMAL AND PHOTOCATALYTIC REACTIONS BY SADDLE-DISTORTED PORPHYRINS

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Among organic photocatalysts, porphyrins are good candidates owing to their optical and redox properties based on the 18π aromatic macrocyclic structure. We have focused on a diprotonated saddle-distorted dodecaphenylporphyrin (**H_4DPP^{2+}**), which can be applied as a photoredox catalyst to photocatalytic oxidation of substrates based on the photodynamics and electron-transfer (ET) properties of **H_4DPP^{2+}**. In this talk, I would like to present our recent progress[1-4] in thermal and photocatalytic reactions using **H_4DPP^{2+}** as a photocatalyst.

We successfully achieved the interconversion between O_2 and H_2O_2 using a redox couple of an *N*21,*N*23-dimethylated saddle-distorted porphyrin (***syn*-Me_2P**) and the corresponding isophlorin derivative (***syn*-Me_2Iph**).[2] While ***syn*-Me_2Iph** reacted with O_2 to afford H_2O_2 selectively, ***syn*-Me_2P** could also react with H_2O_2 to afford ***syn*-Me_2Iph** and O_2, achieving the isophlorin-O_2/porphyrin-H_2O_2 interconversion. On the basis of kinetic analysis on the reaction of ***syn*-Me_2P** with H_2O_2, the formation of a two-point hydrogen bonded adduct of ***syn*-Me_2P** with H_2O_2 was proposed as a reaction intermediate in the interconversion, which was also elucidated by DFT calculations.

Under visible-light irradiation, efficient O_2 reduction reactions proceeded to produce H_2O_2 by **H_4DPP^{2+}** as a photocatalyst.[3] The quantum yield (12%), the turnover number (3000 for 6 h), and the turnover frequency (500 h^{-1}) are achieved in the photocatalytic system based on a free-base porphyrin for the first time. The photocatalytic reaction mechanism has been revealed by ns-laser flash photolysis and the kinetic analysis.

Highly efficient near-infrared (NIR) light-driven H_2 evolution has been developed by a combination of **H_4DPP^{2+}** as a photosensitizer and platinum nanoparticles as a H_2-evolving catalyst.[4] The quantum yield of H_2 evolution at 710 nm was determined to be 17%, which is the highest value among photocatalytic H_2-evolution systems ever reported.

Acknowledgements. This work was supported by Grants-in-Aid from the Japan Society of Promotion of Science (JSPS) and CREST from Japan Science and Technology Agency (JST) (JPMJCR16P1).

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Short Biography. I recieved my B.S. (Prof. Yoshihiko Ito), M.S. (Prof. Hisanobu Ogoshi) and Ph. D. (Prof. Jun-ichi Yoshida) from Kyoto University, where I studied molecular recognition and regioselective functionalization of carbohydrates by synthetic host molecules. I then moved to Nagoya University for postdoctoral work with Prof. Minoru Isobe, where I studied metalloenzymes isolated from silkworm diapause eggs. Then, I joined Institute for Molecular Science as an assistant professor. Two years ago I joined University of Nagasaki, Siebold as an associate professor and was then promoted to professor this April. My research interests include a design and synthesis of new molecular catalysts, and the development of a new fine-bubble reaction system suitable for molecular catalysts.

Five Selected Publications of Relevance to Catalysis Science.

- Kurahashi, T.; *Inorg. Chem.* **2018**, *57*, 1066–1078.
- Kurahashi, T.; *Inorg. Chem.* **2015**, *54,* 8356–8366.
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DIOXYGEN ACTIVATION BY MN(III) COMPLEXES UNDER ORGANIC/AQUEOUS BIPHASIC CONDITIONS

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Atmospheric dioxygen is an ideal oxidant, but the use of dioxygen for oxidation reactions is still limited. One of the problems is that dioxygen activation for use as an oxidant usually required a costly sacrificial reductant such as NADPH in the case of biological oxidations by heme enzymes. The present study shows that a manganese(III) complex with a Schiff base ligand is converted to di-μ-oxo manganese(IV) complex under biphasic conditions using aqueous alkaline solution.[1] According to the isotope labeling studies, the resulting di-μ-oxo manganese(IV) complex contains oxygen atoms from both dioxygen and water (Figure 1). A low-temperature homogeneous reactions between the manganese(III) complex with OH^- generates a distinct species, which was thoroughly investigated various methods including ESR (electron spin resonance), ^2H NMR, and resonance Raman spectroscopy. The data indicate the formation of an anionic $[Mn(III)(OH)_2]$– species. But the CV (cyclic voltammetry) measurements show that the reducing ability is not enough to activate dioxygen.[2] Indeed, the di-μ-oxo manganese(IV) complex was not detected under homogeneous reactions, indicating that organic/aqueous biphasic conditions are important in this system. To apply the present findings to catalytic reactions, I am now investigating a new reaction system using dioxygen fine bubbles that mix organic and aqueous phase to emulsion solution under moderate dioxygen pressure. My expectation is to expand the interface between organic, aqueous and gas phase for effective aerobic oxidation using a metal complex as a catalyst.

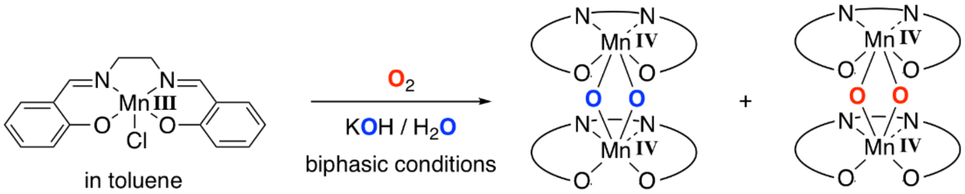

Figure 1. Dioxygen activation under organic/aqueous biphasic conditions.

Acknowledgements. This work was supported by JST, PRESTO (Grant Number JP17937445) and JSPS KAKENHI (Grant Numbers 23550086 and 15K05462).

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Short Biography. Takahiro Matsumoto received his PhD at Kanazawa University in 2007. After a post-doctoral fellow from 2007 at Kyushu University, He was made Assistant Professor in 2009, and Associate Professor in 2014 at Kyushu University. He received young scientists' awards; the Young Scientists' Prize, Japan Society of Coordination Chemistry (2016) and the Young Scientists' Prize, Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology (2018). His research interest focuses on homogeneous catalysts for activation of small molecules such as dihydrogen, dioxygen, and recently, in particular, methane. Homogeneous molecular catalysts, that have been made as a model for oxygen-tolerant [NiFe]hydrogenases, are capable of oxidizing dihydrogen gas and reducing dioxygen gas to water. The oxygen-tolerant [NiFe]hydrogenases are known for acting as hydrogenase and oxidase. We could synthesize such enzyme mimics, and then applied them to anode and cathode catalysts of hydrogen fuel cell. In recent years, he particularly focuses on methane activation based on homogeneous catalysts by means of light energy. The exited state is able to activate methane to methanol, wherein the reaction mechanism is supported by experimental results and quantum chemical calculations.

Five Selected Publications of Relevance to Catalysis Science.

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- Multifunctional Catalysts for H_2O_2-resistant Hydrogen Fuel Cells, Y. Mori, T. Ando, T. Matsumoto, T. Yatabe, M. Kikkawa, K.-S. Yoon, S. Ogo, *Angew. Chem. Int. Ed.* **2018**, *57*, 15792−15796.
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- [NiFe]Hydrogenase from *Citrobacter* sp. S-77 Surpasses Platinum as an Electrode for H_2 Oxidation Reaction, T. Matsumoto, S. Eguchi, H. Nakai, T. Hibino, K.-S. Yoon, S. Ogo, *Angew. Chem. Int. Ed.* **2014**, *53*, 8895–8898.

Awards

2018	The Young Scientists' Prize, Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology, **Study of Hydrogen Fuel Cell using Molecular Catalyst as Electrode**
2016	The Young Scientists' Prize, Japan Society of Coordination Chemistry, **Molecular Fuel Cell -Dihydrogen and Dioxygen Activation Inspired by Hydrogenase-**

PHOTO-INDUCED AROMATIC C-H FUNCTIONALIZATION BY A TRANSITION METAL COMPLEX

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Photo-induced direct aromatic C-H functionalization has been achieved by means of an organometallic zirconium catalyst with dioxygen gas. The active species of peroxide-bridged zirconium complex is structurally-defined by X-ray analysis, which causing methoxylation of toluene via photo-driven electron transfer. Direct aromatic C-H functionalization is one of the most challenging themes in the field of organic and organometallic chemistry. To data, there have been a few reports of the direct aromatic functionalization,[1,2] however, the catalyst design is limited. Here, we report a new catalyst bearing organometallic $Zr_2(\mu\text{-}O)$ core for the direct functionalization (Figure a).

A dinuclear Zr_2^{IV} oxide complex $[Zr_2^{IV}(\eta^5\text{-}C_5H_5)_4(Cl)_2(\mu\text{-}O)]$ (**1**) was prepared by the literature method,[3] as characterized by X-ray analysis (Figure b). This complex **1** was irradiated by UV light in CH_3OH under O_2 to afford a Zr_2^{IV} peroxide complex $[Zr_2^{IV}(\eta^5\text{-}C_5H_5)_4(Cl)_2(\mu\text{-}O_2)]$ (**3**) (Figure c). This type of Zr^{IV} peroxide complex **3** is the first characterization. The peroxide ligand (O_2^{2-}) can be assigned by the O-O bond distance of 1.516(9) Å. Photo excitation of **3** caused methoxylation of toluene triggered by one-electron transfer from toluene to the excited state of **3**, resulting in the formation of negatively-charged toluene methoxide, which was oxidized by **4** to form toluene methoxide.

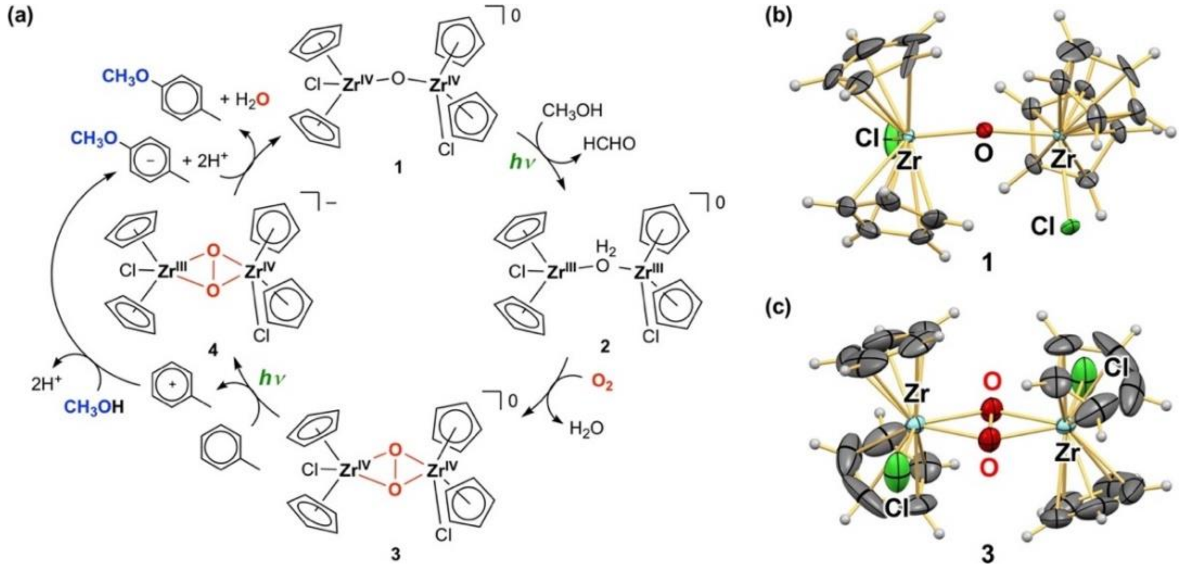

Figure. (a) A proposed mechanism of photo-induced toluene methoxylation by Zr complexes. (b) X-ray structure of **1**. (c) X-ray structure of **3**.

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Short Biography. Ken Motokura (WoS Researcher ID S-4499-2019) received his B.Sc. (2002), M.Sc. (2003), and Ph.D. (2006) degrees from Osaka University. Subsequently, he moved to the University of Tokyo as an Assistant Professor. In 2008, he joined the Tokyo Institute of Technology as an Associate Professor(Lecturer). In 2017, he was promoted to an Associate Professor. He has received a Research Grant Award from the UBE Foundation (2012), Presentation Award at the 111th Annual Meeting of the Catalysis Society of Japan (2013), Young Scholar Lecture Award of the Chemical Society of Japan (2014), Young Scientist Award of the Catalysis Society of Japan (2014), the Chemical Society of Japan Award for Young Chemists (2016), the Challenging Research Award, Tokyo Institute of Technology (2016), and the Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology, the Young Scientists' Prize (2019). He is member of JST PRESTO "Science and Creation of Innovative Catalysts". His research interests include precise designing of multiactive sites on a catalyst surface for efficient organic synthetic reactions including one-pot transformation, detailed characterization of active site environments using several spectroscopic techniques such as XAFS, solid-state NMR, and in-situ FT-IR, and design and development of novel metal complex and organocatalyst systems for CO_2 conversion reactions. His research target also includes selective activation of C-H bonds in simple alkanes for dehydrogenative coupling reactions, such as direct alkylation of benzene with alkanes.

Five Selected Publications of Relevance to Catalysis Science.

- A Resin-Supported Formate Catalyst for the Transformative Reduction of Carbon Dioxide with Hydrosilanes, R. A. Pramudita, Y. Manaka, K. Motokura**,** *Chem. Eur. J.* **2020**, in press.
- Direct Alkylation of Benzene at Low Temperature in the Liquid-Phase: Catalysis by Montmorillonites as Noble-Metal-Free Solid, M. Takabatake, M. Nambo, Y. Manaka, K. Motokura, *ChemPlusChem* **2020**, *85*, 450–453.
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- Formate-Catalyzed Selective Reduction of Carbon Dioxide to Formate Products Using Hydrosilanes, K. Motokura, C. Nakagawa, R. A. Pramudita, Y. Manaka, *ACS Sustainable Chem. Eng.* **2019**, *7*, 11056–11061.
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Recent Press Releases

"A metal-free, sustainable approach to CO_2 reduction", "A rhodium-based catalyst for making organosilicon using less precious metal", "Direct Alkylation of Benzene at Low Temperatures (ChemistryViews).

LAYERED SOLID ACID FOR ALKYLBENZENE PRODUCTION VIA ACTIVATION OF ALKANES

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Alkylbenzenes are widely used as raw materials for production of chemical compounds such as synthetic detergents.[1] Alkylbenzenes are produced by Friedel-Crafts reaction of alkyl halides and benzene. However, the use of organohalides should be avoided from the viewpoint of green chemistry. Therefore, direct alkylation of benzene with alkane has been studied. This direct alkylation method has two advantages compared to conventional one: (i) halogen-free reaction system, (ii) reduction of synthetic step, costs, and raw substrates for halogenation of alkanes. Noble-metal-containing zeolites have mainly been used as catalysts for the direct alkylation of benzene with alkane at high temperature. For example, alkylation with hexane, Pt-modified ZSM-5 shows 30% conversion and 70% selectivity to hexyl benzenes at 205 °C.[2] Only a homogeneous super strong acid, HF-SbF_5, can promote the reaction selectively at room temperature.[3] However, there are no report on a heterogeneous catalyst without noble metal for selective production of alkylated benzenes at low temperature.

In this study, the direct, liquid phase alkylation reaction of benzene using alkanes at 150 °C was carried out using the cation-exchanged montmorillonites as solid acid catalysts. When aluminum-exchanged montmorillonite (Al-mont) was used for the reaction of *n*-heptane, the target alkylated product with long carbon chain, was selectively obtained: 1.82 % conversion of benzene with 58% selectivity was achieved.[4] The Al-mont showed higher catalytic activity and selectivity to Ph-C7 alkylation products compared with other heterogeneous and homogeneous acids, such as zeolties as H_2SO_4. Not only heptane but also C5-C8 linear and cyclic alkanes reacted with benzene in the presence of Al-mont. Product selectivity analysis during the reaction indicates the carbocation mechanism. Interestingly, this Al-mont-catalyzed dehydrogenative coupling was enhanced significantly in the presence of transition metal co-catalyst. Proposed reaction mechanism will be discussed in presentation.

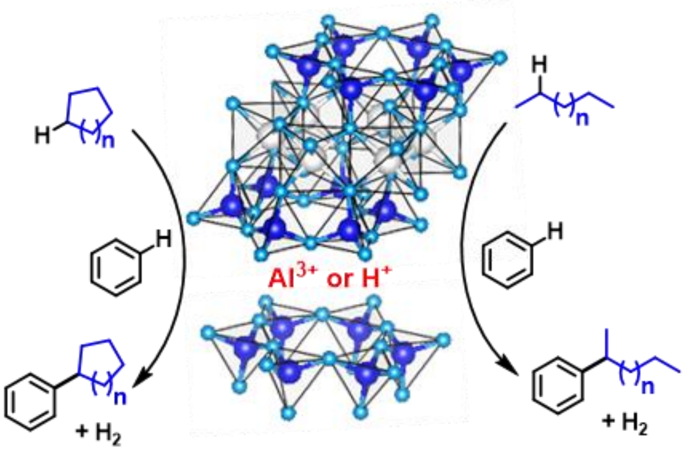

Figure 1. Montmorillonite-catalyzed direct alkylation of benzene with alkanes

Acknowledgements. This work was supported by PRESTO Grant (No. 11328) from the Japan Science and Technology Agency (JST).

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- Photochemical reaction on graphene surfaces controlled by substrate-surface modification with polar self-assembled monolayers, R. Nouchi, K.-i. Ikeda, *Phys. Chem. Phys. Chem.* **2020**, *22*, 1268–1275.
- Adsorbates as a charge-carrier reservoir for electrostatic carrier doping to graphene, R. Nouchi, K.-i. Ikeda, *Appl. Phys. Express* **2020**, 13, 015005.
- Gate-controlled photo-oxidation of graphene for electronic structure modification, R. Nouchi, M. Matsumoto, N. Mitoma, *J. Mater. Chem. C* **2019**, *7*, 1904–1912.
- Dipolar Switching of Charge-Injection Barriers at Electrode/Semiconductor Interfaces as a Mechanism for Water-Induced Instabilities of Organic Devices, R. Nouchi, *Adv. Mater. Interfaces* **2018**, *5*, 1801261.

ELECTRICAL MONITORING OF METHANE OXIDATION USING ATOMICALLY THIN FILMS OF TRANSITION-METAL OXIDE NANOSHEETS

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A change in electrical resistance is a facile platform for monitoring chemical reactions. However, a reaction-induced change in resistance is usually masked by a high bulk conductivity of the sensing layer. Thus, an ultrathin sensing layer is desired to enhance the surface sensitivity. In addition, the sensitivity originates from reactivity and/or catalytic activity of the sensing layer towards a chemical reaction to be sensed. Therefore, an atomically thin material that possesses reactivity towards a target chemical reaction should be employed as the sensing layer to achieve electrical monitoring of the reaction. Methane (CH_4) has been regarded as an alternative carbon source to petroleum for producing useful chemicals. Oxidation (dehydrogenation) is the first step to produce the chemicals, but CH_4 possesses the most stable C–H bond among all hydrocarbons. Thus, a lot of efforts have been devoted to finding a material that enables facile dehydrogenation of CH_4. Recently, Weaver *et al.* reported that CH_4 undergoes dehydrogenation at low temperatures on a surface of IrO_2 single crystals.[1]

In this study, the electrical monitoring of CH_4 oxidation is achieved by employing monolayered films of IrO_2 nanosheets[2] as an atomically thin sensing layer. Two types of changes in electrical resistance were observed upon CH_4 exposure, depending on the thickness of the sensing layer: (1) a decrease in a monolayered film due to (partial) reduction of the iridium oxide nanosheets (bulk resistivity: IrO_2 > Ir[3]) [Fig. 1(a)], and (2) an increase in a thicker film due to increased surface scattering[4] upon adsorption of CH_4 and/or reaction products [Fig. 1(b)]. The observation of the resistance decrease with a monolayered film is a verification of the occurrence of the CH_4 oxidation reaction.

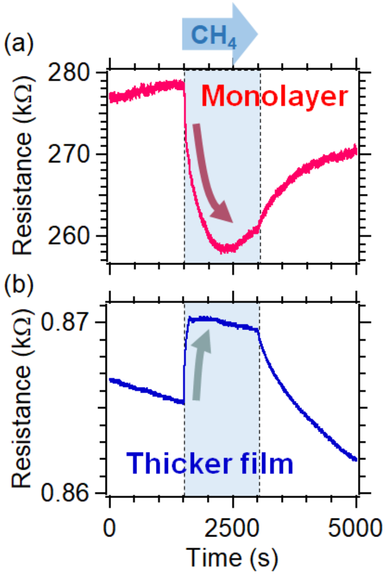

Figure 1. Change in electrical resistance of (a) monolayered and (b) thicker films of IrO_2 nanosheets upon CH_4 exposure.

Acknowledgements. This work was supported by JST PRESTO Grant Number JPMJPR17S6 and JSPS KAKENHI Grant Number JP19H02561.

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His research interest focuses on developments of highly active catalysts for hydrogen and valuable chemicals (*e.g.* olefins and aromatics) productions from unutilized abundant feedstocks, such as natural gas and biomass. He also investigates the novel low-temperature electro-catalytic reaction systems to utilize an unutilized low-temperature waste heat. Currently, he applies the low-temperature electro-catalytic reaction system to carbon dioxide conversions.

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Recent Press Releases

"New method converts carbon dioxide to methane at low temperatures",
"New, low cost alternative for ethylene production".

AMBIENT-TEMPERATURE OXIDATIVE COUPLING OF METHANE OVER CERIUM PHOSPHATE NANOROD CATALYST IN AN ELECTRIC FIELD

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Oxidative coupling of methane (OCM) is an attractive catalytic process for direct production of useful C_2 hydrocarbons from methane and oxygen in air. However, activation of methane requires high temperatures over 973 K due to its tetrahedral stable structure, and non-selective oxidation easily proceeds at such high temperatures. To resolve the difficulties described above, we adopted an unconventional catalytic system, a catalytic reaction in an electric field, in anticipation of methane conversion at low temperatures.[1,2] We have recently developed Ce–W–O system catalysts for OCM at low temperature with imposing an electric field.[3-5] However, these systems have several drawbacks: (i) the need for a CeO_2 support leads to difficult structure control of surface active Ce sites, (ii) low surface areas (~ 4 m^2 g^{-1}) and (iii) the resulting insufficient C_2 yield (~6%). Herein, we focus on the OCM activity of a monoclinic $CePO_4$ nanorod catalyst with structurally controlled uniform active sites.[6] Figure 1 shows the time course of the C_2 hydrocarbon yield for OCM over various Ce-based catalysts in the electric field (7 mA) without external heating. Among the catalysts tested, the $CePO_4$ nanorod catalyst showed the highest C_2 yields (18%) and durability.[6] The OCM activity of the $CePO_4$ catalyst at ambient temperature in the electric field is comparable to that of the Mn–Na_2WO_4/support system catalysts at 1073 K, which is one of the highest performance catalysts. In addition, the $CePO_4$ catalyst showed very low OCM activity without the electric field even at the high temperature of 1073 K, indicating that the $CePO_4$ catalyst can activate methane only when the electric field is applied.

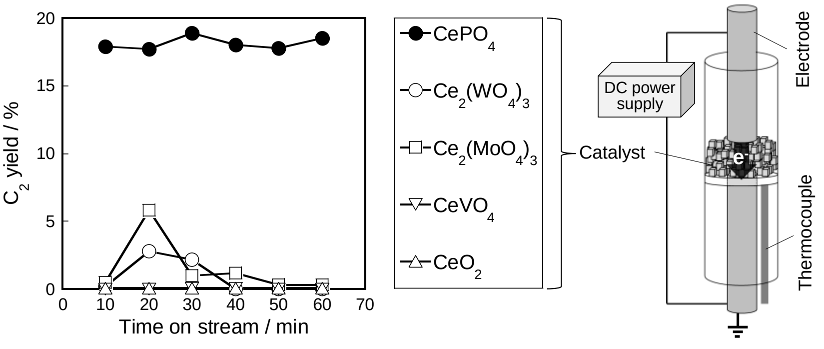

Figure 1. Time course of the C_2 hydrocarbon yield for OCM over various cerium-based catalysts at ambient temperature in the electric field.[6]

Acknowledgements. This work was supported by JST PRESTO program (Grant No. JPMJPR16S4, JPMJPR15S3).

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- Hemoproteins Reconstituted with Artificial Metal Complexes as Biohybrid Catalysts, K. Oohora, A. Onoda, T. Hayashi, *Acc. Chem. Res*. **2019**, *52*, 945–954.
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- Catalytic Cyclopropanation by Myoglobin Reconstituted with Iron Porphycene: Acceleration of Catalysis due to Rapid Formation of the Carbene Species, K. Oohora, H. Meichin, L. Zhao, M. W. Wolf, A. Nakayama, J. Hasegawa, N. Lehnert, T. Hayashi, *J. Am. Chem. Soc.* **2017**, *139*, 17265–17268.

HYDROXYLATION OF C–H BONDS BY HEMOPROTEIN-BASED ARTIFICIAL METALLOENZYME

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A variety of natural metalloenzymes efficiently and/or selectively catalyze the difficult reactions in aqueous media under a mild condition. In the natural metalloenzymes, sophisticated protein matrices serve as the reaction fields for active metal centers, whereas the specificity for the natural substrate and some fragile property for modification, however, limit the applications in the reactions for non-natural substrates. In this context, creation of artificial metalloenzymes have been focused on to overcome these points.[1] Our group especially demonstrates the engineering of hemoprotein, a useful metalloprotein containing iron porphyrin (heme) as a cofactor, with artificial cofactors. Heme in the hemoprotein is replaced by artificial cofactors to afford the reconstituted protein as an artificial metalloenzyme. The several reconstituted hemoproteins remarkably enhance the catalytic activities compared with original hemoprotein.[2] The present study demonstrates an artificial metalloenzyme to catalyze H_2O_2-dependent C–H bond hydroxylation via detectable high-valent oxo-species.[3] A manganese complex of porphycene, a constitutional isomer of porphyrin, and myoglobin, an oxygen storage hemoprotein, are employed as an artificial cofactor and a protein matrix, respectively (Figure 1). The obtained artificial metalloenzyme and its mutant show catalytic activity of C–H bond hydroxylation for the small alkane substrates such as propane and ethane with good selectivity for over oxidation. X-ray crystal structure analysis indicates that the mutant providing relatively high turnover number possesses the cavity for substrate binding. An active intermediate of this artificial metalloenzyme is assigned as a Mn(V) species by EPR and kinetics using stopped flow technique. Further experiments reveal the enhancement of the reactivity of the intermediate by the mutation.

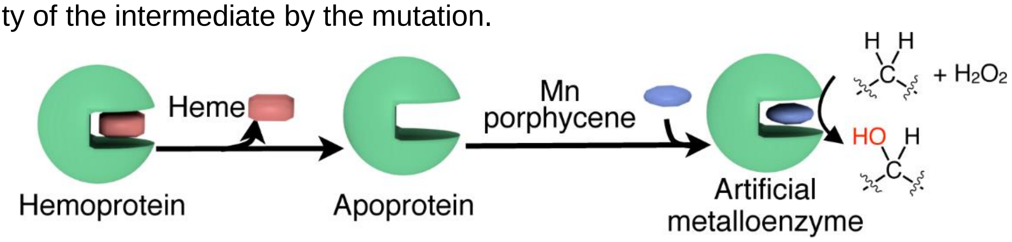

Figure 1. Schematic representation of preparation of artificial metalloenzyme.

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Five Selected Publications of Relevance to Catalysis Science.

- Data-Driven Identification of the Reaction Network in Oxidative Coupling of the Methane Reaction via Experimental Data, I. Miyazato, S. Nishimura, L. Takahashi, J. Ohyama, K. Takahashi, *J. Phys. Chem. Lett.* **2020**, *11*, 787–795.
- High-Throughput Experimentation and Catalyst Informatics for Oxidative Coupling of Methane, T. N. Nguyen, T. T. P. Nhat, K. Takimoto, A. Thakur, S. Nishimura, J. Ohyama, I. Miyazato, L. Takahashi, J. Fujima, K. Takahashi, T. Taniike, *ACS Catal.* **2020**, *10*, 921–932.
- Catalyst Acquisition by Data Science (CADS): a web-based catalyst informatics platform for discovering catalysts, J. Fujima, Y. Tanaka, I. Miyazato, L. Takahashi, K. Takahashi, *React. Chem. Eng.,* in press.
- Visualizing Scientists' Cognitive Representation of Data through the Application of Ontology, L. Takahashi, K. Takahashi, *J. Phys. Chem. Lett.* **2019,** *10*, 7482–7491.
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Recent Press Releases

“High-Throughput Experimentation and Catalyst Informatics for Oxidative Coupling of Methane.”, “Catalyst Acquisition by Data Science (CADS): a web-based catalyst informatics platform for discovering catalysts.”.

THE RISE OF CATALYSTS INFORMATICS: HIGH THROUGHPUT EXPERIMENT AND DATA SCIENCE FOR OXIDATIVE COUPLING OF METHANE

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Recent advancements in the novel field materials informatics have now begun to expand towards catalysis over the past several years. This movement has developed into the establishment of catalysts informatics. A main focus of catalysts informatics is to design catalysts via combining catalysts data with data science techniques, including those relating to machine learning as shown in Figure 1. Here, a high throughput experimental device is designed and developed for the oxidative coupling of methane (OCM) reaction where 20 catalysts can be evaluated under various experimental conditions. With the device, over 12,000 OCM catalysts are able to be evaluated within a timespan of three days. This approach has resulted in the accumulation of catalyst data that is ten times greater than what has been collected for the OCM reaction over the past 30 years. This catalyst big data is then coupled with machine learning techniques. Machine learning successfully interpolate the experimental condition in OCM as shown in Figure 2. Moreover, this result made it possible to then continue to predict catalysts that may possess a high C2 yield. The details of the high throughput experimental device as well as the manner in which machine learning is able to predict the experimental conditions and catalysts are introduced. Lastly, developed catalysts informatics platform "CADS" is also introduced.

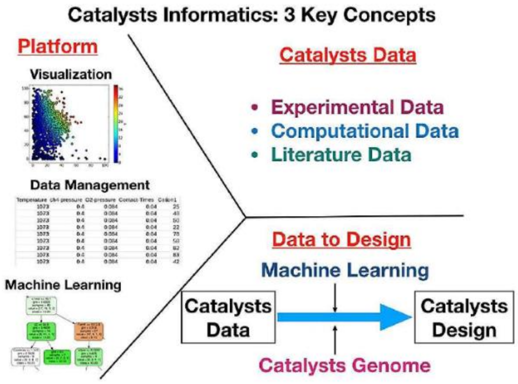

Figure 1. Concept of Catalysts Informatics.[1]

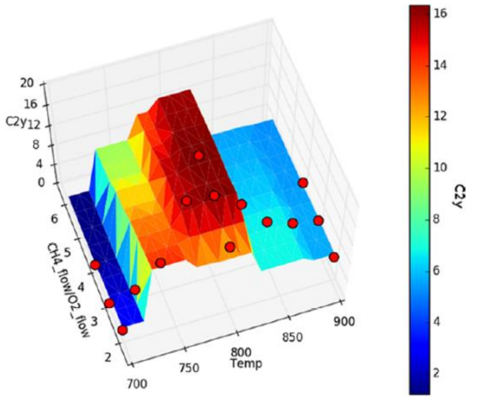

Figure 2. Interpolation filling of experimental space in OCM via machine learning.[2]

Acknowledgements. This work is funded by Japan Science and Technology Agency (JST) CREST Grant Number JPMJCR17P2, JSPS KAKENHI Grant-in-Aid for Young Scientists (B) Grant NumberJP17K14803.

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Five Selected Publications of Relevance to Catalysis Science.

- Data Driven Identification of the Reaction Network in Oxidative Coupling of the Methane Reaction via Experimental Data, I. Miyazato, S. Nishimura, L. Takahashi, J. Ohyama, K. Takahashi, *J. Phys. Chem. Lett.* **2020**, *152*, 787–795.
- High-Throughput Experimentation and Catalyst Informatics for Oxidative Coupling of Methane, T. N. Nguyen,T. T. P. Nhat, K. Takimoto, A. Thakur, S. Nishimura, J. Ohyama, I. Miyazato, L. Takahashi, J. Fujima, K. Takahashi, T. Taniike, *ACS Catal.* **2020**, *10*, 921–932.
- Visualizing Scientists' Cognitive Representation of Data through the Application of Ontology, L. Takahashi, K. Takahashi, *J. Phys. Chem. Lett.* **2019**, *151*, 7482–7491.
- Creating Machine Learning-Driven Material Recipes Based on Crystal Structure, K. Takahashi, L. Takahashi, *J. Phys. Chem. Lett.* **2019**, *151*, 283–288.
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Recent Press Releases

"High-Throughput Experimentation and Catalyst Informatics for Oxidative Coupling of Methane.", "Catalyst Acquisition by Data Science (CADS): a web-based catalyst informatics platform for discovering catalysts.".

STANDARDIZING CATALYST DATA AND CATALYST-RELATED KNOWLEDGE THROUGH THE IMPLEMENTATION OF ONTOLOGY

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Data has become a central player in current chemical and catalyst research and development due to increasingly successful applications of data science towards catalyst and chemical research, resulting in new fields chemoinformatics and catalyst informatics.[1,2] Issues such as data quality, lack of database standardization, and individualized recording practices have made it difficult to fully utilize data science techniques. Additionally, there is a growing need to be able to process and extract knowledge from large datasets. Ontology is therefore proposed as a viable approach towards addressing these concerns where a series of vocabulary and relationships can be explicitly defined using description logic.[3] Such a system allows for underlying data semantics to be defined and structured in a way that is both easier to understand by researchers and machines alike. It also becomes possible to query data and extract specific information based on given sets of conditions or restrictions, making it possible to survey large quantities of data, which can be particularly useful when attempting to design catalysts. By implementing ontology, data is reshaped into a data web of relationships, helping to reduce the static nature of current datasets as well as help fill in information gaps.[4] Ontology can also be used to define and visualize the experiences and knowledge of researchers that influence research and scientific discoveries. By doing so, scientific discoveries can become less reliant on aha! moments and accidents and become more governed by rules, thereby providing structure and more intention to scientific discoveries. Thus, ontology can improve database construction and management in chemical and catalyst research while also laying the foundation for semantics-based data science applications in chemoinformatics and catalyst informatics.

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Short Biography. Prof. Kazuhiro Takanabe is Professor in the Department of Chemical System Engineering at The University of Tokyo. He previously worked at King Abdullah University of Science and Technology (KAUST) from 2010 to 2018. Before he joined KAUST, he was Assistant Professor in the Department of Chemical Systems Engineering at the University of Tokyo (2008-2010). Upon receipt of his doctoral degree in engineering from the Tokyo Institute of Technology in 2006, he served as a Postdoctoral Fellow at the University of California at Berkeley from 2006-2008. During his doctoral study, Prof. Takanabe studied at the University of Twente in the Netherlands as an exchange student (2002-2004). He is currently Editor of the Journal of Catalysis since September 2017.

Five Selected Publications of Relevance to Catalysis Science.

- Photocatalytic water splitting: Quantitative approaches toward photocatalysis by design, K. Takanabe, *ACS Catal.* **2017**, *7*, 8006–8022.
- Integrated in situ characterization of molten salt catalyst surface: Evidence of sodium peroxide and OH radical formation, K. Takanabe, A. M. Khan, Y. Tang, L. Nguyen, A. Ziani, B. W. Jacobs, A. M. Elbaz, S. Mani Sarathy, F. Tao, *Angew. Chem. Int. Ed.* **2017**, *56*, 10403–10407.
- In-operando elucidation of bimetallic CoNi nanoparticles during high-temperature CH_4/CO_2 reaction, B. Al-Sabban, L. Falivene, S. Kozlov, A. Aguilar-Tapia, S. Ould-Chikh, J.-L. Hazemann, L. Cavallo, J.-M. Basset, K. Takanabe, *Appl. Catal., B* **2017**, *213*, 177–189.
- An oxygen-insensitive hydrogen evolution catalyst coated by molybdenum-based layer for overall water splitting, A. T. Garcia-Esparza, T. Shinagawa, S. Ould-Chikh, M. Qureshi, X. Peng, N. Wei, D. H. Anjum, A. Clo, T.-C. Weng, D. Nordlund, D. Sokaras, J. Kubota, Kazunari Domen, K. Takanabe, *Angew. Chem. Int. Ed.* **2017**, *56*, 5780–5784.
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INTEGRATING OH RADICAL GENERATOR IN METHANE OXIDATION FOR IMPROVING C-C COUPLING UNDER FUEL-RICH CONDITION AT HIGH TEMPERATURES

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Oxidative coupling of methane (OCM) is an attractive reaction that can generate C_2 hydrocarbons from methane in a single reactor. The OCM has attracted both industrial and academic interests and a large number of catalysts have been investigated to improve the OCM yield. Benchmarking C_2 yield is often considered to be ~30% (C basis).[1] It is commonly accepted that the reaction proceeds via methane reacting with catalytically activated surface oxygen species to form methyl radicals, which recombines to achieve C-C bond formation. Among the catalysts investigated, some Na-based catalysts including (Mn/)Na_2WO_4/SiO_2 catalyst were proposed to exhibit high C_2 yield.[2,3] We ascribed the high product yield to be a distinctive reaction mechanism on this catalyst, where H_2O, instead of CH_4, is activated on the catalyst surface to generate OH radical.[2,4] The generated OH radicals, in turn, react with gas-phase CH_4 to produce methyl radicals, which then lead to C-C coupling to form C_2H_6.[2] Impact of OH radical has been elucidated experimentally,[3] and by numerical modeling[5] using the state-of-the-art gas phase CH_4-O_2 reaction network (Figure 1). The presentation will discuss the details of reaction mechanism, the nature of active site, and future perspectives of the OH radical-mediated chemistry for CH_4 conversion in OCM and more.

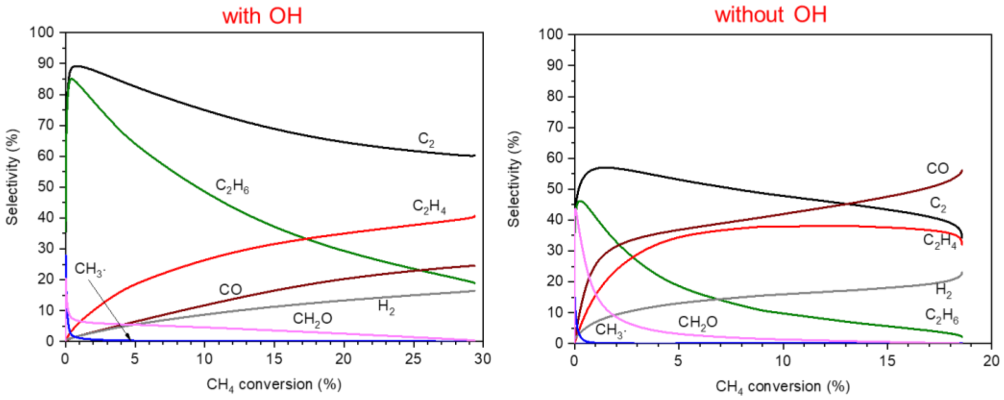

Figure 1. Numerical simulation using CHEMKIN for product distribution from CH_4/O_2 mixture at 800 °C isothermal, 1 atm, CH_4/O_2 ratio of 6 without any dilution. The gas-phase chemical kinetic model employed here is the (KAUST-Aramco PAH Mech 1-GS, KAM1-GS). The extent of OH• involvement was assessed by arbitrarily varying the rate constant of the reaction $O_2 + 2\,H_2O \xrightarrow{K} 4\,OH\cdot$.

Acknowledgements. PRESTO JST for funding.

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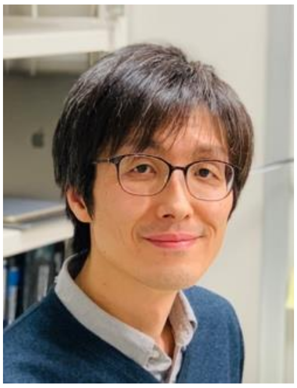

Short Biography. Dr. Jun Takaya (born in 1977) received his PhD from Tokyo Institute of Technology under the direction of Prof. Nobuharu Iwasawa (2004). After a JSPS postdoctoral period (2004-05) with Prof. John F. Hartwig at Yale University, he was appointed to an Assistant Professor of the research group of Prof. Nobuharu Iwasawa at Tokyo Institute of Technology in 2005, and promoted to Associate Professor in 2014. He has also been working as a PRESTO researcher of the Japan Science and Technology Agency (JST) from 2017. He received Incentive Award in Synthetic Organic Chemistry, Japan in 2013, the Banyu Chemist Award in 2014, Merck-Banyu Lectureship Award in 2014, Thieme Chemistry Journal Award 2015, and The Young Scientist's Prize in 2016. His current research interests are mainly on the development of new transition metal complexes and their utilization in synthetic chemistry to achieve new molecular transformations. He has developed new synthetic reactions of carbon dioxide and unsaturated hydrocarbons utilizing newly designed transition metal catalysts bearing a heavier group 14 element-centered pincer type ligand. Mechanistic investigations clarified unique non-innocent behavior of the silyl ligand, which enables unprecedented bond activation/formation mechanisms. He also achieved transition metal-catalyzed direct C-H bond carboxylation reactions of arenes and alkenes with carbon dioxide as a C1 source. He has recently developed new bimetallic complexes and demonstrated their unique reactivity and catalysis in synthetic chemistry utilizing precisely designed multidentate ligands as a scaffold for the metal-metal bond.

Five Selected Publications of Relevance to Catalysis Science.

- Photo-promoted Skeletal Rearrangement of Phosphine-Borane Frustrated Lewis Pairs Involving Cleavage of Unstrained C–C σ-Bonds, T. Ito, N. Iwasawa, J. Takaya, *Angew. Chem., Int. Ed.*, DOI: 10.1002/anie.202004444.
- Rhodium-Catalyzed C−H Activation Enabled by an Indium Metalloligand, R. Yamada, N. Iwasawa, J. Takaya, *Angew. Chem., Int. Ed.* **2019**, *58*, 17251.
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- Synthesis, Structure, and Catalysis of Palladium Complexes Bearing a Group 13 Metalloligand: Remarkable Effect of an Aluminum-Metalloligand in Hydrosilylation of CO_2, J. Takaya and N. Iwasawa, *J. Am. Chem. Soc.* **2017**, *136*, 6074.

TUNING TRANSITION METAL CATALYSIS WITH METALLOLIGANDS

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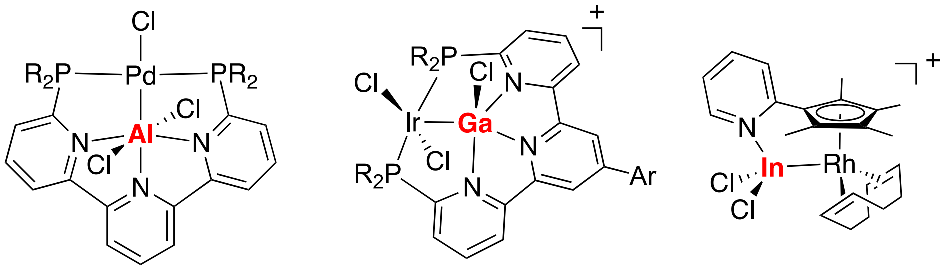
Z-type ligands, which serve as a σ-acceptor via dative bonding from a transition metal, have recently emerged as a useful tool for controlling reactivity of transition metal catalysts. We have successfully synthesized a series of palladium complexes having a Z-type, group 13 metalloligand utilizing 6,6''-bis(phosphino)-2,2':6',2''-terpyridine derivatives as an efficient scaffold for M–E bonds (E = Al, Ga, In). Systematic investigation revealed unique characteristics of the Al-metalloligand in both structure and reactivity, which exhibited the highest catalytic activity for hydrosilylation of CO_2 ever reported (TOF = 19300 h^{-1}).[1] We have also achieved synthesis of an Ir complex having a pincer-type gallylene ligand through the complexation-induced reduction of Ga^{III} by Ir^{I} utilizing the *N*,*P*-multidentate ligand.[2,3] The pincer-type structure enabled various reactions at Ir with keeping the gallylene ligand intact. For examples, two-electron reduction with KC_8 afforded a neutral Ir^{I} complex having another Ga–metalloligand, $GaCl_3$, on Ir, which is promising for cooperative molecular activation with Ir, Ga^{I}, and Ga^{III}. Furthermore, we recently developed rhodium complexes having an In-metalloligand utilizing a pyridine-tethered cyclopentadienyl ligand as a support for an In–Rh bond.[4] The In-metalloligand dramatically changes the electronic and redox properties of the rhodium metal, awakening its catalysis for an sp^2C–H bond activation reaction. These studies are highly promising to explore new transition metal catalysis with rationally designed Z-type metalloligands in synthetic chemistry.



Tuning reactivity of transition metals with group 13 metalloligands toward efficient CO_2 fixation and C–H bond transformations

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Short Biography. Masazumi Tamura recieved his B.S. (2003) at School of Science from Kyoto University (Thesis Director: Prof. K. Maruoka) and received M.S. (2005) at Graduate School of Engineering from The University of Tokyo (Thesis Director: Prof. M. Fujita). From 2005 to 2012 he was a researcher working at Kao Corporation, and during that period he obtained his Ph.D. (2012) at Graduate School of Engineering from Nagoya University (Thesis Director: Prof. A. Satsuma). From 2012 to 2020, He worked as an assistant professor at School of Engineering in Tohoku University (Tomishige Lab.), and during the period he also worked as a researcher for JST-PRESTO from 2015 to 2019. He became an associate professor from 2020 at Research Center for Artificial Photosynthesis (ReCAP) in Osaka City University. Recently, he received Research Award in Aoba Foundation for the Promotion of Engineering (2015), Catalysis Society of Japan Award for Young Researchers (2017), The Young Scholar Lectures of The Chemical Society of Japan (2017), The Japan Petroleum Institute Award for Encouragement of Research and Development (2018), The Young Scientists' Prize, The Commendation for Science and Technology by the MEXT (2018) and Intelligent Cosmos Research Encouraging Award (2020). His interests focus on transformation of CO_2, biomass-derived materials and plastics to valuable chemicals by using heterogenous catalysts. Moreover, he has recently studied hybrid catalysts composed of heterogeneous and homogeneous components with multi-catalytic functions for organic synthesis.

Five Selected Publications of Relevance to Catalysis Science.

- Direct Synthesis of Unsaturated Sugars from Methyl Glycosides, J. Cao, M. Tamura, Y. Nakagawa, K. Tomishige, *ACS Catal.* **2019**, *9*, 3725–3729.
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- Transformation of Sugars to Chiral Polyols over a Heterogeneous Catalyst, M. Tamura, N. Yuasa, J. Cao, Y. Nakagawa, K. Tomishige, *Angew. Chem. Int. Ed.* **2018**, *57*, 8058–8062.
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STRONG BASE CATALYST OF NITRILE-MODIFIED CERIUM OXIDE FOR ORGANIC REACTIONS

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Rational design of active sites is essential for catalysts to obtain high activity and selectivity in organic synthesis. However, formation of uniform active sites over heterogeneous catalysts is generally difficult, and development of a new methodology for fine tuning of the active sites over heterogeneous catalysts is highly required. Modification of heterogeneous catalysts with organic modifiers such as self-assembled monolayer (SAM) attracts is one promising method,[1] but modification of metal oxides with organic modifiers is quite rare in spite of metal oxides being durable and stable for heating, and widely used as acid/base catalysts in industry. Herein, we found that the self-assembled heterogeneous and homogeneous hybrid catalyst composed of CeO_2 and nitriles, particularly 2-cyanopyridine, was effective for base-catalyzed organic reactions such as hydromethoxylation of acrylonitrile,[2,3] transesterification,[2] Knoevenagel condensation,[2] carbonate derivative synthesis from CO_2 such as organic carbonates, carbamates, ureas and polycarbonates.[4] For example, the hybrid catalyst of CeO_2 and 2-cyanopyridine (Figure 1) showed about 2000-fold higher activity than CeO_2 in the hydromethoxylation of acrylonitrile. The basicity over the hybrid catalyst of CeO_2 and 2-cyanopyridine was much higher than that over CeO_2 by a factor of 109, and the pK_a (in CH_3CN) was estimated to be ~21, which puts it in the superbase category. In this talk, I will introduce the catalysis of the hybrid catalyst composed of CeO_2 and nitriles for various organic reactions.

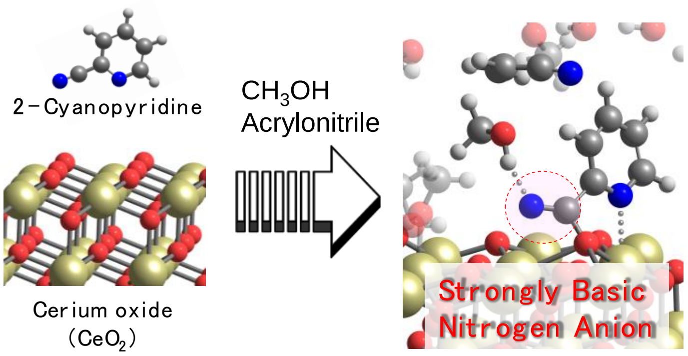

Figure 1. Formation of strong base site by combination of CeO_2 and 2-cyanopyridine.

Acknowledgements. This work was supported by JST PRESTO Grant Number JPMJPR15S5 and JPMJPR16S8, Japan.

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Short Biography Atsushi Urakawa (ORCID: 0000-0001-7778-4008) is Professor at the Department of Chemical Engineering and Leader of Catalysis Engineering Section at Delft University of Technology (TU Delft). He is enthusiastic about fundamental as well as highly applied research, always seeking for new ideas and strategies to make a difference in industry to guide the technological trends towards greener society by means of innovative catalytic processes. His current major research activities are centered on catalysis for environmental protection (e.g. automotive catalysis) and synthesis of future chemical energy carriers such as hydrogen and methanol. Notably, his team actively researches on CO_2 conversion catalysis and recently reported the most efficient process to produce methanol and dimethyl ether from carbon dioxide and hydrogen using high-pressure approach with granted patents. The practical relevance of the catalysts and processes developed by his team is of utmost importance and he actively collaborates with industry partners. Furthermore, to facilitate rational catalyst and process design, his team develops new spectroscopic and analysis tools to gain fundamental insights into the catalytically active sites and active species under catalysts' working (*operando*) conditions, aiming to establish catalyst structure-activity relationships.

Five Selected Publications of Relevance to Catalysis Science.

- From CO or CO_2?: Space-resolved insights into high-pressure CO_2 hydrogenation to methanol over $Cu/ZnO/Al_2O_3$, R. Gaikwad, H. Reymond, N. Phongprueksathat, P. Rudolf von Rohr, A. Urakawa, *Catal. Sci. Technol.*, DOI: 10.1039/D0CY00050G.
- Deciphering key intermediates in the transformation of carbon dioxide into heterocyclic products, R. Huang, J. Rintjema, J. González Fabra, E. Martín, E. C. Escudero-Adán, C. Bo, A. Urakawa, A. W. Kleij, *Nat. Catal.* **2019**, *2*, 62.
- Lewis acidic supports promote the selective hydrogenation of carbon dioxide to methyl formate in the presence of methanol over Ag catalysts, J.J. Corral-Pérez, C. Copéret, A. Urakawa, *J. Catal.* **2019**, *380*, 153.
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UNDERSTANDING CATALYTIC PERFORMANCE THROUGH PHYSICOCHEMICAL GRADIENTS ON THE REACTOR SCALE

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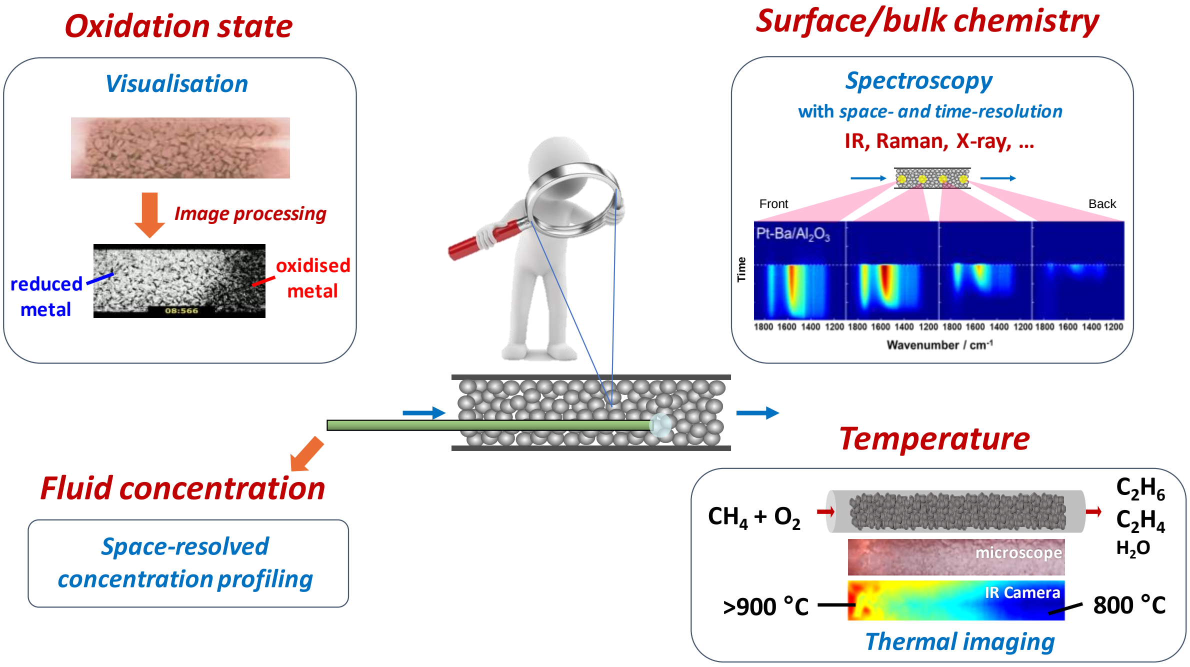
Various types of gradients (temperature, concentration, material state, surface species, etc.) are present in catalytic reactors under continuous operation. For example, when the conversion of a reactant is 90%, the atmosphere a catalyst experiences is completely different near the fluid inlet or the outlet (e.g. of a packed-bed reactor) due to the obvious gradient of the concentration of chemical species in the reaction fluid. This consequently affects the type and concentration of surface chemical species present on the catalyst, inducing its spatial variation within a reactor. Furthermore, reactions are generally exothermic or endothermic, and even multiple reactions take place simultaneously, inducing non-negligible temperature gradients in reactors.

In this talk, I highlight the importance of elucidating such gradients to understand *what happens where* for steady-state processes, taking oxidative coupling of methane as an example, and to understand *what happens where and when* for unsteady-state processes such as CO_2 capture-conversion and automotive catalysis. Through these examples, I will explain how these gradients can be studied by *operando* methodologies and catalytic performance, namely reactant conversion and product selectivity, is shaped and can be holistically understood.



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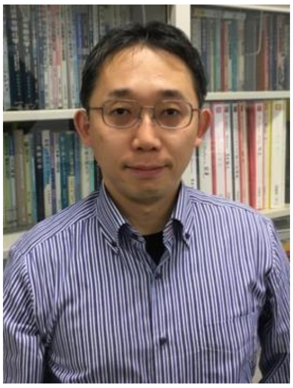

Short Biography. Yasuyuki Yamada received his B.S. (1998, supervisor: Prof. Renji Okazaki), M.S. (2000, supervisor: Prof. Hiroshi Nishihara), and Ph. D. (2003, supervisor: Prof. Mitsuhiko Shionoya) degrees from the University of Tokyo. From 2003 to 2004, He worked as a pos-doc researcher in the group of Prof. Jean A. Chmielewski at Purdue University in U.S.A. He began his academic career at Tokyo University of Science as an Assistant Professor in the group of Prof. Shin Aoki from 2004. After He moved to Nagoya University as an Assistant Professor (Prof. Kentaro Tanaka's group) in 2007, he promoted to an Associate Professor in 2014. His research background covers coordination chemistry, supramolecular chemistry, electrochemistry, DNA and peptide chemistry. He received "The chemical Sciety of Japan Lecture Award for Young Chemists„ in 2014, "Symposium Award of International Congress on Pure & Applied Chemistry (ICPAC)„ in 2018, "SHGCS Japan Award of Excellence„ in 2019. His current research interests includes 1) development of bio-inspired supramolecular catalysts, 2) design and synthesis of molecular assemblies with unique topological structures, and 3) synthesis of molecular spin devices and single molecular magnets, especially by using metallo-porphyrinoids as key components.

Five Selected Publications of Relevance to Catalysis Science.

- Development of Functional Molecular Assemblies Based on Programmable Construction of Face-to-Face Assemblies of Metallo-Porphyrinoids, Y. Yamada, K. Tanaka, *J. Incl. Phenom. Macrocycl. Chem.* **2020**, *96*, 197–213.
- Catalytic Methane Oxidation by Supramolecular Conjugate Based on μ-Nitrido-Bridged Iron Porphyrinoid Dimer, Y. Yamada, K. Morita, N. Mihara, K. Igawa, K. Tomooka, K. Tanaka*, *New J. Chem.* **2019**, *43*, 11477–11482.
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- Dynamic Molecular Invasion into Multiply Interlocked Catenane, Y. Yamada, R. Itoh, S. Ogino, T. Kato, K. Tanaka, *Angew. Chem. Int. Ed.* **2017**, *56*, 14124–14129.
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SUPRAMOLECULAR APPROACH TO HIGHLY POTENT MOLECULAR CATALSYT FOR DIRECT C–H ACTIVATION OF METHANE

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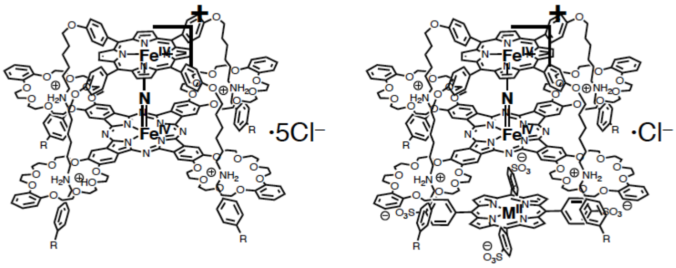
Effective molecule-based catalysts for direct C–H activation of methane has been extensively investigated both from social demands to reduce our dependence on petroleum resources and from scientific interests in high catalytic activity of natural oxygenases such as methane monooxygenases. In spite of the continuous challenge to mimic the active centers of natural oxygenases that can activate C–H bonds of methane under mild reaction conditions, artificial molecule-based catalysts show much less catalytic activities than both of natural enzymes and inorganic heterogeneous catalysts. Inspired by the fact that some oxygenases successfully enhance the catalytic activity of molecular metal-oxo species by utilizing coordinating ligands with the help of their higher order structures of proteins, we sought for a supramolecular approach for enhancing the catalytic activity of a μ-nitrido-bridged iron porphyrinoid dimer, which is known as one of the most potent molecule-based catalyst for direct C-H activation of methane reported so far.[1]

We first confirmed that a μ-nitrido-bridged dinuclear iron complex of a supramolcular cofacial heterodimer of a porphyrin and a phthalocyanine in which these two porphyrioids are assembled through a fourfold rotaxane structure (**1**$^{5+}\cdot$5Cl^{-} in **Figure 1**) actually catalyzed the conversion of methane into methanol, formaldehyde, and formic acid in an acidic aqueous solution in the presence of H_2O_2 at 60 °C.[2-4] Since **1**$^{5+}\cdot$5Cl^{-} has four peripheral ammonium cations, an additional tetrasulfonate M(II)-porphyrin (**M(II)-TPPS^{4-}**) stacked on the top of the phthalocyanine of **1**$^{5+}$ to give an assembly **2**$\cdot$Cl^{-} through quadruple ionic interaction. **2**$\cdot$Cl^{-} was found to show higher catalytic methane oxidation activity than **1**$^{5+}\cdot$5Cl^{-}. We concluded that extension of the π-stacked structure was the key for activation of **1**$^{5+}$ because the catalytic activity of **2**$\cdot$Cl^{-} did not depend on the kinds of the central metal ion of **M(II)-TPPS^{4-}** in **2**$\cdot$Cl^{-}. A more potent catalyst with a simplified structure designed based on this finding will also be presented.



1$^{5+}\cdot$5Cl^{-} **2**$^{+}\cdot$Cl^{-}

Figure 1. Structures of **1**$^{5+}\cdot$5Cl^{-} and **2**$\cdot$Cl^{-}.

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Short Biography. Ulf-Peter Apfel (WoS Researcher ID R-6779-2017) received his Ph.D. from the Friedrich-Schiller University Jena (Germany) in 2010 in the group of W. Weigand. After a postdoctoral stay with S. J. Lippard at MIT (USA; 2011/2012) as a Humboldt fellow, he started his independent career at the Ruhr University Bochum (Germany) funded by the “Fonds der Chemischen Industrie” and the German research council as an Emmy Noether group leader. He now holds a professorship in inorganic chemistry at the Ruhr University Bochum since 2019 and is head of the department Think Tank/Electrosynthesis at Fraunhofer UMSICHT. He is a member of the scientific advisory board of the RSC flagship journal Chemical Science. His research interests are in the field of technical electrochemistry with a special emphasis on energy conversion applications. This research includes the catalyst design, synthesis as well as electrode and reactor engineering. Especially the activation of CO_2 and formation of H_2 are main topics and projects involve enzyme driven reactions and the synthesis of novel homogenous and heterogenous electro- and photocatalytic materials as functional bioinspired mimics for carbon monoxide dehydrogenases and hydrogenases. In addition, the manufacturing of industrial relevant electrodes and electrochemical reactors, together with our partners from industry, is within the focus of the group.

Five Selected Publications of Relevance to Catalysis Science.

- Local surface structure and composition control the hydrogen evolution reaction on iron nickel sulfides. C. L. Bentley, C. Andronescu, M. Smialkowski, M. Kang, T. Tarnev, B. Marler, P. R. Unwin, U.-P. Apfel, W. Schuhmann, *Angew. Chem. Int. Ed*. **2018**, *5*7, 4093–4097.
- Influence of the Fe : Ni Ratio and Reaction Temperature on the Efficiency of $(Fe_xNi_{1-x})_9S_8$ Electrocatalysts Applied in the Hydrogen Evolution Reaction. S. Piontek, C. Andronescu, A. Zaichenko, B. Konkena, K. junge Puring, B. Marler, H. Antoni, I. Sinev, M. Muhler, D. Mollenhauer, B. Roldan Cuenya, W. Schuhmann, U.-P. Apfel, *ACS Catalysis*, **2018**, *8*, 987–966.
- Bio-Inspired Design: Bulk Iron-Nickel Sulfide Allows for Efficient Solvent-dependent CO_2 Reduction. S. Piontek, K. junge Puring, D. Siegmund, M. Smialkowski, I. Sinev, B. Roldan Cuenya, U.-P. Apfel, *Chem. Sci.* **2019**, *10*, 1075–1081.
- Seleno-Analogous of Pentlandite ($Fe_{4.5}Ni_{4.5}S_{8-Y}Se_Y$, Y = 1-6): Tuning bulk Fe/Ni Sulphoselenides for Hydrogen Evolution. M. Smialkowski, D. Siegmund, K. Pellumbi, L. Hensgen, H. Antoni, M. Muhler, U.-P. Apfel, *Chem. Comm.* **2019**, *55*, 8792–8795.
- Enhancing the CO_2-electroreduction of Fe/Ni-pentlandite Catalysts by S/Se exchange. K. Pellumbi, M. Smialkowski, D. Siegmund, U.-P. Apfel, *Chem. Eur. J.*, DOI:10.1002/chem.202001289.

Recent Press Releases

“Affordable catalyst for CO_2 recycling”, “How oxygen destroys the core of important enzymes”, “Robust and inexpensive catalysts for hydrogen production”. “Chemiker verwandeln CO_2 in Alkohol”.

POWER-TO-X TECHNOLOGIES:
BIOINSPIRED CATALYSTS AND DEVICE DESIGN

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The efficient reduction of protons and CO_2 under mild conditions is a current challenge for modern society. Nature utilizes enzymatic machineries that comprise iron- and nickel-containing active sites to perform these transformations.[1] Recently, we reported on the formidable HER-activity of bulk $Fe_{4.5}Ni_{4.5}S_8$ electrodes revealing similar structural and functional properties as the enzymes.[2,3] We herein set out to explore the influence of the Fe : Ni ratio on the performance of the electrocatalyst.[4] Using linear sweep voltammetry, we show that the increase in Fe or Ni content, respectively, lowers the activity of the bulk electrocatalyst towards HER. Additionally, with increasing Se content in $Fe_{4.5}Ni_{4.5}S_{8-x}Se_x$, the HER performance is significantly lowered, leading to the conclusion that electronic as well as geometric properties of the active sites can decisively be influenced by homologous substitution.[5] In addition, we show that a temperature increase leads to a significant decrease of the overpotential. Furthermore, due to the resemblance of such sulfides with CO_2 converting enzymes, we likewise investigated $Fe_{4.5}Ni_{4.5}S_8$ electrodes to perform CO_2 reduction.[6] In non-aqueous conditions, this material is indeed a potential catalyst affording CO as main product with high Faradaic yields. Notably, the reactivity of the pentlandite materials can be further tuned by the reactor environment as well as the electrodes shape which was found to be equally.

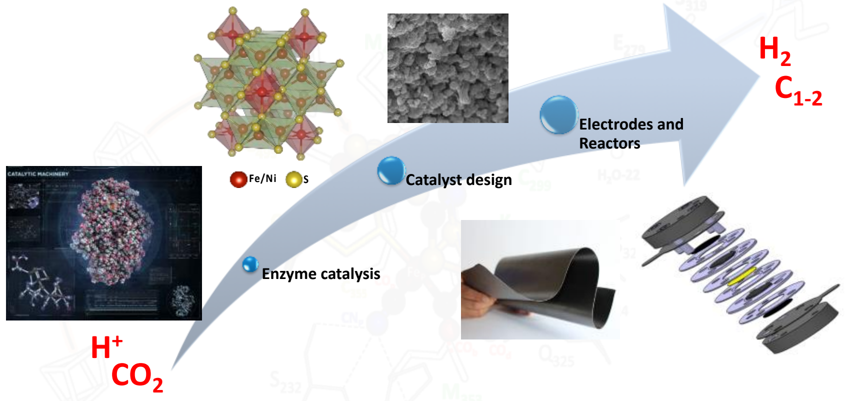

Figure. From enzymes to functional materials - utilizing metal sulfides as biomimetic heterogenous models/catalysts.

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Short Biography. Rosa Arrigo (WoS Researcher ID L-6676-2016) is lecturer in Inorganic Chemistry at the University of Salford in Manchester (UK) and honorary research scientist at the UK' s synchrotron facility Diamond Light Source. Her research interests are focused on the design of nanostructured catalytic systems for applications in green chemistry and energy storage and conversion. Her research strategy consists of establishing molecular level structure-function relationships through the controlled synthesis of tailored materials, testing and thorough structural characterisation, including but not limited to the extensive use of innovative in situ synchrotron-based techniques such as X-ray photoelectron spectroscopy and X-ray absorption fine structure spectroscopy. Current projects focus on the development of hybrid organic/inorganic supported metal and metal oxide nanostructures mimicking structures and functions of biological systems for the conversion of carbon dioxide. Recently, she is investigating the host/guest chemistry in metal-organic frameworks for the delivery of *Aspergillus* derived drugs.

Five Selected Publications of Relevance to Catalysis Science.

- Elucidating the mechanism of the CO_2 methanation reaction over Ni/hydrotalcite-derived catalysts via surface sensitive in situ XPS and NEXAFS, G. Giorgianni, C. Mebrahtu, M. E. Schuster, A. I. Large, G. Held, P. Ferrer, F. Venturini, D. Grinter, R. Palkovits, S. Perathoner, G. Centi, S. Abate, R. Arrigo, *Phys. Chem. Chem. Phys.*, DOI: 10.1039/D0CP00622J.
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- On the High Structural Heterogeneity of Fe-Impregnated Graphitic-Carbon Catalysts from Fe Nitrate Precursor, R. Arrigo, M. E. Schuster, *Catalysts* **2019**, *9*, 303–309.
- Operando X-ray absorption fine structure study of the electrocatalytic reduction of carbon dioxide over Ferrihydrite on nitrogen-doped carbon, C. Genovese, M. E. Schuster, E. K. Gibson, D. Gianolio, V. Posligua, R. Grau-Crespo, G. Cibin, P. P. Wells, D. Garai, V. Solokha, S. Krick Calderon, J. Velasco Velez, C. Ampelli, S. Perathoner, G. Held, G. Centi, R. Arrigo, *Nat. Commun.* **2018**, *9*, 935.
- In situ observation of reactive oxygen species forming on oxygen-evolving iridium surfaces, V. Pfeifer, *T. E. Jones, J. J. Velasco Vélez, R. Arrigo**,** S. Piccinin, M. Hävecker, A. Knop-Gericke, R. Schlögl, *Chem. Sci.* **2017**, *8*, 2143–2149.

Recent Press Releases

"Take a Tour of the Diamond Light Source" in Chemistry world,
"Carbon Dioxide Conversion to Hydrocarbon: Thinking Big to See Small Things",
"Understanding Catalysts and Catalysis".

IN SITU SPECTROSCOPY TO ELUCIDATE THE MECHANISM OF THE CO_2 METHANATION REACTION OVER NICKEL-IRON CATALYSTS

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The renewable energy market from wind power and photovoltaics is rapidly growing and integrated storage technologies are becoming key elements for stabilizing the electricity networks. Amongst the emerging storage technologies, the power to gas (P2G) process has been the subject of intensive studies due to its high potential in terms of storage capacity and duration.[1] A typical P2G system involves the sustainable formation of H_2 from H_2O electrolysis, which is used to catalytically reduce CO_2 to methane via methanation reaction. This contribution is concerned with the CO_2 methanation reaction. Oxide-supported Ni-catalysts are mostly investigated owing to their high activity, high selectivity to methane at relatively lower reaction temperatures (≤ 350 °C) and lower price compared to the noble metals (Ru, Rh, and Pd).[2] However, the deactivation of these catalytic systems under these reaction conditions remains a limiting factor.[2]

Synthetic strategies to improve the catalysts´ performances involve, for example, promotion of Ni with non-noble metals, among which, Fe has shown to be particularly beneficial.[2] In the present study, we undertake a comparative synchrotron based spectroscopic analysis of the electronic structure dynamics of hydrotalcite derived Ni and Ni-Fe systems with the aim to provide a molecular level understanding of the deactivation mechanism and clarify the promotion and stabilizing effect of Fe. By means of surface sensitive in situ ambient pressure X-ray photoelectron spectroscopy (APXPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy under reduction and reaction conditions carried out at the VERSOX beamline, we were able to identify the progressive hydroxylation of the metallic Ni surface causing the switch of the selectivity from methane selective to carbon monoxide selective and the role of Fe in retarding the Ni hydroxylation.[3]

A multi-length scale analysis of the characterization of these systems by means of operando nanoprobe X-ray absorption spectroscopy and electron microscopy is underway, which was carried out using the facility at DLS and Johnson Matthey to provide the atomic scale spatial resolution which will help localize the interfacial dynamics during this catalytic reaction under different conditions of different selectivity.

Acknowledgements. The authors thank DLS for beamtime allocation (proposal SI19472 and MG23844).

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Short Biography. Prof. Bandarenka is a W3 associate professor working at Technical University of Munich since May 2014. He obtained his PhD in Chemistry in 2005 from Belarusian State University. Afterwards, he was a post-doc at the University of Twente in the Netherlands, where he worked on new proton conducting electrolytes. In 2008 he moved to the Technical University of Denmark where he worked on electrocatalysis for energy provision. Between 2010 and 2014 he was a group leader in the Center for Electrochemical Sciences at Ruhr University Bochum, Germany. Prof. Bandarenka conducts research in the area of physics of energy conversion and storage. His main topics include the design and implementation of functional materials and better understanding and characterization of electrified interfaces. The material design is based on so-called bottom-up approach using input from electrochemical surface science and starting from model surfaces. Prof. Bandarenka is the author and co-author of more than 120 publications in refereed journals. He is also currently one of the editors of Applied Surface Science journal (Elsevier).

Five Selected Publications of Relevance to Catalysis Science.

- Enhancing the hydrogen evolution reaction activity of platinum electrodes in alkaline media using Ni-Fe clusters, S. Xue, R. W. Haid, R. M. Kluge, X. Ding, B. Garlyyev, J. Fichtner, S. Watzele, S. Hou, A. S. Bandarenka, *Angew. Chem. Int. Ed*. **2020**, *59*, 10934–10938.
- Tailoring the oxygen reduction activity of Pt nanoparticles through surface defects: a simple top-down approach, J. Fichtner, S. Watzele, B. Garlyyev, R. Kluge, F. Haimerl, H. El-Sayed, W.-J. Li, F. Maillard, L. Dubau, R. Chattot, J. Michalicka, J. Macak, W. Wang, D. Wang, T. Gigl, C. Hugenschmidt, A. S. Bandarenka, *ACS Catal.* **2020**, *10*, 3131–3142.
- Optimizing the size of platinum nanoparticles for enhanced oxygen electro-reduction mass activity, B. Garlyyev, K. Kratzl, M. Rück, T. Kratky, S. Günther, O. Tomanec, R. Zboril, M. Cokoja, A. S. Bandarenka, A. Gagliardi, R. A. Fischer, *Angew. Chem. Int. Ed.* **2019**, *58*, 9596–9600.
- The nature of active centers catalyzing oxygen electro-reduction at platinum surfaces in alkaline media, Y. Liang, D. Mclaughlin, C. Csoklich, O. Schneider, A. S. Bandarenka, *Energy Environ. Sci.* **2019**, *12*, 351–357.
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Recent Press Releases

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Ernst-Haage prize

Water Electrolysis

DETERMINATION OF ELECTROACTIVE SURFACE AREA OF NICKEL-, COBALT-, IRON-, AND IRRIDIUM-BASED OXIDE ELECTROCATALYSTS

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Metal oxides are important functional materials with a wide range of applications, especially in the field of electrocatalysis. However, quick and accurate assessment of their real electroactive surface area (ECSA), which is of paramount importance for the evaluation of their performance, remains a challenging task. In the presentation, I will present a relatively simple strategy for an accurate in situ determination of the ECSA of commonly used metal oxide catalysts, namely: Ni-, Co-, Fe-, Pt- and Ir-based oxides. Similar to the well-established practice in electrocatalysis, the method is based on the phenomenon of specific adsorption. It uses the fact that at the electrode potentials close to the onset of the oxygen evolution reaction (OER), specifically adsorbed reaction intermediates manifest themselves through so-called adsorption capacitance, which is unambiguously detectable using electrochemical impedance spectroscopy.[1,2] With simple impedance measurements, experimentalists can acquire the adsorption capacitance values and accurately estimate the real electroactive surface area of the above-mentioned oxide materials, including nanostructured electrocatalysts. Additionally, as illustrative examples, I will demonstrate an application of the method for the determination of the ECSA of oxide catalyst nanoparticles.

Acknowledgements. Financial support from Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany´s Excellence cluster “e-conversion” and TUM IGSSE cohort 11 (ActiveElectroCat, Project 11.01) are gratefully acknowledged.

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Short Biography: Dr. Clotilde S Cucinotta, EPSRC fellow, early career. Following her Master in theoretical condensed matter physics and her PhD in surface functionalization with organic molecules (2006), Dr. Cucinotta spent four years at ETHZ (CH), where she pioneered new molecular dynamics techniques to model mass diffusion processes and chemical transformation in solids, liquids and at their interface. Here she also matured an interest for the energy problem, studying Hydrogen storage in light weight alloys. Subsequently, Dr. Cucinotta moved to Trinity College Dublin (IE) where she worked on different electron transport problems as well as on energy conversion in solid oxide fuel cells. There she also developed new models for environmental stability of 2D materials. In May 2018 Dr. Cucinotta moved to Imperial College London with an independent fellowship, founded by EPSRC. Here she established her research group and work to develop a new methodology to simulate electrochemical devices - such as electrochemical cells, batteries, memristors and sensors – in operation, including the effect of an applied potential and electric currents. She uses this to study problems like electrochemical water splitting, CO2 reduction, intercalation in anodes for Na-ion batteries, memristive switching and corrosion.

Five Selected Publications of Relevance to Catalysis Science.

- The nanoscale structure of the Pt-water double layer under applied potential revealed, R. Khatib, A. Kumar, S. Sanvito, M. Sulpizi, C. S. Cucinotta, *under review, https://arxiv.org/abs/1905.11850*.
- Liquid exfoliation of solvent-stabilized few-layer black phosphorus for applications beyond electronics, D. Hanlon, C. Backes, E. Doherty, C. S. Cucinotta, N. C. Berner, C. Boland, Z. Gholamvand, P. Lynch, A. Harvey, S. Zhang, K. Wang, G. Moynihan, A. Pokle, Q. M. Ramasse, N. McEvoy, W. Blau, J. Wang, S. Sanvito, D. O’Regan, G. S. Duesberg, V. Nicolosi, J. N. Coleman, *Nat. Commun.* **2015**, *6*, 8563. *DOI*:10.1038/ncomms9563.
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Recent Press Releases

https://www.imperial.ac.uk/news/189848/bringing-electricity-chemistry-together-with-16m/

IMPROVING THE DESIGN OF ELECTROCHEMICAL DEVICES WITH THEORY AND MODELLING

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In this talk I will highlight my research on materials and fundamental atomic process that underpin different areas of energy and nanotechnology, such as in electrolysers, batteries and memristors. I will introduce some issues connected with the simulation of electrified interfaces at the nanoscale focusing on modelling the effect of an applied potential to a cell by simulating charged electrodes [1]. I will present some recent progress in our understanding of the interactions of the electrolyte with the metal under applied potential in the technologically relevant Pt-water interface.

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[1] The nanoscale structure of the Pt-water double layer under applied potential revealed, R. Khatib, A. Kumar, S. Sanvito, M. Sulpizi and C. S. Cucinotta, *https://arxiv.org/abs/1905.11850*.

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Short Biography. Emma Gibson (https://orcid.org/0000-0002-7839-3786) is a LKAS Research Fellow at the University of Glasgow, since moving back in 2017. Her interests lie in applying synchrotron techniques and vibrational spectroscopy to study heterogeneous catalysts under reaction conditions. After doing a PhD with Prof David Lennon in Glasgow (2007) she held several PDRA positions, in France (2007-2011), the Netherlands (2011-2012) and finally spent 4 years at the UK Catalysis Hub labs in Harwell (2013-2017). The campus hosts the UK's central facilities, the ISIS Neutron and Muon Source, the Diamond Light Source and the Central Laser Facility. At Harwell she was involved in several projects developing reactor setups to investigate catalysts under *operando* conditions using X-ray or vibrational spectroscopy techniques. In her current post at Glasgow, she is PI on an EPSRC iCASE funded PhD Studentship with Johnson Matthey and has another student co-funded with ISIS. In addition, she is Co-I on an Industry Academia Partnership Programme from the Royal Academy of Engineering and the Newton Fund organising XAFS workshops in Cape Town, SA, and on a Royal Society International Exchanges Cost Share 2017 China (NSFC) award. She continues to be involved with the UK Catalysis Hub, leading a project in the Core theme on reactor development for synchrotron experiments and continues to serve as PI of the UK Catalysis Hub BAG access route to the core XAFS beamline (B18) at DLS (2016-2020).

Five Selected Publications of Relevance to Catalysis Science.

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A MULTISCALE INVESTIGATION OF ASH LOADED GASOLINE PARTICULATE FILTERS

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Sustainable fuel sources such as pure-electric and fuel cell powered systems have the potential to provide transport solutions that emit near-zero tailpipe gases and particles. However, until these solutions become wide spread, emissions standards for gasoline and diesel vehicles must be met to limit pollution levels in the short term. After-treatment solutions, such as three-way catalysts (TWC) and selective catalytic reduction (SCR), are currently used in gasoline and diesel engines to minimise the emissions of harmful products such as CO, nitrogen oxides (NOx) and volatile organic compounds (VOCs) and particulate matter (PM).[1] PM consists of soot from the incomplete combustion of fuel and incombustible material (ash- Ca, P, S, Zn) mainly due to lubricant oils. This PM has a carcinogenic effect on the respiratory system, especially if in the form of nanoparticles. One solution to tackle particulate emissions from gasoline engines is to coat a Gasoline Particulate Filter (GPF) with the three-way catalyst, to both reduce NOx and limit particulate emissions in one unit. However, one concern is the build-up of ash components, ~60% of which accumulates on the filter walls where it may interact with the catalyst. Taking a multiscale approach to this problem, we performed XAFS measurements averaging results over a 200x200 μm area of the monolith wall, nanoprobe XRF mapping (50 nm resolution) and STEM-EDS imaging (Å-resolution). Samples were analysed pre and post ageing treatment to simulate use of the GPF after > 100,000 km. All of the measurements were performed on the Harwell campus using the Diamond Light Source and so hopefully showcases some of the wide variety of techniques available and their use in heterogeneous catalysis research.

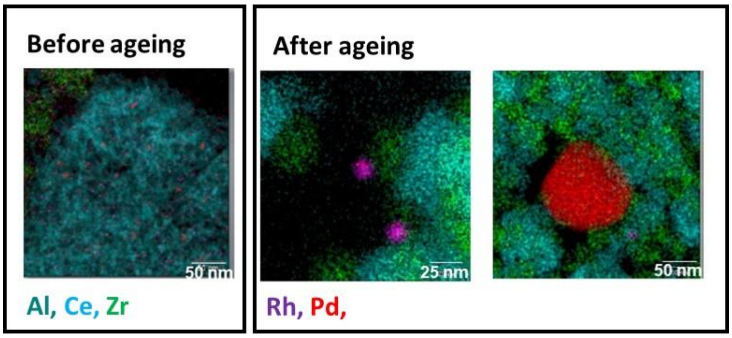

Figure. STEM-EDX on pre and post aged samples was conducted on the JEOL JEM-2800 at Johnson Matthey Technology Centre, Sonning.

Acknowledgements. Funding for M Panchal's PhD is from an EPSRC Industrial CASE award (Project Partner: Johnson Matthey PLC), EP/R512138/1.

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Jun.-Prof. Dr. rer. nat.

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Short Biography. Stephan C. Hammer (ORCID IC 0000-0002-3620-9362) holds the Junior-Professor position (W1 tt W2) for Organic Chemistry and Biocatalysis at the Bielefeld University. His research combines methods from organic chemistry, protein biochemistry and directed evolution to engineer, apply and understand new enzyme function. Completely new catalytic reactions can be envisioned in enzymes, because their macromolecular structure provide a very high level of molecular recognition to control catalytic cycles. Reaction discovery and development in enzyme active sites benefit from the ability to precisely bind substrates in defined conformations, to guide competing reactions pathways and to control highly reactive intermediates such as carbocations and radicals. Stephan's research group aims to develop a new class of catalysts for synthetic organic chemistry that is protein-based, fully genetically encoded and catalyzes fundamental C-C, C-N and C-O bond formations that do not have a good catalytic solution. These new enzymes will potentially be applied in organic synthesis, increase our understanding in enzymology and can expand the metabolism in living organisms. Currently, he is leading the DFG-funded Emmy-Noether research group: New catalytic reaction development by laboratory evolution of protein-based catalysts.

Five Selected Publications of Relevance to Catalysis Science.

- Asymmetric Enzymatic Hydration of Unactivated, Aliphatic Alkenes, R. M. Demming, S. C. Hammer, B. M. Nestl, S. Gergel, J. Pleiss, B. Hauer, *Angew. Chem. Int. Ed.* **2019**, *58*, 173–177.
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Recent Press Releases

Enzymes beats catalysts at the oxidation game

Chemistry of the Year 2017 – Evolved Oxidizer

Dr. Stephan Hammer has been elected for the Emmy Noether Program

ASYMMETRIC ANTI-MARKOVNIKOV ALKENE FUNCTIONALIZATION ENABLED BY ENZYME-CONTROLLED RADICAL AND CARBOCATION CHEMISTRY

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In comparison to heterogeneous and small molecule catalysts, enzymes offer a very high level of molecular recognition. Biocatalysts provide a multitude of precise substrate interactions enabling tight control of substrate conformations, transition states and reaction pathways. We aim to generate highly optimized enzyme active sites that use their molecular recognition to control challenging carbocation and radical chemistry.

Here we show laboratory evolutions of new enzymes that convert terminal as well as internal alkenes to their anti-Markovnikov carbonyl compounds, a challenging reaction in catalysis.[1,2] These anti-Markovnikov alkene oxygenases (aMOx) are derived from P450 monooxygenases that are well-known to catalyze alkene epoxidations in nature. Experimental and computational studies reveal that aMOx catalyze a direct anti-Markovnikov oxene transfer with a hydride migration as key step to generate the corresponding carbonyl product (unpublished). The alkene epoxidation is discriminated since the evolved active sites lock highly reactive radical and carbocation intermediates in specific conformations that are unproductive for the epoxidation pathway. In addition, we observed that the hydride migration is highly regio- as well as enantioselective. This opens the door to asymmetric anti-Markovnikov alkene oxidations – an unexplored area in catalysis. To investigate scope and limitation in synthesis, we combined an evolved aMOx for internal alkenes with other biocatalysts to perform redox hydration and hydroamination of alkenes (unpublished). This yields chiral anti-Markovnikov alcohols and amines from alkenes, a transformation that currently lacks efficient catalytic protocols.

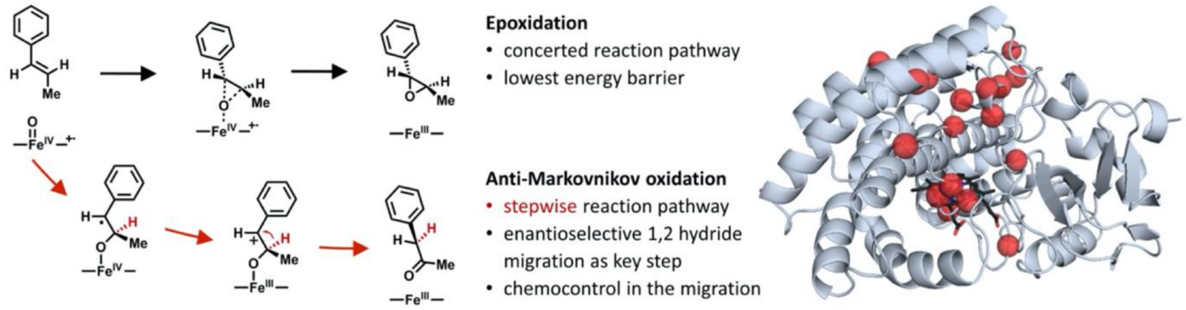

Figure 1. Anti-Markovnikov alkene oxidation by metal-oxo–mediated enzyme catalysis.

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Short Biography: Corinna Hess received her undergraduate degree (BS Chemistry) from the University of Chicago. She subsequently pursued her PhD studies in the field of bioinorganic chemistry, supervised by Professor Harry Gray, at the California Institute of Technology. As part of her PhD project, she carried out electrochemical studies with an amine oxidase. Following postdoctoral positions at the University of California, Berkeley, and the Max Planck Institute for Bioinorganic Chemistry, she joined the Chemistry Department at Durham University as a lecturer (2010). In 2014 she was appointed assistant professor of bioinorganic chemistry at the Technical University of Munich (TUM). Research in the Hess lab centers on the development of catalysts for multi-electron transformations, including H_2 production and O_2 activation, as well as the development of earth-abundant photocatalysts.

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DEVELOPMENT OF EARTH-ABUNDANT PHOTOCATALYSTS BASED ON THE MACROCYCLIC MABIQ LIGAND

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Photoredox catalysts are increasingly being employed in organic synthesis, and particularly in conjunction with organometallic catalysts, have enabled numerous novel reactivities. However, the photoactive metal complexes in these systems are commonly Ru- and Ir-based complexes. A key goal within the realm of sustainable chemistry is to replace these noble metal complexes with inexpensive, earth-abundant alternatives. Our own work in this area has focused on studies with a series of late, first-row transition metal complexes coordinated by a macrocyclic ligand, Mabiq. The M^{II}-Mabiq complexes in this series are photoactive, and can be photochemically reduced to the formally M^{I}-Mabiq forms. The Zn^{II}-Mabiq complex acts as a $^1O_2$ sensitizer, while the Ni analogue was successfully employed in a photoredox catalyzed cyclization reaction. A series of bimetallic Mabiq complexes also have been synthesized and likewise, are photoactive. The photophysical properties and reactivity of the M_n-Mabiq compounds will be presented.

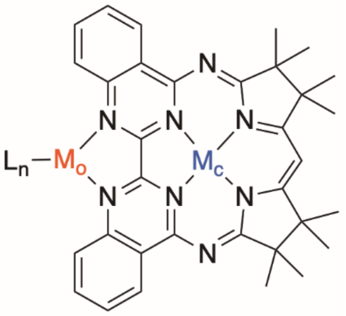

Figure. Macrocyclic Mabiq ligand contains two available coordination sites.

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Short Biography: Søren Kegnæs (WoS Researcher ID E-1891-2011) holds the Chair of Inorganic and Catalysis at the Department of Chemistry at Technical University of Denmark (DTU). The research group of Søren Kegnæs is part of The Centre for Catalysis and Sustainable Chemistry at DTU. The primary scientific field of Søren Kegnæs is within the design of functional nanomaterials, their characterization and application in heterogeneous catalysis and energy conversion. His research interest includes on framework materials like zeolites, MOFs, polymers. He has a specific focus on the synthesis of functional nanoparticles and materials with high surface area and controlled porosity. The core competence and strength of his research group are based on the synthesis skills combined with understanding of heterogeneous catalysis. Therefore, the aim in group of Søren Kegnæs is to develop materials which are optimized and adapted to the target applications in heterogeneous catalysis and energy conversion.

Five Selected Publications of Relevance to Catalysis Science.

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METAL NANOPARTICLES CONFINED IN POROUS MATERIALS FOR SELECTIVE CATALYSIS

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In spite of the great technological, environmental and economic interests, general methods for the stabilization of nanoparticles against sintering are missing. Although for some specific systems, it has been achieved by optimizing the interaction of nanoparticles with a support material or by encapsulation of the metal particles.[1-3] However, these known catalytic systems are in general rather expensive and difficult to synthesize and they can't be produced in industrial scale. Therefore, the development of novel sintering stable heterogeneous nanoparticle catalysts, which find use in the chemical industry, is of great importance.

Recently, we have developed several different catalytic systems where metal nanoparticles are confined in different porous materials including zeolites,[3-5] porous polymers (POP)[6], and carbon materials[7]. Here, we give an overview of the progress, which has been made, on the synthesis of metal nanoparticles confined in different porous materials and their application in catalysis. The confinement of nanoparticles in porous materials can, beside thermal stability, also contribute active to the catalytic reaction by improving the catalysts activity or selectivity for instance by controlling the accessible or type of activity sites.[3,5]

We have tested the produced materials as catalysts in different selective oxidation and hydrogenation reactions. For instance, Ni particles encapsulated in zeolites, see Figure 1, where highly active in methanisation of CO_2 to CH_4.[5] Furthermore, the location of the metal particles have a great influence on the catalyst activity. Additionally, the encapsulation of other nanoparticles, like Cu, Ru, Pd and Pt were demonstrated to be highly active and selective in various gas-phase reactions including catalytic oxidation of ethanol to acetaldehyde and hydrogenation of alkenes.[4,8] All materials were characterized by various techniques including SEM, in situ TEM, STEM, TEM tomography, XPS, XRF, BET and XRD.

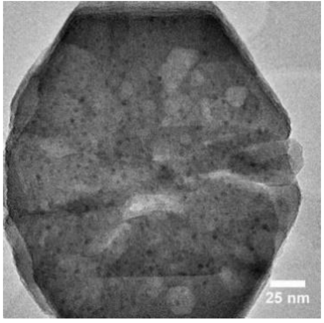

Figure 1. TEM image of nickel nanoparticles encapsulated in MFI zeolite.

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NANOSCALE CATALYSTS' PROPERTIES REVEALED BY IN-SITU SCANNING PROBE MICROSCOPY

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(Photo-) Electrocatalysts represent dynamic entities with their morphology, composition and oxidation state being subject to change under liquid-phase reaction conditions and external stimuli. At present, deficient understanding of nanoscale materials properties and lacking structure-property correlations under reaction conditions impede the rational design of robust, active and selective catalysts for key catalytic reactions including (photo-) electrochemical CO_2 reduction (CO_2RR). The potential of in-situ scanning probe microscopy-based methods (SPM; EC-AFM / STM)[1] will be discussed in the context of prevailing questions in (photo-) electro-catalysis: How do electrocatalytic materials evolve under reaction conditions and which factors impact catalyst dynamics at the nanoscale? How do catalytic selectivity and activity correlate with structure / composition / oxidation state of catalysts? What are the underlying chemical and physical reaction mechanisms?

Selected results will be presented starting with the potential-dependent morphology of copper-based electrodes during CO_2RR.[2] Our results reveal distinct surface morphologies over wide potential ranges upon electrode exposure to electrolytes and during CO_2RR, which can be understood by surface mobility and specific adsorption. Morphological changes are followed *in-situ* in potentiostatic image series and atomically stepped surfaces can be established under reducing conditions. With the combination of electrochemical electrode characterization and local real space structure and morphology information, light is shed into the general behaviour of polarized electrode surfaces. Further, recent insights into interface dynamics associated with electrochemical stimuli will be shared.[4] In addition, results on investigating interfacial electron transfer processes at electrified solid-liquid interfaces with nanometer spatial resolution will be presented as well as atomic-scale insights into hybrid organic-inorganic catalysts for CO_2RR be provided. Strategies will be discussed how fundamental findings combined with complementary microscopic and spectroscopic characterization can be translated into novel synthetic strategies for the design of next-generation CO_2RR catalysts.

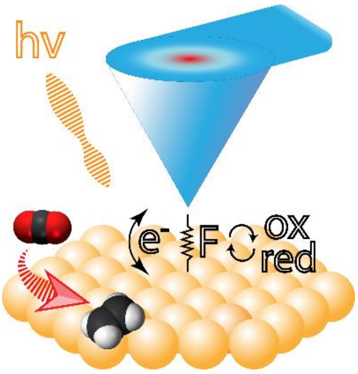

Figure. Revealing in-situ morphological, electrical, and catalytic properties of CO_2RR catalysts at the nanoscale.

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Five Selected Publications of Relevance to Catalysis Science.

- Influence of local defects on the dynamics of O-H bond breaking and formation on a magnetite surface, A. Bourgund, B. A. J. Lechner, M. Meier, C. Franchini, G. S. Parkinson, U. Heiz, F. Esch, *J. Phys. Chem. C* **2019**, *123*, 19742.
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TOWARDS ATOM-BY-ATOM CATALYST DESIGN: FUNDAMENTAL INSIGHTS FROM REAL-TIME MICROSCOPY

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In heterogeneous catalysis, a high catalytic activity is sometimes caused by the internal structural fluxionality of supported clusters,[1] while sintering into larger particles typically leads to catalyst deactivation. The atomic-scale mechanisms underlying these processes are far less well-understood than one might expect. If we precisely understood the correlation between catalyst dynamics and activity, however, we could design stable, yet intrinsically dynamic (i.e. structurally fluxional) catalysts.

To this purpose, we have accelerated our scanning tunneling microscopy (STM) to video frame rates,[2] thus allowing us to investigate the dynamics of clusters on single crystalline supports. In the case of Pd_n ($1 \leq n \leq 19$) on a hexagonal boron nitride nanomesh, we successfully monitored reversible cluster isomerization *in situ* and found that while an atom diffuses rapidly along the rim of pores, a small cluster jumps between six sites around the pore center.[3] In contrast, Pt_n clusters on a magnetite $Fe_3O_4(001)$ surface do not exhibit lateral or internal dynamics and instead appear to sink into the surface with increasing temperature, indicating a change in cluster–support interface.

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His research focuses on the computational modelling of catalytic materials, and is divided between two complementary themes of software development and chemical materials simulation. Computational catalysis is a fast-growing and exciting field due to the possibility of testing and tuning reactive systems on the computer before exhaustive laboratory investigation. Currently, he is a co-investigator on the EPSRC Centre-to-Centre grant "New trimetallic nanoparticles as catalysts for the conversion of carbon dioxide to renewable fuels", and he has on-going interests in:

- the structure and reactivity of multi-element metal nanoparticles for chemical synthesis;
- the catalytic chemistry of defective and doped metal oxide surfaces;
- the structure and application of zeolites for MTH and biomass transformation;
- the upgrading of ethanol to butanol using transition-metal homogeneous catalysts.

His work to develop state-of-the-art computational models is realised through the hybrid quantum/molecular mechanical (QM/MM) approach, which opens up exciting opportunities for high-level theory or the modelling electronically charged systems, all of which are infeasible with common methods.

Five Selected Publications of Relevance to Catalysis Science.

- Role of the Support in Gold-Containing Nanoparticles as Heterogeneous Catalysts, S. Meenakshisundaram, Q. He, R. V. Engel, M. A. Sainna, A. J. Logsdail, A. Roldan, D. J. Willock, N. Agarwal, C. J. Kiely, G. J. Hutchings, *Chem. Rev.* **2020**, *120*, 3890.
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- Hydride Pinning Pathway in the Hydrogenation of CO_2 into Formic Acid on Dimeric Tin Dioxide, P. J. Sarma, S. D. Baruah, A. J. Logsdail, R. C. Deka, *ChemPhysChem* **2019**, *20*, 680.
- Computational QM/MM investigation of the adsorption of MTH active species in H-Y and H-ZSM-5, S. A. F. Nastase, A. J. O'Malley, C. R. A. Catlow, A. J. Logsdail, *Phys. Chem. Chem. Phys.* **2019**, *21*, 2639.
- Computational investigation of CO adsorbed on Au_x, Ag_x and $(AuAg)_x$ nanoclusters ($x = 1 – 5, 147$) and monometallic Au and Ag low-energy surfaces, A. L. Gould, C. R. A. Catlow, A. J. Logsdail, *Eur. Phys. J. B* **2018**, *91*, 32.

COMPUTATIONAL INSIGHT INTO THE INITIAL STAGES OF THE METHANOL-TO-HYDROCARBON PROCESS

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Reducing society's fossil fuel dependence is at the forefront of current research efforts, with alternative carbon sources, such as biomass, showing great potential due to viable, sustainable production routes being developed for their conversion to fuels and fine chemicals. Various routes for biomass valorisation are currently of academic and commercial interest; for instance, methanol can be produced from biomass-derived syngas, which can then be converted to a wide range of useful hydrocarbons using zeolite catalysts.[1] This Methanol-to-Hydrocarbons (MTH) process is one of the promising technologies to bypass crude oil in the production of fuel and light olefins and is now used on industrial scale;[2] however controlling the product selectivity and deactivation rate remains a challenge, especially due to a lack of clear understanding of how the catalyst influences the formation of the first C-C bond.

Experimental characterisation of the MTH reaction, and catalyst influence, is challenging due to the fast and complex nature of the sequential catalysed reactions; thus, computational approaches have proven pivotal in providing insight to reaction mechanisms, and allow *in silico* refinement of catalyst materials and reaction conditions in order to improve efficiency. In this work, we present our investigations on the initial steps of the MTH process, including zeolite framework methoxylation, formation of dimethyl ether and then formation of the first C-C bonds.[3-5] We use a combination of state-of-the-art static and dynamical approaches to show that acid site distribution and reactant loading make a significant difference to reactivity, with a key initial step being abstraction of the framework Brønsted proton. The outcomes from our simulations lay the foundations for on-going efforts to tailor zeolite catalysts for optimal efficiency in the MTH process.

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Short Biography. Sandra Luber is professor in theoretical and computational chemistry at the University of Zurich. She carried out her PhD studies at ETH Zurich (2007-2009). Afterwards she joined the Biozentrum Basel, Yale University, and BASF. The habilitation thesis was finished in 2016. Her research interests focus on development of theoretical methods at the interface of chemistry, biology, physics, and materials science with emphasis on approaches derived from quantum mechanics. Main recent research directions have included spectroscopy, catalysis, and *in silico* design of functional compounds. In the field of catalysis, she has mainly been working on the development of artificial water splitting embedded in the priority program “Solar light to chemical energy conversion”. Besides e.g. informed design approaches, her current work in catalysis has dealt with an improved description of dynamic and environmental effects in catalysis as well as accurate electronic structure for the simulation of highly involved transition metal compounds. She has been honored with numerous awards. Selected awards since 2017 include the Clara Immerwahr Award (first theoretician awarded), Hans G. A. Hellmann Award and Robin Hochstrasser Award (first woman awarded), Werner Prize of the Swiss chemical society, Carl Duisberg Memorial Award of the German chemical society, OpenEye Outstanding Junior Faculty Award of the American chemical society, and the Jochen Block Prize of the German catalysis society.

Five Selected Publications of Relevance to Catalysis Science.

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- Zooming in on the O-O bond formation – An Ab Initio Molecular Dynamics Study Applying Enhanced Sampling Methods, M. Schilling, R. A. Cunha, S. Luber, *J. Chem. Theory Comput.* **2020**, *16*, 2436–2449.
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- Discovery of Open Cubane Core Structures for Biomimetic $LnCo_3(OR)_4$ Water Oxidation Catalysts, M. Schilling, F. Hodel, S. Luber, *ChemSusChem* **2017**, *10*, 4561–4569.

Selected Recent Media and Press Releases

“Catalysis and Design – Jochen Block Prize”, “Using sunlight to produce energy from water”,
Interview in ChemCatChem.

COMPUTATIONAL STUDIES AND DESIGN IN THE FIELD OF BIO-INSPIRED ARTIFICIAL WATER SPLITTING

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Solar energy is an inexhaustible energy source for a sustainable solution to the global energy consumption. The storage of large amounts of light energy can be achieved by conversion into chemical energy saved in biomass. Artificial photosynthesis permits the splitting of water into molecular hydrogen and oxygen and is therefore a very promising strategy to meet the increasing worldwide need for clean energy. This requires the development of high-performance water-reduction and water-oxidation catalysts where the latter is currently the main bottleneck for efficient photocatalytic water splitting. Detailed analysis of the catalytic functioning and the factors determining the efficiency of catalysts is a prerequisite for the design of more efficient catalysts. We present our recent research for the in-depth study of water splitting catalysis using forefront computational methods. In particular, we go beyond standard computational approaches using very accurate wavefunction-based electronic structure methods as well as high-performance ab initio molecular dynamics. The latter allows for an improved inclusion of solvent and environmental effects at ambient conditions, which have been shown to have a decisive influence on the behaviour of the catalysts, and paves the way for highly sophisticated complete free energy surfaces and elucidation of reaction networks using enhanced sampling methods.

In close collaboration with experimental groups, we have recently investigated in detail for instance bio-inspired water oxidation catalysts, which feature a cubane core in analogy to the oxygen-evolving complex in nature’s photosystem II. Other projects have dealt with the study of reaction networks and in silico design of bio-inspired Ru-based water oxidation catalysts or Co-based water reduction catalysts.

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Five Selected Publications of Relevance to Catalysis Science.

- Site Specific and Localized Structural Displacements in Open Structured Multimetallic Oxides, T. Lunkenbein, L. Masliuk, M.Plodinec, G. Algara-Siller, S. Jung, M. Jastak, P. Kube, A. Trunschke, R. Schlögl, *Nanoscale* **2020**, 12, 6759–6766.
- Visualizing the Importance of Oxide-Metal Phase Transitions in the Production of Synthesis Gas over Ni Catalysts, L. E. Sandoval-Diaz, M. Plodinec, D. Ivanov, S. Poitel, A. Hammud, H. C. Nerl, R. Schlögl, T. Lunkenbein, *J. Energy Chem.* **2020**, *50*, 178–186.
- Insights into Chemical Dynamics and their Impact on the Reactivity of Pt Nanoparticles during CO Oxidation by Operando TEM, M. Plodinec, H. C. Nerl, F. Girgsdies, R. Schlögl, T. Lunkenbein, *ACS Catal.* **2020**, *10*, 3183–3193.
- A Versatile Homebuilt Gas Feed and Analysis System for Operando TEM of Catalysts at Work, M. Plodinec, H. C. Nerl, R. Farra, M. G. Willinger, E. Stotz, R. Schlögl, T. Lunkenbein, *Microsc. Microanal.* **2020**, *26*, 220–228.
- A Quasi in-situ TEM Reactor for Decoupling Catalytic Gas Phase Reaction and Analysis, L. Masliuk, M. Swoboda, G. Algara-Siller, R. Schlögl, T. Lunkenbein, *Ultramicroscopy* **2018**, *195*, 121–128.

OPERANDO ELECTRON MICROSCOPY – VISUALIZING DIFFERENT CONTRIBUTIONS OF CHEMICAL DYNAMICS

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Heterogeneous catalysis has emerged to a ubiquitous technology in chemical industry. Its protagonists are metastable nanomaterials that adapt to the chemical potential of the environment.[1] Their working structures form during reaction, can vary on the local scale and are often only stable under one specific condition. Recent developments for *operando* electron microscopy experiments (OPEX) allow studying catalysts in their working environment and visualizing *in situ* generated morphologies and phases on the nanoscale.[2],[3] Such reaction induced morphological and structural alterations are part of chemical dynamics that can be divided into reversible (dynamic) and irreversible (transformation) contributions.[4]

Here we will present how OPEX supports untangling different contributions of chemical dynamics using CO oxidation over Pt nanoparticles and synthesis gas production over Ni catalysts as an example. The experiments were conducted inside an aberration corrected transmission electron microscope (TEM) or a modified environmental scanning electron microscope (ESEM). As we will show for CO oxidation, at low activity morphological transformations dominate, while at high activity structural dynamics prevail.[5] Morphological transformations and structural dynamics are characterized by the exposure of low-index surface facets and the occurrence of frustrated phase transitions, respectively. In addition, OPEX reveals that for a specific reaction morphological transformations and structural dynamics can have an opposite effect on the performance. For instance, while morphological transformations lead to deactivation, structural dynamics are needed to maintain a high activity. Chemical dynamics have also been observed for the synthesis gas production over Ni catalysts. For this reaction morphological surface transformations lead to a change of the reaction mechanism, while reversible oxide-metal phase transitions modulate the activity.[6]

In summary, OPEX allows investigating catalysts at work and disentangling different contributions of chemical dynamics as well as their assignments to different activity regimes. Prospectively, OPEX will enhance our understanding on the origin of the function of heterogeneous catalysts.

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Five Selected Publications of Relevance to Catalysis Science.

- Covalent Organic Framework Films through Electrophoretic Deposition-Creating Efficient Morphologies for Catalysis, J. M. Rotter, S. Weinberger, J. Kampmann, T. Sick, M. Shalom, T. Bein, D. D. Medina, *Chem. Mater*. **2019**, *31*, 10008–10016.
- Switching On and Off Interlayer Correlations and Porosity in 2D Covalent Organic Frameworks T. Sick, J. M Rotter, S. Reuter, S. Kandambeth, N. N. Bach, M. Döblinger, J. Merz, T. Clark, T. B. Marder, T. Bein, D. D. Medina, *J. Am. Chem. Soc.* **2019**, *141*, 12570–12581.
- Oriented Thin Films of Electroactive Triphenylene Catecholate-Based 2D Metal-Organic Frameworks, A. Mähringer, A. C. Jakowetz, J. M. Rotter, B. J. Bohn, J. K. Stolarczyk, J. Feldmann, T. Bein, D. D. Medina, *ACS Nano*, **2019**, *13*, 6711–6719.
- Oriented Films of Conjugated 2D Covalent Organic Frameworks as Photocathode for Water Splitting, T. Sick, A. G. Hufnagel, J. Kampmann, I. Kondofersky, M. Calik, J. M. Rotter, A. Evans, M. Döblinger, S. Herbert, K. Peters, D. Böhm, P. Knochel, D. D. Medina, D. Fattakhova-Rohlfing, T. Bein, *J. Am. Chem. Soc.* **2018**, *140*, 2085–2092.
- Directional Charge-carrier Transport in Oriented Benzodithiophene Thin Films, D. D. Medina, M. L. Petrus, A. N. Jumabekov, J. T. Margraf, S. Weinberger, J. M. Rotter, T. Clark, T. Bein, *ACS Nano*, **2017**, *11*, 2706–2713.

COVALENT ORGANIC FRAMEWORK FILMS THROUGH ELECTROPHORETIC DEPOSITION-CREATING EFFICIENT MORPHOLOGIES FOR CATALYSIS

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The ability to grow covalent organic framework (COF) films allows for studying their properties as solid layers and enables their incorporation into a variety of functional devices. [1] Here, the fabrication of COF films and coatings by electrophoretic deposition (EPD) is presented. We demonstrate that the EPD technique is suitable for depositing COFs featuring two- and three-dimensional structures linked by imine or boronate ester bonds on charged electrode. Through EPD, within 2 min, large-area films (up to 25 cm^2) exhibiting an inherent textural porosity are obtained on smooth or corrugated surfaces. By controlling the deposition parameters such as duration and applied potential, deposits of precise thickness can be produced. Furthermore, co-depositions of different COFs as well as COF/Pt nanoparticles from mixed suspensions are illustrated. The film morphologies obtained by EPD are shown to be advantageous for catalysis, as demonstrated for sacrificial agent-free photoelectrochemical water reduction. Here, the imine-linked BDT-ETTA COF (consisting of tetraphenylethylene and benzodithiophene) photocathodes show a strongly increased photocurrent density compared to the respective dense and oriented films.[2] Furthermore, BDT-ETTA COF/Pt nanoparticle hybrid films exhibit photocurrent densities of over 100 μA cm^{-2}. The rapid and scalable deposition of COF particles as films and coatings through EPD is a versatile addition to the toolbox of COF film fabrication techniques, allowing for tailoring COF film architectures for desired functionalities. [3]

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Short Biography. Florian Meirer was born in Vienna, Austria and studied technical physics at the Vienna University of Technology with special emphasis on X-ray physics, especially synchrotron radiation induced X-ray fluorescence analysis and absorption spectroscopy in total reflection geometry in the group of Prof. C. Streli. He graduated in 2008 and started a postdoctoral research fellowship (Erwin Schrödinger fellowship, Austrian Science Fund) at the Stanford Synchrotron Radiation Lightsource, Menlo Park, USA in the group of Prof. P. Pianetta. In 2010 he obtained a Marie-Curie Cofund fellowship and joined the team of Dr. M. Bersani at the Fondazione Bruno Kessler, Trento, Italy focusing on dopant activation research for advanced CMOS technology.
Since 2013 he is employed as Assistant Professor in the Inorganic Chemistry and Catalysis group at Utrecht University, reinforcing the group of Prof. B.M. Weckhuysen, in the field of (X-ray) spectro-microscopy and data mining. His past and current research focuses on development and application of spectro-microscopic techniques for obtaining insights about nanoscale processes that are critical for understanding how advanced functional materials, such as semiconductor materials or catalysts, operate at multiple length scales, but also how certain agents behave in or impact the environment. Here a strong focus is on mass transport phenomena at multiple length scales. His field of expertise in the area of atomic spectroscopy includes X-ray spectroscopic techniques, especially absorption spectroscopy in combination with 2D and 3D imaging or special experimental setup geometries (e.g. grazing incidence or grazing exit geometries), and, not limited to X-ray spectroscopy, multi-variate analysis of large spectroscopic data sets including network analysis and machine learning.

Five Selected Publications of Relevance to Catalysis Science.

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- Correlated X-ray Ptychography and Fluorescence Nano-Tomography on the Fragmentation Behavior of an Individual Catalyst Particle during the Early Stages of Olefin Polymerization, K. W. Bossers, R. Valadian, S. Zanoni, R. Smeets, N. Friederichs, J. Garrevoet, F. Meirer, B. M. Weckhuysen, *J. Am. Chem. Soc.* **2020**, *142*, 3691–3695.
- Unraveling Structure Sensitivity in CO_2 Hydrogenation over Nickel, C. Vogt, E. Groeneveld, G. Kamsma, M. Nachtegaal, L. Lu, C. J. Kiely, P. H. Berben, F. Meirer, B. M. Weckhuysen, *Nat. Catal.* **2018**, *1*, 127–134.
- Spatial and temporal exploration of heterogeneous catalysts with synchrotron radiation, F. Meirer, B.M. Weckhuysen, *Nat. Rev. Mater.* **2018**, *3*, 324–340.
- Single-Molecule Fluorescence Microscopy Reveals Local Diffusion Coefficients in the Pore Network of an Individual Catalyst Particle, F. C. Hendriks, F. Meirer, A. V. Kubarev, Z. Ristanovic, M. B. J. Roeffaers, E. T. C. Vogt, P. C. A. Bruijnincx, B. M. Weckhuysen, *J. Am. Chem. Soc.* **2017**, *139*, 13632–13635.

PORE-SPACE EXPLORATIONS USING X-RAY MICROSCOPY AND SINGLE-PARTICLE TRACKING

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Mass transport of reactant molecules through the porous matrix of catalyst particles plays a key role in heterogeneous catalysis, as it directly affects catalyst efficiency in diffusion-limited systems. In order to measure and properly model diffusion in these complex pore structures, we use a combination of 3D correlated X-ray microscopy (3D XRM)[1-3] and single-molecule fluorescence / single-particle tracking (SMF/SPT)[4,5] that provide highly complementary information (Figure 1). Based on this information, mass transport simulations are performed studying in-diffusion of reactants, their conversion into products at the zeolite domains, and subsequent out-diffusion of those products.[6] Our results not only reveal active sites accessibility but allow a quantification and visualization of reactant and product diffusion inside the three-dimensional pore network of a single catalyst particle over time.

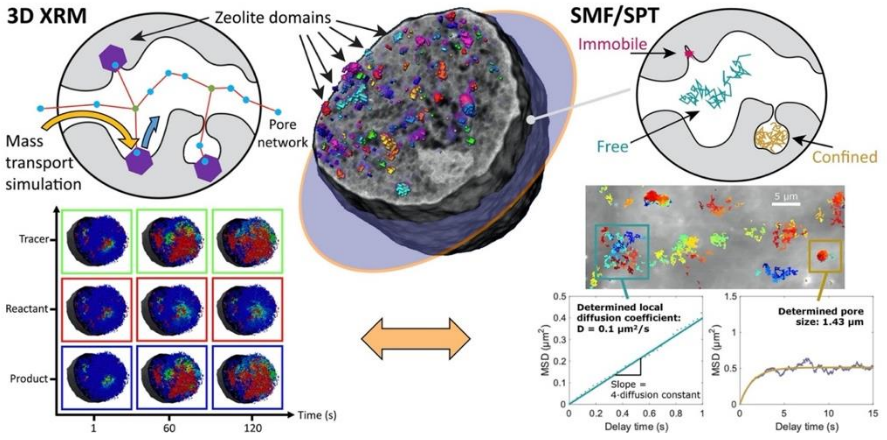

Figure 1. 3D X-ray microscopy (3D XRM) and single-molecule fluorescence / single-particle tracking (SMF/SPT) exploring a catalyst particle's pore space.

Correlated XRM provides 3D information about the pore space and the distribution of a catalyst's components – here an individual fluid catalytic cracking catalyst (FCC) particle. A pore network is established and used for mass transport simulations, including the change of a feedstock molecule into a product at the zeolite domains.[6] These simulations are cross-checked with SMF/SPT experiments via super-resolution fluorescence microscopy inspecting one virtual slice through an FCC catalyst particle and providing highly complementary information at the length scale of the individual random walker.[5]

Acknowledgements. The work is supported by a Netherlands Organization for Scientific Research (NWO) VIDI Grant No. 723.015.007 and the NWO Gravitation program, Netherlands Center for Multiscale Catalytic Energy Conversion (MCEC).

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Short Biography. Marcus Rose (Researcher ID F-6784-2013, ORCID: 0000-0001-8196-1353) holds the Chair of Chemical Technology II at the Technical University of Darmstadt (TUDa) since 2017 and is currently the Dean of Studies of the Department of Chemistry. He studied Chemistry and got his PhD at Dresden University of Technology with research stays at the Georgia Institute of Technology and the Max-Planck-Institut für Kohlenforschung. Before being appointed full professor at TUDa he was research group leader at the RWTH Aachen University in the Department of Chemical Technology.
Currently he is editorial board member of the Journal *Materials* and co-organizer of the South-West-German Catalysis Course. He is co-author of Key Topic Collection for Catalysis Teaching of the German Catalysis Society. He was awarded the RWTH Innovation Award and the Hochschullehrer-Nachwuchs-Preis of the DECHEMA.
His research interest covers heterogeneous catalysis, reaction engineering and separation technologies based on novel functional materials and for the utilization of renewable resources. His group develops novel nanoporous organic framework and polymer materials with specific functions and textural properties. Applications focus on tuning catalytic active sites and their separation performance based on selective adsorption and membrane nanofiltration mainly for liquid phase systems such as in biorefineries. Novel synthetic routes for catalytic materials and innovative catalyst shaping by additive manufacturing are explored. Catalytic investigations aim to establish new value-added chains in biomass utilization. Experimental approaches range from basic catalyst and reaction parameter screening in batch pressure reactors up to investigation and modeling of reaction kinetics to understand reaction networks and mechanistic features. Also, mass transfer properties and limitations are unraveled and catalytic performances are investigated using advanced continuously operated reactor setups in the gas and liquid phase. The major goal is to prove the feasibility and competitiveness of novel catalysts and reaction routes and advance the field by combining sustainable chemistry, materials design and catalysis engineering.

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ORGANIC FRAMEWORKS AS SOLID MOLECULAR CATALYSTS

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Nanoporous organic materials offer unique properties and opportunities to extend applications in catalysis beyond conventional zeolites, carbons and other porous materials due to chemically well-defined surface functions and active sites that are tunable on a molecular level.[1] In this contribution three strategies are presented regarding advances of organic frameworks as solid molecular catalysts:

1) Tin-based organic frameworks as “organozeolite” catalysts show an unexpected catalytic activity and an “inverse” selectivity in isomerization of monosaccharides compared to conventional tin-based zeolites.[2] The materials consist of a three-dimensional framework of aromatic linkers that are covalently connected by Sn-atoms. The inverted selectivity is mechanistically investigated with isotopically labelled substrates. Different reaction mechanisms are revealed that result from the different chemical nature of the active tin-sites and their different chemical environment in the nanopores. In current work the synthesis is improved to enable tailor-made active sites in combination with advanced characterization tools such as *dynamic nuclear polarization* (DNP) MAS NMR.

2) Amine-based organic frameworks enable for the first time heterogeneously catalyzed metal-free hydrogenation reactions based on the concept of frustrated Lewis-pairs.[3] An insoluble hypercrosslinked polyamine-based organic framework as solid Lewis base serves as support for tris(pentafluorophenyl)borane (BCF) as the Lewis acidic counterpart. The Lewis adduct, “frustrated” and thus, highly reactive due to sterical hindrance, is able to activate hydrogen and catalytically hydrogenate alkenes. The materials structure, the Lewis acid-base-interactions and their catalytic performance were comprehensively analyzed.

3) In a third approach solid polyphosphine organic frameworks are applied as nanoporous macroligands for the immobilization of metal complexes by coordination within the phosphine-functionalized framework. The resulting catalysts are active heterogenized molecular catalysts for the hydroformylation of alkenes.

Overall, these approaches proof the suitability of organic frameworks catalysts to bridge the gap between homogeneous and heterogeneous catalysis by combining the advantageous features of molecular and solid metal- and organocatalysts.

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CONTROLLING THE FORMATION OF ACTIVE CU-OXO NANOCLUSTERS FOR DIRECT METHANE OXIDATION TO METHANOL

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Cu-oxo nanoclusters hosted in zeolites are able to convert selectively methane into methanol at moderate temperatures in a three-stage reaction.[1] Cu-exchanged mordenite (MOR) catalysts show the highest methanol yields, attributed to a preferential formation of active Cu_3O_3 clusters in its 8-MR pores.[2] In our previous work we have shown that by adjusting synthesis parameters, it is possible to achieve the homogeneous formation of these active Cu_3O_3 sites in MOR.[3] Here we apply an analogous strategy to other zeolite frameworks, in order to study the role of topology in the formation of Cu-oxo active species.

Similarly to MOR, Cu species hosted in MEL and FER zeolites showed a linear increase of activity with Cu loading (Figure 1). This indicates that a controlled speciation of Cu into formation of Cu-oxo active nanoclusters has been achieved. Cu-FER shows an offset of activity indicating that the preferred Cu exchange positions at low loadings, identified via IR spectroscopy, are inactive. Spectroscopic characterization shed light into the structure and location of these Cu active species in 8- and 10-MR zeolites.

Results of this study show that the interplay of synthesis and activation parameters with the thermodynamically preferred ionic exchange positions - affected by local environment and zeolite properties - determines the formation of active Cu-oxo clusters in zeolites.

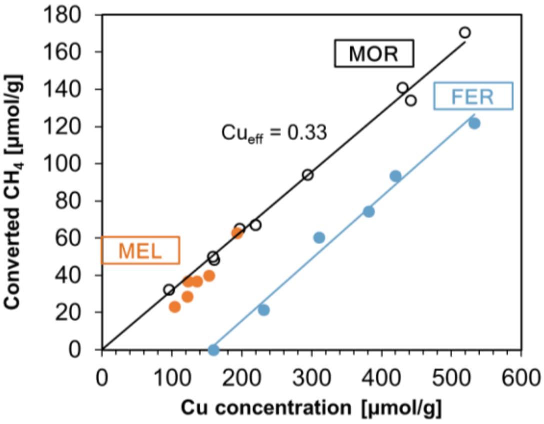

Figure 1. Yield of CH_4 converted in one reaction cycle (activation in O_2 at 450 °C followed by 4 h CH_4 loading at 200 °C) for different Cu-zeolites. Cu efficiency (Cu_{eff}) is defined as mol CH_4 activated per mol Cu. Selectivity to methanol within 75-80 % for all samples.

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Short Biography. Juliane Simmchen (ORCID 0001-9073-9770) is currently a Freigeist Fellow at the TU Dresden. Her lab focusses on catalytically active colloidal materials and the physical principles governing their interactions. The basic principle is to construct micromotors from innovative material combinations to confer activity to them through catalytic and photocatalytic processes. Applications range from energy supply of microscale machining to drug delivery and environmental remediation, not to forget investigations on information transport as well as communication strategies on both, the individual particle level and in swarms. This highly multidisciplinary research area bridges chemistry, surface science, (bio)-physics and engineering.

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Recent Press Releases

Mikropartikel mit Licht antreiben, Synchronized swimming under the microscope,

MOTILE MICROSCALE CATALYSTS

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Synthetic active matter has become a core interest in physics which is mostly due to its ability to emulate living systems. Since these systems operate constantly out of equilibrium, new physics had to be developed to understand autonomous motion at the microscale. Colloidal particles can achieve microscale motility using different physicochemical mechanisms. For instance, if an asymmetric spherical particle acts as a catalyst on one hemisphere, a molecular solute concentration gradient accumulates in the surrounding fluid and subsequently propels the particle via self-diffusiophoresis.

Using chemically active Pt@SiO_2 Janus particles in a peroxide solution, a robust catalytic system was developed to observe behaviors in a series of conditions. As one example, we explored that the presence of actively moving colloids induces self-assembly processes of passive particles in their surroundings.[1]

The motion of chemically active colloids is conditioned by a chemical field as well as a hydrodynamic flow field which determine both, the motility as well as the influence on their surroundings. Nearby particles would respond by phoresis to the chemical field and simultaneously they are dragged by the flow. Using highly active, ultrafast light-driven swimmers,[2] this effect becomes more pronounced and a robust formation of large, ordered structures are observed.[3,4] However, these intrinsically chemical phenomena are not yet frequently considered by chemists or catalysis researchers and I envision exciting findings through this connection.

Acknowledgements. This research was funded by a Freigeist grant (91619) granted by the Volkswagen foundation.

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Short Biography. Jennifer Strunk received her diploma and PhD degree in Industrial Chemistry from the Ruhr-University Bochum, Germany, in 2004 and 2008, respectively. After a postdoctoral stay at UC Berkeley (2008-2010) and employment as junior research group leader at Ruhr-University (2010-2014) and as research group leader at the Max-Planck-Institute for Chemical Energy Conversion (2014-2016), she became head of the new Department of Heterogeneous Photocatalysis at the Leibniz Institute for Catalysis (LIKAT) in Rostock, Germany, in January 2017. She is also appointed as Professor (W2) for Catalysis at the University of Rostock, Germany, and member of the Board of Directors at LIKAT. Since January 2019 she additionally serves as Editor for *Applied Surface Science* (Elsevier). Her prime research interest is to develop reliable and reproducible research methodologies to understand the basic elementary processes and active sites in heterogeneous photocatalysis.

Five Selected Publications of Relevance to Catalysis Science.

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Recent Press Releases

Vom Klimagas zum Rohstoff

ATOMIC SCALE INSIGHT INTO PHOTOCATALYSIS INVOLVING TITANIUM DIOXIDE AND OXYGEN

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In many studies in photocatalysis, only the formation of the product of primary interest, e.g. a solar fuel, and the conversion of the primary reactant, e.g. a greenhouse gas, is quantified and studied mechanistically. It would be desirable, on the other hand, to close the mass balance by tracing the atoms in all reactants and products involved in the reaction. This leads to mechanistic insight and the identification of limiting reaction steps. Such a challenging co-reactant and byproduct is oxygen, which is particularly difficult to trace if oxide-based semiconductors are used. Here, new atomic scale insight is presented into the reaction and fate of oxygen over TiO_2-based photocatalysts.

On bare TiO_2, CH_4 is the known primary product of photocatalytic CO_2 reduction. The stoichiometrically required byproduct O_2 is much less frequently detected. When added to the gas phase, it inhibits CH_4 formation almost completely[1]. In a similar manner, when TiO_2 is modified with IrO_2 to accelerate oxygen evolution, gaseous dioxygen can indeed be detected, but CO_2 reduction is no longer possible, so water splitting is the only feasible reaction. The stoichiometric 2:1 ratio of H_2:O_2 is reached after some time, but in the initial phases, certain amounts of oxygen are missing in the gas phase. Long term CO_2 reduction experiments with bare TiO_2 revealed that CH_4 formation terminates at a point, when roughly the same amounts of oxygen should have been evolved. This leads to the conclusion that CH_4 formation in photocatalytic CO_2 reduction is only possible as long as TiO_2 can act as a "scavenger" for evolved oxygen, possibly by filling native oxygen vacancies.[2] In photocatalytic alcohol oxidation with Au/TiO_2 under UV irradiation, the alcohol can react with the photogenerated holes over the titania interface directly, but the electrons can only be transferred to oxygen effectively when gold is present[3]. Thus, a predominantly *catalytic* role of the gold nanoparticles is indicated. Using *ab initio* calculations at finite temperature under consideration of the fluctuating nature of the gold nanoparticles, the primary function of gold is discovered to be the activation of dioxygen (Figure 1). The oxygen molecule is split with lower activation barrier and at shorter bond lengths at the gold nanoparticle as compared to bare titania surface.[4]

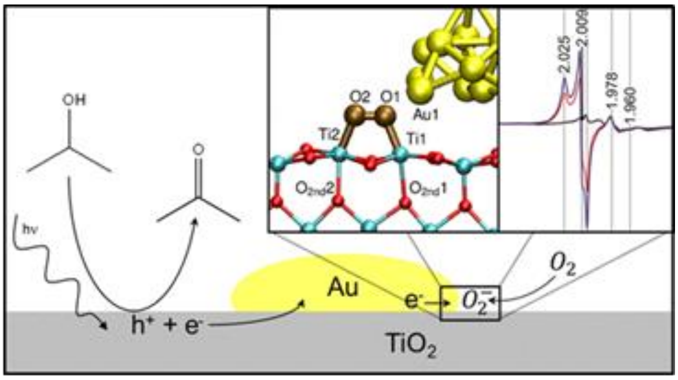

Figure 1. Mechanistic understanding of oxygen activation and superoxide formation during selective oxidation on Au/TiO_2.

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Five Selected Publications of Relevance to Catalysis Science.

- Supported bismuth halide perovskite photocatalyst for selective aliphatic and aromatic carbon-hydrogen bond activation, Dai, Y.; Poidevin, C.; Ochoa-Hernández, C.; Auer, A. A.; Tüysüz, H., *Angew. Chem. Int. Ed.* **2020**, *59*, 5788.
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Recent Press Releases

https://kofo.iwww.mpg.de/kofo/en/current-topics/news/2020/200318-harun-tueysuez-receives-dechema-prize-2019

HALIDE PEROVSKITE PHOTOCATALYSTS FOR SELECTIVE C–H BOND ACTIVATION

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Inorganic halide perovskites with a general formula of ABX_3 (A = Rb, Cs; B = Ge, Pb, Sn; and X = Cl, Br, I) have gained considerable research interest because of their unique physicochemical properties.[1] Due to the quick growth in the field of halide perovskite solar cells, different research areas on halide perovskites have emerged that are now being deeply explored.[2] Although solid halide perovskites have distinctive features and potential as catalysts on the nanoscale, they are barely explored in catalysis. We have employed nanostructured halide perovskite as new class of catalyst for polymerization,[3] oxidation and ring opening reactions of organic substrates.[4]

Herein, we design a series of stable lead-free halide perovskites nanoparticles with a size of 2-5 nm within the pore channels of mesoporous silica and demonstrate their novel photocatalytic functionalities for C–H bond activation (Figure 1). *Under* visible light irradiation, the composite photocatalysts can effectively oxidize aromatic and aliphatic hydrocarbons with very good selectivities towards aldehydes and ketones, without forming any over oxidation products. The isotopic labelling, *in-situ* spectroscopic studies and density functional theory calculations supported to propose a reaction mechanism. The interaction between hydrocarbons and under-coordinated metal center of halide perovskite can stimulate C-H bond activation and results in a high catalytic conversion rate.[5]

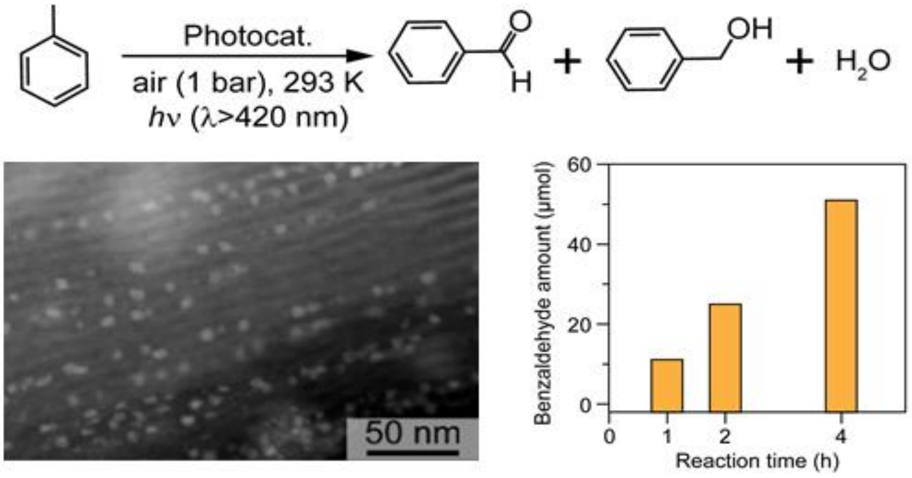

Figure 1. TEM image of supported halide perovskite (left), photocatalytic conversion of solvent-free toluene to benzaldehyde as the main product (right).

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