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E-ABSTRACT BOOK

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4TH INTERNATIONAL SYMPOSIUM ON SINGLE-ATOM CATALYSIS

Plenary

SA-PL-01

Single-Atom Catalysis: A Game of Coordination Environment

Aiqin Wang,* Tao Zhang*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China
**Email: aqwang@dicp.ac.cn; taozhang@dicp.ac.cn*

ABSTRACT

Single-atom catalysis has become one of the most active frontiers in catalysis in the past decade.[1,2] It has now been widely accepted that the coordination environment, including the inner shell and outer shell comprised of the support, reactants, and environmental molecules, determines the electronic and geometric properties of central atoms and in turn the catalytic performance of SACs. In some cases, the neighboring atoms on the support can be directly involved in the catalysis in a metal-support concerted catalysis manner. Therefore, the coordination environment not only serves as an effective descriptor of the structure-performance relationship, but also provides great opportunities to fabricate better-performed SACs through modulation of the coordination.
In this presentation, I will highlight the recent advances in our group in the identification and modulation of the coordination environment of SACs.[3-6] First, the heterogeneity of the coordination environment of SACs is discussed regarding the non-uniform structure and composition of the support. Then, various approaches to tune the inner-shell and outer-shell coordination environment are shown for the effective improvement of the catalytic performance of SACs. Finally, the structure evolution of SACs driven by the external stimuli and reactant/products is discussed. The atomic understanding of the coordination environment of SACs will help to elucidate the nature of single-atom catalysis and enrich the theoretical aspects of heterogeneous catalysis.

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SA-PL-02

Versatile and Robust Single Atom Catalysts

Abhaya K. Datye*

Dept. of Chemical & Biological Engineering, University of New Mexico
Albuquerque, NM 87131, USA
**Email: datye@unm.edu*

ABSTRACT

A major challenge in the field of single atom catalysis is their thermal stability and low volumetric reactivity (due to low metal loadings). As we demonstrated, atom trapping provides strong anchoring sites, making atomically dispersed Pt stable at 800 °C in air on ceria [1], and more recently even atomically dispersed Rh on alumina. In these catalysts, we can also achieve metal loadings of 3 wt% on supports such as ceria or alumina. However, in many cases, the strongly bound single atom sites are not very active as heterogeneous catalysts due to their strong covalent bonding to the support [2]. Hence, it may be necessary to modify the support to achieve a balance of high stability and reactivity. By stabilizing metals in the form of single atoms, it is possible to perform reactions not possible with the bulk metal. For example, Ni is a well-known catalyst for reactions such as dry reforming, or hydrogenation, but not for reactions such as CO oxidation, methane oxidation or for selective hydrogenation of acetylene. Also, Ni catalysts are known to suffer from challenges such as coke formation, which leads to formation of carbon filaments and plugging of the reactor, or from difficulties in handling reduced Ni catalysts due to their pyrophoric nature. In this presentation, we will describe the synthesis of single atom catalysts that are stable in oxidizing environments as well as under steam/H_2, and how single atom catalysts can perform a range of reactions, under oxidizing and reducing conditions, without needing any activation [3,4].

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AC-PL-03

Theoretical Foundations of Single-Atom Catalysis

Jun Li*

Theoretical Chemistry Center, Department of Chemistry, Tsinghua University, Beijing, China
**Email: junli@tsinghua.edu.cn*

ABSTRACT

Catalysis science and technology have played a key role in chemical industries, biological transformation, atmospheric processes, environment, energy, and human health. Conventionally, catalysts are discovered based on trial-and-error experiments, which calls for rational understanding of the active sites and microscopic mechanisms of catalytic reactions. In recent years, heterogeneous single-atom catalysts (SACs) and single-cluster catalysts (SCCs) have aroused significant interest in the catalysis community [1-3]. These new types of catalysts offer well-defined atomically precise active sites that enable manipulation and design of heterogeneous catalytic reactions [4,5]. In this talk, we will provide an overview and perspective of atomically precise heterogeneous catalysis (APCat) via SACs and SCCs. The theoretical foundations of the stability and reactivity of SACs and SCCs will be discussed. Possible applications in thermo-, electro- and photo-catalysis of critical catalytic reactions will be highlighted.

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SA-PL-04

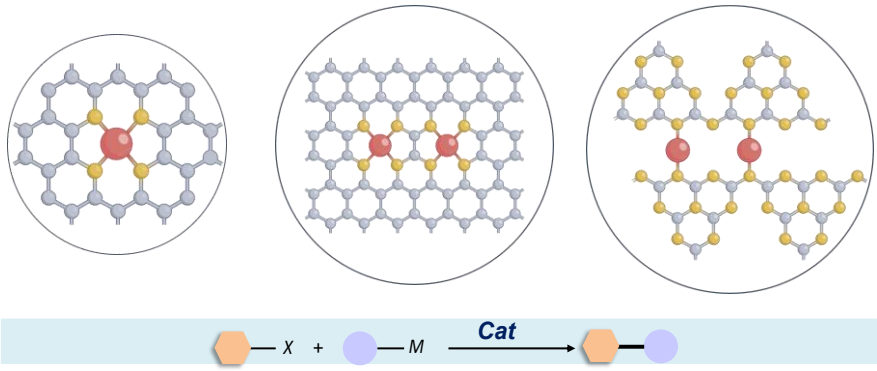
Sustainable chemical synthesis: from single-atom to geminal-atom catalysis with tailored dynamics

Jiong Lu*

Department of Chemistry, Institute for Functional Intelligent Materials, National University of Singapore
**Email: chmluj@nus.edu.sg*

ABSTRACT

A global shortage of energy and resources, and the push for clean manufacturing processes, means that economical and sustainable production methods of fine chemicals and pharmaceutical are urgently needed. Despite the huge success in homogenous catalysis, the development of heterogeneously catalysed processes is highly attractive for large-scale production to facilitate catalyst separation, recovery, and reuse, and improve adaptability for continuous-flow synthesis. In this talk, I will discuss the rational design and synthesis of atomic-precision catalysis, inspired by atomic-scale investigations. I will then introduce novel heterogeneous catalysts with well-defined active sites including artful single-atom catalysts (ASAC) and geminal-atom catalysts (GACs), characterized by tailored dynamic behaviors for a wide range of cross coupling reactions. These advancements pave the way for the development of next-generation atomic-precision catalysis with the potential to transform chemical production and energy conversion, contributing to a more sustainable future.



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Keynote

SA-KL-01

The Cooperation of Single-Atom and Frustrated Lewis Pairs for Catalyzing Two-Molecule Reactions

Chun-Ran Chang (常春然)*

School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an, China
** Email: changcr@mail.xjtu.edu.cn*

ABSTRACT

Direct conversion of methane is of great significance for the development of new petrochemical routes using natural gas/shale gas as raw materials. Either its nonoxidative coupling or co-conversion with another molecule all needs simultaneous activation of two molecules. Herein, we propose the construction of single-atom coupled frustrated Lewis pair (SA-FLP) dual active site catalysts to enhance the co-activation of two molecules and the subsequent coupling reactions. The SA-FLP dual active sites are successfully constructed on the surface of CeO_2 through metal doping and oxygen vacancy regulation strategies using density functional theory (DFT) calculations and ab initio molecular dynamics (AIMD) simulations [1]. It is found that SA-FLP dual active sites can simultaneously activate two molecules of methane, thereby achieving nonoxidative coupling of methane to produce ethane and ethylene [2]. In addition, the applications of SA-FLP dual active sites are extended in the co-conversion of methane and other small molecules, for example, SA-FLP dual active sites can simultaneously activate CH_4 and HCHO, and efficiently co-convert them to ethanol [3]; The SA-FLP dual active sites can efficiently activate CH_4 and H_2O simultaneously, and achieve the co-conversion of them into methanol [4-5]; The SA-FLP dual active sites can simultaneously activate CH_4 and CO_2, and selectively co-convert them into acetic acid [1]. Overall, SA-FLP dual-active-site catalysts show great potential in the direct conversion of methane as well as other two-molecule reactions.

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SA-KL-02

Metal cluster catalysis in the gas phase

Sheng-Gui He

Institute of Chemistry, Chinese Academy of Sciences
Zhongguancun North First Street 2, Beijing 100190, PR China
Email:shengguihe@iccas.ac.cn

ABSTRACT

Metal clusters with limited number of atoms and unsaturated chemical bonds are often superior in catalytic reactivity to their bulk counterparts. Metal clusters can be isolated in the gas phase and their structures and catalytic reactions can be characterized under well controlled and reproduceable conditions. Catalytically active single-atoms such as Ir, Rh, Au, Pt, and so on can also be anchored on gas phase metal clusters with precise number of atoms. Mass spectrometric and spectroscopic instruments with state-of-the-art reactors for gas phase cluster reactions have been developed to study a few important catalytic reactions: (1) CO oxidation by O_2, H_2O, and NOx,[1-3] (2) CO_2 reduction by H_2,[4,5] and (3) partial oxidation of CH_4 by O_2 and CO_2.[6-8] Elementary reactions to construct catalytic cycles in the gas phase were experimentally determined and then computationally studied with quantum chemistry methods. Good matches between experiments and calculations for exactly the same chemical systems were achieved to reveal mechanisms of chemical transformation at a strictly molecular level.

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SA-KL-03

Construction and Application of Atomically Dispersed Catalysts

Daojian Cheng *

State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China
**Email: chengdj@mail.buct.edu.cn*

ABSTRACT

Atomically dispersed catalysts (ADCs) have attrated much attention in catalysis region due to its nearly 100% atomic utilization rate. However, developing universal construction method and precise regulation of the coordination environment are the main difficulties to the development of ADCs[1]. To solve these problems, we put forward some facile approaches for the accurate and universal preparation of ADCs. Notably, for carbon-based carriers, Ru, Pt, Rh, Ir, Au, Mo, etc. ADCs could be fabricated by a facile room temperature impregnation method [2, 3]. More importantly, a volcano-type relation between oxidation states and hydrogen evolution activity could be observed by controlling the local coordination environments of metal atoms, further suggesting the importance of local coordination regulation [3]. In addition, for metal oxide/hydroxide carriers, 34 kinds of ADCs could also be synthesized by a one-step electroreduction method [4, 5]. A library of atomically dispersed catalysts is constructed and the coordination reconstruction mechanism for ADCs is emphasized. The developed atomically dispersed catalysts in our works could display excellent activity in many reaction systems, mainly including water splitting [2-5], hydrogenation[6], hydroformylation reaction[7] and so on. We believe the developed construction methods and the understanding of structure-activity relationship contribute to guide the development of highly active and low cost catalysts in the future.

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SA-KL-04

Integrative Catalytic Pairs – the Smallest Catalytic Units to Drive Complex Chemical Reactions

Bin Liu

Department of Materials Science and Engineering
City University of Hong Kong
Email: bliu48@cityu.edu.hk

ABSTRACT

Single-atom catalysts (SACs) refer to catalysts with a single type of reactive atoms anchored on a host support through various interactions, which have garnered significant research attention due to their combined advantages of homogeneous and heterogeneous catalysts, including close to 100% atom utilization efficiency, well-defined structure, and high catalytic activity/selectivity. However, the homogeneity of isolated active sites in SACs may limit their applications in complex chemical reactions that involve multiple reaction intermediates. To address the challenge of a single type of active sites in SACs, we have proposed another novel type of catalysts, which compose of integrative catalytic pairs (ICPs), featuring adjacent binary active centers that exhibit synergistic catalytic effects in addition to their mutual regulation of electronic structure, offering the smallest catalytic units to drive complex chemical reactions.

SA-KL-05

Metal-support frontier orbital interactions in single-atom catalysis

Junling Lu*

Key Laboratory of Precision and Intelligent Chemistry, Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China
**Email: junling@ustc.edu.cn*

ABSTRACT

Single-atom catalysts (SACs) with maximized metal utilization and discrete energy levels, hold promise for broad applications in heterogeneous catalysis, energy conversion, environmental science, and biomedicine. The activity and stability of SACs are governed by the pair of metal-adsorbate and metal-support interactions. However, the understanding of these interactions with their catalytic performance in nature is challenging, correlations of activity with the charge state of metal atoms have frequently reached controversial conclusions. Here we report that the activity of palladium (Pd) SACs exhibit a linear scaling relationship with the positions of the lowest unoccupied molecular orbital (LUMO) of oxide supports across 14 types of semiconductors. Elevation of the LUMO position by reducing the support particle size to a few nanometers boosts a record high activity along with excellent stability in the semihydrogenation of acetylene. We unveil that the elevated LUMO of support reduces its energy gap with the highest occupied molecular orbital (HOMO) of Pd_1 atoms, which promotes Pd_1–support orbital hybridizations for high stability and further amends the LUMO of anchored Pd_1 atoms to enhance Pd_1–adsorbate interactions for high activity. These findings consist with the frontier molecular orbital (FMO) theory and provide a general descriptor for the rational selection of metal-support pairs with predictable activity.

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SA-KL-06

A Short History of *Single-Atom Alloy* Catalysts; From Birth in a Chilly Vacuum to Application in a Fiery Reactor

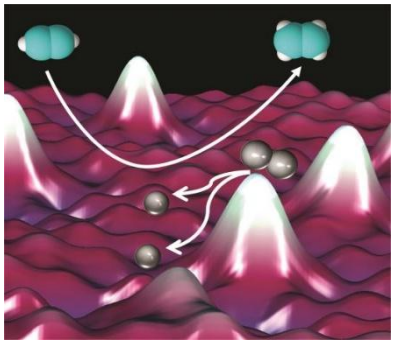
E. Charles H. Sykes*

Department of Chemistry, Tufts University, 62 Talbot Ave, Medford, MA 02155, USA

**Email: Charles.sykes@tufts.edu*

ABSTRACT

In this talk I will discuss a new class of heterogeneous catalysts called *Single-Atom Alloys* in which precious, reactive metals are utilized at the ultimate limit of efficiency.1-7 These catalysts were discovered by combining low-temperature scanning tunneling microscopy with more traditional ultra-high vacuum surface science approaches to study surface-catalyzed chemical reactions. This research provided links between atomic-scale surface structure and reactivity which are key to understanding and ultimately controlling important catalytic processes. In collaboration with Maria Flytzani-Stephanopoulos these concepts derived from our surface science and theoretical calculations were first used to design *Single-Atom Alloy* nanoparticle catalysts that are shown to perform industrially relevant reactions at realistic reaction conditions. For example, alloying elements like platinum, palladium and rhodium with cheaper, less reactive host metals like copper enables 1) dramatic cost savings in catalyst manufacture, 2) more selective hydrogenation, dehydrogenation and oxidation reactions, 3) reduced susceptibility to CO poisoning, and 4) higher resistance to deactivation by coking. I go on to describe very recent theory work by collaborators Stamatakis (Oxford University), Michaelides (Cambridge University) and Montemore (Tulane University) that predicts reactivity trends for a wide range of *Single-Atom Alloy* combinations for important reaction steps like H-H, C-H, N-H, O-H, and CO2 activation. I end with two demonstrations of new nonintuitive *Single-Atom Alloy* nanoparticle formulations that were predicted *a priori* and proven in reactors. Overall, I hope to highlight that this combined surface science, theoretical prediction, synthesis and testing approach provides a new and somewhat general method for the design of new heterogeneous catalysts.



Scanning tunneling microscope image showing atomically-dispersed palladium atoms in a copper surface. The palladium atoms activate hydrogen enabling the industrially important acetylene-ethylene conversion with 100% selectivity

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SA-KL-07

Single-atom catalysts for energy applications

Qiang Xu*

Department of Chemistry, Southern University of Science and Technology, Shenzhen, China

ABSTRACT

Single-atom catalysts (SACs) exhibit extraordinary activity and selectivity for various reactions. Recently, we have synthesized a number of non-noble metal single-atom catalysts using metal-organic frameworks (MOFs) as precursors and used them for energy applications.[1] A double-solvent method has been used to introduce $FeCl_3$ along with dicyandiamide into MIL-101-NH_2, of which the pyrolysis produces atomically dispersed Fe/N-doped hierarchical carbon architectures showing extremely efficient electrocatalytic performance for oxygen reduction reaction (ORR).[2] The thermolysis of energetic MOF MET-6 results in the formation of large carbon networks with hierarchical porosity and single Fe and Co atoms, which exhibit excellent catalytic performance for ORR under both alkaline and acidic conditions.[3] A SiO_2 template has been used to control the morphology of Fe-doped ZIF-8 crystals, of which the pyrolysis leads to the formation of single-atom iron catalysts on overhang-eave carbon cages, showing high catalytic activity and durability for ORR and excellent performance as cathode for zinc-air batteries.[4] A dual-atom iron catalyst has been synthesized using a heteroatom modulator approach, which catalyzes efficient oxygen evolution reaction (OER).[5] Most recently, we have developed a simple universal method to synthesize a series of noble-metal single atoms on non-noble metal oxides, which show high activities for OER and hydrogen evolution reaction (HER) under acidic condition.[6] Dual Fe/I single atoms anchored on N-dopedcarbon nanorods (Fe/I-N-CR) have been synthesized via a metal–organic framework (MOF)-mediated two-step tandem-pyrolysis method, which shows excellent ORR activity and stability and high performance as catalysts for wide-temperature quasi-solid-state Zn-air batteries.[7] Through a photodeposition method, Cu single-atom sites and atomically Cu-doped Au nanoparticles are simultaneously anchored on a photoactive MOF with mesoporous channels, closely integrating distinct sites within a confined environment. Thanks to the electron accumulation of plasmonic metal nanoparticles and the synergy among different active sites, this MOF composite achieves efficient photocatalytic CO_2 reduction to C_2H_6 with a production rate as high as 69.9 μmol g^{-1} h^{-1} and a selectivity as high as 71.1%.[8] In this talk, discussions on the recent progress of single-atom catalysts for energy applications will be given.

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SA-KL-08

Dual-Atom Catalysts for Effective Bond-Formation and Bond-Cleavage Transformations in Artificial Photosynthesis

Ke R. Yang*[1,2]

[1] *Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin, China 300071*
[2] *Frontier Science Center for New Organic Matter, Nankai University, Tianjin, China 300071*
**Email: ke.yang@nankai.edu.cn*

ABSTRACT

Single-atom catalysts have become increasingly important in the catalysis community because they not only maximize the utilization of metal atoms, but also provide a good platform for mechanistic investigation and performance optimization. Artificial photosynthesis is the mimic of photosynthesis to convert solar energy into chemical energy through two important reactions, namely the water oxidation reaction (WOR) and CO_2 reduction reaction (CO_2RR). These reactions involve bond formation and cleavage, e.g. O–O bond formation in WOR and C–O bond cleavage in CO_2RR, which should conceptually work better with two catalytically active metal centers. In this talk, we will discuss a special class of single-atom catalysts when two catalytically active atoms approach each to form a dimer, the so-call dual-atom catalysts or dinuclear heterogeneous catalysts and demonstrate their excellent performance in WOR and CO2RR by promoting the O–O bond formation and C–O bond cleavage through the synergy between two neighboring metal atoms. Detailed mechanistic insights through computational investigation and their implications for solar fuel production will also be discussed.

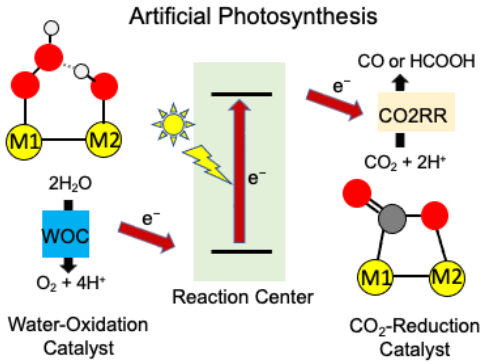

Figure 1. Dual-atom catalysts for effective O–O bond formation and C–O bond cleavage in the water-oxidation reaction and CO2-reduction reaction.

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SA-KL-09

Catalysis at Interfaces: Atom-Efficient Metal Catalysts Based on Single Atoms, Clusters and Nanpparticles

Emiel J.M. Hensen*[1]

1 Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, Het Kranenveld 14, 5612 AZ Eindhoven, The Netherlands
**Email: e.j.m.hensen@tue.nl*

ABSTRACT

Efficient utilization of transition metals is one of the most important requirements for heterogeneous catalysts. Design rules for nanoparticle catalysts are well established and often imply that sub-optimal metal dispersion is desired for high activity. Metal-support interactions can strongly impact the catalytic performance of metal nanoparticles. Specific sites at the metal-support interface can give rise to unusually high reactivity. In this contribution, I will demonstrate the possibility to tune metal-support interfaces towards high CO_2 hydrogenation and CO oxidation activity. The approach entails experimental work involving the synthesis of uniform active phases, operando characterization, and transient kinetic analysis augmented with density functional theory calculations of mechanisms and microkinetic simulations. Three different cases will be presented: (i) single atoms of Pd on nanosized CeO_2 crystallites for optimum CO oxidation and (ii) Co clusters stabilized on CeO_2 and CoO/CeO_2-ZrO_2 composites and (iii) inverse CeO_{2-x}/Co catalysts for CO_2 methanation.

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SA-KL-10

Theory-Guided Design of Metal-Nitrogen Doped Carbon Single and Dual Atom Catalysts for Efficient Electrocatalytic Reactions

Jeong Woo Han*

Department of Materials Science and Engineering, Seoul National University, Seoul 08826, Republic of Korea
**Email: jwhan98@snu.ac.kr*

ABSTRACT

Metal-nitrogen doped carbon (M-N-C) with atomically dispersed single and dual sites can orchestrate critical redox processes for sustainable CO_2 utilization, high-efficiency fuel cells, and advanced biosensing technologies. A central challenge is the atomic-level modulation of coordination environments across such diverse reactions, as this governs reaction intermediate adsorption energetics.To address this, we developed a theory-guided framework to design M-N-C catalysts with tailored metal nuclearity and coordination geometry, enabling cross-reaction adaptability.

High-throughput density functional theory (DFT) screening revealed coordination control and orbital configuration as key design strategies[1], identifying Fe, Co, and Ni single-atom sites for CO_2 reduction (CO_2RR)[2]. Carbon support with mesoporosity and graphitic character further enhanced Ni-N_4 activity for CO2RR by decoupling electron transport and reactant diffusion[3]. Cu-N4C8 sites confined in micropores achieved 96% CO Faradaic efficiency through d-orbital modulation[4]. To access new electronic structures and reaction pathways, we extended our approach to dual-atom systems. Orbital-coupled Fe_2-N-C catalysts showed a twofold increase in CO_2RR turnover frequency over their single-site counterparts[5], while FePd-N-C[6] and FeCo-N-C[7] catalysts achieved high oxygen reduction reaction (ORR) activity with half-wave potentials exceeding that of commercial Pt/C. Mn-N_3 nanozymes exhibited stronger oxidase, peroxidase, and glutathione oxidase activities than Mn-N_4, enabling high-sensitivity biosensing[8].

These findings establish atomic coordination as a core design principle. By uniting computational screening, atomic-resolution synthesis, and machine learning, we unlock a general strategy to rationally engineer redox-active sites, bridge disparate application domains, and accelerate catalyst discovery for sustainable energy and biosensing.

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SA-KL-11

The Application of Synchrotron Radiation X-ray Spectroscopy in Single Atom Catalysis

Zheng Jiang*[1]

[1] *National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230026, P. R. China*
**Email: jiangz@ustc.edu.cn*

ABSTRACT

Synchrotron Radiation X-ray Spectroscopy (SRXS) techniques, including X-ray absorption fine structure (XAFS) and X-ray emission spectroscopy (XES), have emerged as powerful tools for investigating structure-activity relationships in energy materials, particularly in single-atom catalysts. XAFS has established itself as an indispensable characterization method in single-atom catalysis, providing critical insights into local structural parameters such as valence state, symmetry, ligand number, and coordination type, offering accurate theoretical models in theorical simulations. Recent advancements in this field have witnessed the development of cutting-edge techniques such as *in situ/operando* XAFS detection combined with sophisticated analytical methods including difference spectra (Δμ) analysis and wavelet transformed EXAFS. These innovations enable real-time monitoring and precise characterization of dynamic structural evolution in catalysts under operational conditions, thereby facilitating the establishment of accurate structure-performance correlations. High-energy resolution spectroscopic approaches such as XES and high-energy-resolution fluorescence-detected XANES (HERFD-XANES) have further enhanced our capability to probe fine electronic structures near the Fermi level. These techniques demonstrate exceptional sensitivity in detecting subtle charge transfer processes, identifying ligand species, and characterizing minor local structural distortions, positioning them as increasingly vital characterization tools in energy catalysis research. This presentation will also introduce the state-of-the-art spectroscopy platforms at the Shanghai Synchrotron Radiation Facility (SSRF) and the upcoming Hefei Advanced Light Facility (HALF), both developed under the author's leadership. These advanced SRXS systems have significantly accelerated research progress in single-atom catalysis by providing unprecedented spatial and temporal resolution for mechanistic studies of catalytic processes.

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SA-KL-12

Small molecules activation by photon-phonon co-driven catalysis

Junwang Tang

Department of Chemical Engineering, Tsinghua University, Beijing China 100084
**E-mail: jwtang@tsinghua.edu.cn*

ABSTRACT

Photon-driven small molecules activation, eg. H_2O splitting, methanol reforming and methane conversion is scientifically and industrially of significance as it promises an efficient pathway for solar energy utilization and a green approach for chemical synthesis. However it is kinetically very challenging due to a multi-electron/hole process [1]. To achieve this potential, efficient activation of these small molecules (e.g. N_2, H_2O and CH_4 etc) are important while rather challenging.

Our early study on charge dynamics in inorganic catalysts reveals that the current low solar to fuel/chemical conversion efficiency is due to both fast charge recombination and sluggish oxidation reaction [2], we thus developed effective material strategies to improve the activities of catalysts. Importantly, we discovered that coupling photons with phonons to co-drive catalytic reactions is significantly more efficient and selective compared to solely relying on photocatalysis, which has been demonstrated in a few scenarios, including methane conversion to formaldehyde on Ru single atoms loaded on ZnO [3], methane to C_2H_6 over Au-immobilised TiO_2 [4] etc, all with extremely high conversion and selectivity. Typically, we also found that photon-phonon co-driven process over single atom catalysts could dramatically improve H_2 production from methanol reforming [5]. Very recently, we developed a new concept of an intramolecular junction, which is composed of alternate benzene and triazine motifs in CTF polymer. Such structure can facilitate fast charge separation and is characterised by spatially separated reduction and oxidation sites in one molecular unit, thus substantially improving the methane conversion to ethanol and mitigating the overoxidation to CO_2, resulting in an unprecedented ethanol yield and selectivity of 80% operated under ambient condition [6].

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SA-KL-13

Controllable Synthesis and Application Exploration of Single-Atom Catalysts

Yuen Wu*[1,2]

[1]*State Key Laboratory of Precision and Intelligent Chemistry, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, Anhui 230026, China*
[2]*Department of Dermatology, The First Affiliated Hospital of USTC, Division of Life Sciences and Medicine, University of Science and Technology of China, Hefei, Anhui, 230000, China*
**Email: yuenwu@ustc.edu.cn*

ABSTRACT

Single-atom catalysts (SACs), characterized by the isolation of metal atoms on supports, have emerged as a frontier in heterogeneous catalysis, offering unparalleled advantages such as maximum atomic utilization efficiency, unique electronic structures, and tunable coordination environments.[1] This abstract summarizes our recent research progress in the controllable synthesis of SACs and their applications in diverse catalytic reactions. We have developed several novel strategies to precisely control the dispersion and coordination of single atoms. For instance, by using the strong metal-support interaction and atomic layer deposition techniques, we can accurately manipulate the loading and spatial distribution of single atoms on various supports, including carbon materials, metal oxides, and zeolites.[2-4] These methods not only improve the stability of SACs but also endow them with excellent catalytic performance.

Regarding applications, SACs have demonstrated remarkable performance in numerous reactions. In the field of electrocatalysis, our designed single-atom catalysts exhibit high activity and durability for oxygen reduction reaction, hydrogen evolution reaction, and carbon dioxide reduction reaction, providing potential solutions for energy conversion and storage.[5,6] In addition, in the area of environmental catalysis, SACs show excellent activity in the degradation of pollutants and the removal of harmful gases, contributing to environmental protection and remediation.

This abstract not only deepens our understanding of the structure-activity relationship of SACs but also provides practical guidance for the rational design and large-scale preparation of high-performance single-atom catalysts. Future research will focus on further optimizing the synthesis methods, exploring new application scenarios, and elucidating the reaction mechanisms at the atomic level to promote the commercialization of single-atom catalysts.

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SA-KL-14

Mechanistic insights into catalytic conversion of methane from DFT computational studies

Qingfeng Ge*

School of Chemical and Biomolecular Sciences, Southern Illinois University Carbondale, IL 62901, USA
**Email:qge@chem.siu.edu*

ABSTRACT

The catalytic conversion of methane to fuels and commodity chemicals is essential for sustainable development. The emergence of single-atom catalysts provided a new opportunity for the selective activation and conversion of methane. In this talk, I will highlight our research on methane activation and conversion using various catalysts, particularly focusing on systems characterized by single-atom catalysts. We employed DFT calculations to explore reaction mechanisms and emphasized the potential of both noble (Pd) and non-noble (Cr) single-atom catalysts in facilitating the conversion of methane into valuable chemicals like methanol and ethanol. Our findings demonstrate that single chromium (Cr) atoms anchored on anatase titanium dioxide (TiO_2) and within UiO-66 metal-organic frameworks can catalyze the direct conversion of methane to methanol. The former reaction can occur using a mild oxidant, hydrogen peroxide (H_2O_2), while the latter requires the formation of a Cr-oxo species. The anionic oxyl radicals created at the Cr site serve as active species for methane activation through a homolytic mechanism, leading to a reaction that proceeds via the Eley-Rideal mechanism. Additionally, we showed that a single palladium (Pd) atom on indium oxide (In_2O_3) can catalyze the production of ethanol (CH_3CH_2OH) through the atom-economic coupling of formaldehyde (HCHO) and methane (CH_4). These studies provide valuable insights into modern catalytic strategies for methane conversion, paving the way for future research and development in this critical area of chemical engineering.

SA-KL-15

AI-Driven Theory of Metal Catalyst Stability based on Metal-Support Interaction

Wei-Xue Li*

State Key Laboratory of Precision and Intelligent Chemistry, Department of Chemical Physics, School of Chemistry and Materials Science, University of Science and Technology of China; Hefei, 230026, China.

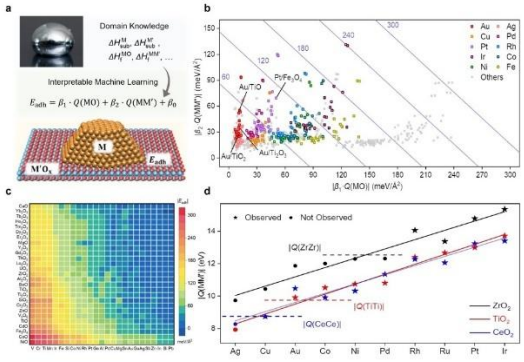
**Email: wxli70@ustc.edu.cn*

ABSTRACT

Achieving high stability in metal catalysts is critical for their practical application in industry, yet remains a long-standing challenge due to sintering and chemical degradation under working conditions. Traditional approaches often fall short in systematically understanding and tuning the complex interplay between catalyst structure, composition, and environment.

Our team has developed an AI-driven theoretical framework to address this challenge. By integrating big data with interpretable artificial intelligence, we unified the theory of catalyst growth kinetics and established a Sabatier-like principle for tuning metal–support interactions (MSI) to enhance sintering resistance. This framework allows for rational support selection based on MSI strength and catalyst performance. To go further, we constructed a massive space of over 30 billion mathematical expressions and, using experimental data, identified a physically transparent MSI control equation. This equation successfully describes a wide range of catalytic interfaces, including oxide-supported nanoparticles, single-atom catalysts, and metal-on-oxide systems. We also introduced a criterion for strong metal–metal interactions, resolving long-standing experimental puzzles such as the encapsulation of metal catalysts by oxide supports.

This AI-guided approach not only accelerates the discovery of fundamental catalytic principles but also provides powerful design rules for building next-generation catalysts with both high activity and long-term stability under industrial conditions.



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SA-KL-16

Single-Atom Catalysis: Insights from Model Systems

F. Kraushofer,*[1] L. Puntscher,[1] P. Sombut,[1,2] A. Rafsanjani-Abbasi,[1] F. Buchner,[3] F. J. Lewis,[1] M. Eder,[1] J. Pavelec,[1] E. Rheinfrank,[1], G. Franceschi,[1] V. Birschitzky,[2] M. Riva,[1] M. Meier,[1,2] C. Franchini,[2] M. Schmid,[1] U. Diebold,[1] G. K. H. Madsen,[3] G. S. Parkinson[1]

[1]*Insitute of Applied Physics, Technical University of Vienna, Austria*
[2]*Faculty of Physics and Center for Computational Materials Science, University of Vienna, Austria*
[3]*Institute of Materials Chemistry, Technical University of Vienna, Austria*
**Email: florian.kraushofer@tuwien.ac.at*

ABSTRACT

While there are many examples where single-atom catalysts have been successfully synthesized and tested, there is a fundamental disconnect between most experimental work and the theoretical modelling of these systems. While applied catalysts are based on complex powder supports, and are fabricated and used in environments containing various potential ligands and contaminants, theoretical treatment is generally based on density functional theory (DFT) calculations assuming low-index facets on idealized supports, often placing the single catalyst atom in a bulk continuation site.

Studies of single-crystalline supports prepared in ultra-high vacuum offer a direct experimental analogue to DFT models. This can be used as a bridge between modelling and more complex experimental systems, and as validation for the possible sites assumed by theory.

As an example, I will present experimental results on iron oxide surfaces. Several seminal SAC papers have shown high activity for single metal adatoms on FeO_x.[1,2] In these studies, the support is commonly modelled in DFT calculations as a hematite (α-Fe_2O_3) (0001) surface. However, the exact atomic-scale structure of this facet is complex and remains heavily debated.[3,4] We focus instead on the $(1\bar{1}02)$ facet of hematite, which exhibits a well-defined, bulk-truncated (1×1) termination.[5,6] I will show examples of Pt and Rh single atoms dispersed on this surface, and discuss the different mechanisms by which they can be stabilized. Importantly, this always involves either additional ligands or restructuring of the support, rather than simply placing the atoms in a bulk continuation site.[7-9]

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SA-KL-17

Rational Design of Catalysts Accelerated by AI assisted Computational Chemistry

Zhi-Jian Zhao*

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, China
**E-mail: zjzhao@tju.edu.cn*

ABSTRACT

With continuous advancements in computer hardware and breakthroughs in interdisciplinary fields such as quantum mechanics, fluid dynamics, and artificial intelligence (AI), computational simulation methods have garnered significant attention for accelerating the development of industrial catalysts. Mature multi-scale computational methodologies ranging from density functional theory to continuum models have been progressively established. By employing AI-accelerated computational approaches, it becomes possible to overcome the limitations of traditional model-based catalytic systems. This enables the construction of realistic models for complex industrial catalysts under diverse reaction conditions, achieving large-scale and long-term "operational condition" simulations for industrial catalytic systems. Furthermore, by establishing structure-activity relationships of dynamic catalyst surfaces and developing reaction descriptors for rapid prediction of catalytic performance, high-throughput screening of novel catalytic materials can be realized. Intelligentized high-throughput laboratories, integrating automated experimental platforms with data-driven optimization algorithms, further accelerate the design, validation, and process development of new catalysts, significantly shortening R&D cycles and enhancing experimental efficiency.

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SA-KL-18

From single atom catalysis to multielement catalysis

Li-Ming Yang*

School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
**Email: Lmyang@hust.edu.cn*

ABSTRACT

In this talk, firstly, I will introduce some progress we have made in the design and screening the atomic level catalysts and exploration of catalytic reaction mechanisms from the atomistic level. Representative achievements include: 1) Development and establishment of first principles based hierarchical high-throughput screening methods, 2) Design and development of high-throughput screening software with approved 2 software copyright certificates (High throughput screening platform for two-dimensional single atom catalysts in nitrogen reduction and ammonia synthesis reaction [2D-SAC-NRR] V1.0, and High-throughput screening software for two-dimensional single atom catalysts for oxygen reduction reaction [2D-SAC-ORR] V1.0), 3) Design and prediction of a series of atomic level catalysts for energy small molecule catalytic conversion, and elucidation of experimental observations. Some results have been experimentally verified.

Recently, we extend our research from single atom catalysis to multielement catalysis. First, we have established the methods for the structure construction and prediction of high entropy materials in different dimensions (0D, 1D, 2D, 3D) with approved 5 software copyright certificates. Then, these tools are used to produce effective high entropy structures, and are used for the optimization design of catalyst components and the revelation of reaction mechanism. The optimization iteration is used to guide the design of efficient catalysts.

SA-KL-19

Computational Modelling of Single-Atom Surface Sites on Oxide and Bimetallic Catalytic Nanomaterials

Konstantin M. Neyman* [1,2]

1 Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional, Universitat de Barcelona, 08028 Barcelona, Spain
2 ICREA (Institució Catalana de Recerca i Estudis Avançats), 08010 Barcelona, Spain
**Email: konstantin.neyman@icrea.cat*

ABSTRACT

DFT modelling of relevant for catalysis single-atom surface sites on unreducible metal oxides such as MgO [1-3] has begun well before the term "single-atom catalysis" was introduced [4]. A decade ago our DFT calculations demonstrated a very strong binding of atomically dispersed transition metals across the Periodic Table on nanostructured surfaces of typical reducible metal oxide CeO2 [5,6]. Atomic Pt adsorbed on special surface sites of CeO2 in the form of 2+ cations was found even more stable than Pt atoms comprising metallic Pt in bulk and particles. Quite surprisingly, our recent DFT study [7] revealed that already at quite mild oxidation conditions Pt cations in small oxidized PtOx particles supported on CeO2 are at least as stable as the very stable adsorbed single Pt2+ ones. PtOx/CeO2 nanostructures were suggested to trigger catalytic CO oxidation well below 0°C [8]. Results of our on-going DFT calculations will be presented, which explain such low-temperature CO oxidation on the PtOx/CeO2 nanostructures at the atomic level and provide conceivable complete catalytic cycles for these processes. The second part of the talk will deal with DFT modelling findings for single-atom metal alloy catalysts forming nanoparticles composed of hundreds of low-reactive coinage metal atoms with single atoms of active late transition metals emerging on the surface. The focus will be on the notably varied charge states of the single atoms depending on their atomic environment and on monitoring such atoms by vibrational frequencies of the adsorbed CO probe molecules.

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SA-KL-20

Beyond Dispersing Dopants: The Critical Role of the Host Atoms in Selective Hydrogenation of Acetylene on Single Pd Atom Alloys

Xin Xu*[1]

[1]*State Key Laboratory of Porous Materials for Separation and Conversion, Key Laboratory of Molecular Catalysis and Innovative Materials, MOE Key Laboratory of Computational Physical Sciences, Research Center for Chemical Theory, Department of Chemistry, Fudan University, Shanghai 200433, China*
**Email: xxchem@fudan.edu.cn*

ABSTRACT

Single-atom alloys (SAAs),[1] featured by isolated active dopants dispersed within relatively inert host metals, have shown great promise in selective hydrogenation reaction, a process that is essential for fine chemical production. While studies have predominantly focused on the role of the active dopant, the influence of the host metal on catalytic performance, beyond its mere role for dispersing the dopants, remains largely underexplored. Here, we employ the doubly hybrid functional XYGJ-OS,[2-4] validated against experimental temperature-programmed desorption spectra, to investigate the selective hydrogenation of acetylene on Pd_1/Cu and Pd_1/Au SAAs.[3] Our results reveal that while Pd is essential for H_2 activation, the host metal critically modulates the competitive adsorption of acetylene and ethylene, thereby determining catalytic activity and selectivity of the whole process. These results align well with experimental observations for Pd_1/Cu and Pd_1/Au nanoparticles. Conversely, the widely used density functionals such as PBE-D3BJ fail to accurately discriminate the competitive adsorption of reactants, being unable to distinguish the differences for selective hydrogenation of acetylene on Pd_1/Cu and Pd_1/Au SAAs. This study highlights the need for high-precision methods like XYGJ-OS, providing a fundamental understanding of the nuanced role of host metals in SAA catalysts toward the rational design of highly selective catalysts.

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SA-KL-21

Challenges and opportunities in understanding local environments in carbon-based single-atom catalysts

Sharon Mitchell*[1,2] and Javier Pérez-Ramírez[1,2]

[1]*Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich, Switzerland*
[2]*NCCR Catalysis, Switzerland*
**Email: msharon@chem.ethz.ch*

ABSTRACT

Designing single-atom catalysts (SACs) offers unique opportunities to maximize metal utilization and attain molecular-level control over reactivity. Yet, uncovering and tailoring the local environments of isolated metal centers, especially on amorphous or semi-crystalline supports like functionalized carbons or carbon nitrides, remains a major fundamental challenge. In this talk, I will discuss recent advances that have been enabled by combining state-of-the-art synthesis approaches with emerging tools for structural analysis. I will introduce a deep-learning-assisted atom detection tool for interpreting transmission electron microscopy images, which enables accelerated and standardized statistical analysis of metal dispersion.[1] This approach is particularly valuable for confirming atomic isolation at higher metal contents, where clustering becomes more likely yet harder to detect, and to infer the organization of coordination sites from metal distributions, revealing subtle differences across metal species.[2] However, while this method reveals spatial information, it does not resolve the coordination structure of active metal sites. To approach that level of detail, complementary spectroscopic methods are essential. While X-ray absorption spectroscopy is widely used, it suffers from averaging effects and poor sensitivity to light atoms. In collaboration, we have recently applied ^{195}Pt solid-state NMR spectroscopy to provide a direct signature of the coordination environments in Pt SACs. This technique confirms dominant square-planar Pt(II) species in nitrogen-doped carbon supports and reveals local heterogeneity. Quasi in-situ NMR further allows us to track structural evolution during acetylene hydrochlorination. Finally, I will briefly introduce neural network–accelerated EXAFS analysis as a promising emerging approach for gaining more precise, site-specific structural insights. While still under development, it offers potential to overcome current limitations of XAS by enabling improved interpretation of complex spectral data. Together, these efforts will show how we can bridge the gap between theoretical predictions and experimental evidence, illustrate how synthetic and analytical advances must co-evolve, and emphasize the importance of technique integration and developing more controlled supports to achieve structural uniformity in SACs.

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SA-KL-22

Interpreting Heterogeneous Catalysis via Trans-scale Chemistry

Huabin ZHANG*[1]

[1] *Center for Renewable Energy and Storage Technologies (CREST), Physical Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia.*
**Email: Huabin.Zhang@kaust.edu.sa*

ABSTRACT

Heterogeneous catalysis plays a pivotal role in modern society, advancing industrial energy conversion and storage while enabling the synthesis of fine chemicals and pharmaceutical compounds. Despite its critical importance, designing catalysts with high activity, selectivity, and stability for specific chemical reactions remains a formidable challenge. Over the past century, significant advancements in chemistry and physics have profoundly reshaped our understanding of heterogeneous catalysis and the principles underlying catalyst design. Nevertheless, substantial gaps remain between the theories developed across different historical periods, each tailored to address distinct scientific questions and scales, impeding a comprehensive understanding of catalytic processes.

We propose the concept of "trans-scale chemistry" as a holistic framework that renormalize research across multiple scales, emphasizing distinct chemical challenges and physical phenomena at varying scales, while exploring the theoretical connections and transitions between them. This concept “trans-scale” encompasses coupled spatial and temporal dimensions, ranging from the atomic scale to the macroscale in space, and from ultrafast electron transfer processes occurring within picoseconds to slow structural evolution over seconds or longer. Specifically, we will provide a discussion on key topics, including the origin of inherent spatial and temporal complexity in heterogeneous electrocatalysis; a statistical physics perspective across multiple spatial scales; equilibrium and non-equilibrium understanding across temporal scales; the development of design principles informed by trans-scale chemistry and other related sub-topics.

SA-KL-23

Phase Engineering of Nanomaterials (PEN)

Hua Zhang*[1]

[1]*Department of Chemistry, Hong Kong Institute for Clean Energy (HKICE), Hong Kong Branch of National Precious Metals Material Engineering Research Center (NPMM), City University of Hong Kong, Hong Kong, China*
**Email: hua.zhang@cityu.edu.hk*

ABSTRACT

In this talk, I will summarize the recent research on phase engineering of nanomaterials (PEN) in my group, particularly focusing on the rational design and synthesis of novel nanomaterials with unconventional phases for various promising applications. For example, by using wet-chemical methods, for the first time, we have successfully prepared novel Au nanostructures (*e.g.*, the hexagonal-close packed (*hcp*) 2H-Au nanosheets, 4H-Au nanoribbons, and 4H/*fcc* and *fcc*/2H/*fcc* heterophase Au nanorods), epitaxially grown metal nanostructures on the aforementioned unconventional Au nanostructures and 2H-Pd nanoparticles, and amorphous/crystalline heterophase Pd, PdCu, Rh and Rh alloy nanosheets. By using gas-solid reactions, metastable 1T'-phase group VI transition metal dichalcogenides (TMDs), *e.g.*, WS_2, WSe_2, MoS_2, $MoSe_2$, $WS_{2x}Se_{2(1-x)}$ and $MoS_{2x}Se_{2(1-x)}$, have been prepared. Impressively, the 1T'-MoS_2-supported single-atomically dispersed Pt (s-Pt) atoms with Pt loading up to 10 wt% exhibit superior performance in hydrogen evolution reaction. Importantly, 1T'-TMD monolayers can be stabilized on 4H-Au nanowires, which have been used for ultrasensitive SERS detection. Moreover, the salt-assisted 2H-to-1T' phase transformation of TMDs have been achieved, and the phase transformation of TMDs during our developed electrochemical Li-intercalation process has been observed. Impressively, the lithiation-induced amorphization of $Pd_3P_2S_8$ has been achieved. Currently, my group focuses on the investigation of (crystal) phase-dependent physicochemical properties, functions and applications in catalysis, (opto-)electronic devices, clean energy, chemical and biosensors, surface enhanced Raman scattering, photothermal therapy, *etc.*, which we believe are quite unique and very important not only in fundamental studies, but also in future practical applications. Importantly, the concepts of phase engineering of nanomaterials (PEN), crystal-phase heterostructures, and heterophase materials are proposed.

SA-KL-24

Study on the Selective Oxidation of Methane over Confined Single-atom/Two-atom Catalysts under Mild Conditions

Zhen Zhao[1,2*]

[1]*Shenyang Normal University, (Institute of Catalysis for Energy and Environment, Shenyang, China)*
[2]*China University of Petroleum, Beijing (State Key Lab of Heavy Oil Processing, Beijing, China)*
**Email: zhenzhao@cup.edu.cn*

ABSTRACT

Methane is the main component of natural gas, shale gas and coalbed gases, and it is abundantly available worldwide. However, the low polarizability and high dissociation energy of the C-H bond in methane molecules, as well as the high reactivity of the target oxygen-containing compounds, pose significant challenges in achieving a high selectivity conversion of methane under mild reaction conditions. On the one hand, the direct selective conversion of methane possesses significant fundamental scientific importance. On the other hand, methane is a serious greenhouse gas, with its greenhouse effect being 25 times that of carbon dioxide molecule. Therefore, its selective conversion to produce useful oxygen-containing compounds has significant environmental benefits.

Metal-organic framework (MOFs) materials, due to their dispersed metal ions and single organic ligands, make them excellent mimics of enzyme catalytic systems. However, most MOFs materials are not resistant to water. To address this challenge, the hydrophobic polydimethylsiloxane (PDMS) was used through the vapor deposition method to hydrophobically modify the surface of Cu-BTC (Cu-BTC-P-235). This hydrophobic modification not only significantly enhances the catalytic cycling stability of the material in the liquid phase, but also generates coordinatively unsaturated Cu(I) sites to simulate the particulate methane monooxygenase (pMMO), thereby significantly improving the catalytic activity. The Cu-BTC-P-235 catalyst achieved a high production rate of 10.67 mmol/gcat^{-1}h^{-1} for C_1-containing oxygen compounds, with a selectivity of up to 99.6% for C1-containing oxygen compounds, and this catalyst also exhibited excellent reusability [1]. The high yield of C1 oxygenates (CH_3OH, CH_3OOH, $HOCH_2OOH$ and HCOOH) produced by our PDMS hydrophobic-modified MIL-100(Fe) MOFs catalyst reached 83.13 mmol per gram of catalyst per hour. The selectivity for C1 oxygenates was close to 100% [2]. Recently, we reported a new heteronuclear diatomic Fe and Cu center (Fe1/Cu1−C3Nx) catalyst for the direct selective oxidation of methane. Beneffting from the synergistic effects of heteronuclear diatomic, unique N vacancies, and a hierarchically porous structure, enhanced catalytic performance is realized, with a C1 oxygenate productivity of 9.43 mol gFe+Cu $^{-1}$ h^{-1} at 80 °C, nearly 100% selectivity, and an excellent TOF of 543.09 h^{-1} for the production of oxygenates[3]. Using noble metal Au as the methyl coupling catalyst, and by utilizing the geometric strain and bond locking effects induced by the doping of heteroatoms, the electronic structure symmetry of lattice oxygen in ZnO was successfully broken. The introduction of single-atom Ce significantly accelerated the desorption process of methyl and water molecules on ZnO, simultaneously enhancing the construction efficiency of C-C bonds and the removal efficiency of surface residual hydrogen, thereby significantly improving the performance of photocatalytic OCM[4].

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SA-KL-25

Conversion of small molecules on single metal cations in zeolites or on cerium dioxide – insights from computational modeling

Georgi N. Vayssilov,*[1] Hristiyan A. Aleksandrov,[1] Iskra Z. Koleva[1]

[1]*Faculty of Chemistry and Pharmacy, Sofia University "St. Kliment Ohridski", Sofia, Bulgaria*
**Email:gnv@chem.uni-sofia.bg*

ABSTRACT

We applied computational modeling based on density functional theory to clarify the local structure and properties of single metal cations supported on cerium dioxide or in zeolites as well as adsorption and catalytic transformations of small molecules on them.

To contribute to clarification of the mechanism of CO oxidation on Pt/CeO_2 we modeled the process on mononuclear platinum species and platinum clusters using regular $CeO_2(111)$ surface and $Ce_{21}O_{42}$ nanoparticle [1]. Considering both reaction steps, oxidation of CO and restoration of the catalyst via reoxidation, we found that the reaction paths with lowest activation barriers via $Pt^{2+}(CO)_2$ or $Pt^{4+}(CO)$ complexes. For catalysts with atomically dispersed Ru ions anchored to the ceria support using DFT calculations complemented with spectroscopic measurements, the location of Ru(II) ions on the ceria surface and mechanism of NO conversion on them were clarified [2].

In a series of works, we modeled rhodium cations and clusters in zeolites focusing on their complexes with CO, H_2, NO and small organic molecules. For those complexes we identified also the key intermediates and reaction steps and compare them with experimental observations. Particularly interesting is ethene dimerization directly to 1,3-butadiene, which occurs via pentameric cycle involving rhodium [3]. Since copper-exchanged zeolites are among the catalysts for selective reduction of nitric oxide with ammonia, we modeled detailed mechanism of this process in conjunction with comprehensive infrared spectroscopic and catalytic techniques [4]. We have shown that nitrosyl ions, NO^+, in zeolitic micropores are the key intermediates for NO reduction via di-azo compounds, and that the role of Cu(II) ions in Cu/zeolite catalysts is to convert NO to NO^+, which is then reduced by ammonia to water and dinitrogen.

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SA-KL-26

Mesoporous carbon confined single-atom catalysts towards precise Catalysis

Yang Yang[2] , Xiaojuan Zhu[2] , Ying Wan* [1,2]

1School of Materials and Chemistry, University of Shanghai for Science and Technology, Shanghai, People's Republic of China
2Department of Chemistry, Shanghai Normal University, Shanghai, People's Republic of China
**Email: ywan@shnu.edu.cn*

ABSTRACT

Precise catalysis is the core driving force behind transformative breakthroughs in energy and chemical catalysis1 . By precisely designing catalytic active sites and synthesizing mesoporous carbon confined single-atom catalysts, precise control over the atomically economical reaction pathways can be obtained that convert chemical bonds into target products. Our work focuses on the creation of mesoporous confined catalytic materials for precise catalysis2-5 . Here two examples are given. Based on the *d* charge descriptor catalyst designing strategy, an unprecedented cyclohexanone selectivity (>99.9%) in continuous-flow phenol hydrogenation using an electron-deficient Pd catalyst. The Pd atom exists in a unique Pd–N5C4 structure in which it is coordinated with four quasi-planar N atoms and one axial N atom in the first shell and an additional four C atoms in the second shell that lie on the curved surface of a pore in ordered mesoporous carbon. The Pd site has a *d* charge depletion of 1.18 e that prevents cyclohexanone adsorption, which is therefore exclusively produced. In aqueous continuous-flow phenol hydrogenation, it shows record-high cyclohexanone selectivity (>99.9%) and high conversion (>98%), and can stably run for 300 h without deactivation. Bonding the Pd atom to a curved plane of carbon atoms is an effective way to control the *d* charge of Pd and increase its selectivity for the green synthesis of fine chemicals. We have developed a *d*-electron deficient Ru single-atom catalyst supported on an ordered mesoporous titania/carbon composite. The catalyst demonstrates complete conversion of guaiacol to cyclohexanol and methanol under mild conditions (1 MPa H2, water as solvent) with exclusive selectivity. Structural and spectroscopic analyses revealed atomically dispersed Ru in the OMTC support, resulting in a *d*-electron deficiency of 1.30 e, which increased the demethoxylation of the 2-methoxycyclohexanol intermediate during guaiacol hydrodeoxygenation and therefore increased the selectivity to cyclohexanol and methanol. This work highlights a scalable approach to achieving full carbon utilization in the biomass, advancing the development of sustainable biofuels and chemicals.

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Invited

SA-IL-01

Atomically resolved secondary electron imaging for in situ study of atomic structure on nanoparticle surfaces

Xi Liu[1, 2*], Tian Qin[2], Liwei Chen[2]

[1] *Ningxia University, School of Chemistry and Chemical Engineering, Yinchuan 750021, China*
[2] *Shanghai Jiao Tong University, School of Chemistry and Chemical Engineering, In Situ Centre for Physical Sciences, Shanghai 200210, China*
**Email: liuxi@sjtu.edu.cn*

ABSTRACT

In heterogeneous catalysis, the surface atomic structure of nanocatalysts plays a critical role in determining their catalytic performance. However, directly characterizing these surface structures at the atomic level remains a major challenge. While transmission electron microscopy (TEM) offers high-resolution atomic imaging, the signal often contains substantial bulk phase information, limiting its effectiveness for surface-specific studies. Scanning probe techniques, such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM), are primarily suited for characterizing the surfaces of single-crystal metals and are difficult to apply to nanoparticle surfaces, particularly for in situ studies tracking dynamic evolution in the same region. To overcome these limitations, the authors' team developed an atomically resolved secondary electron (SE) imaging technique, enabling direct surface imaging of a wide range of nanomaterials, including oxides, metals, halides, and two-dimensional materials. This method revealed complex surface atomic structures that are inaccessible by conventional TEM and further allowed visualization of their evolution under realistic chemical environments. The findings provide atomic-scale evidence for the nature and dynamics of metastable active sites, offering critical insights into the activation processes and structure–activity relationships in heterogeneous catalysis.

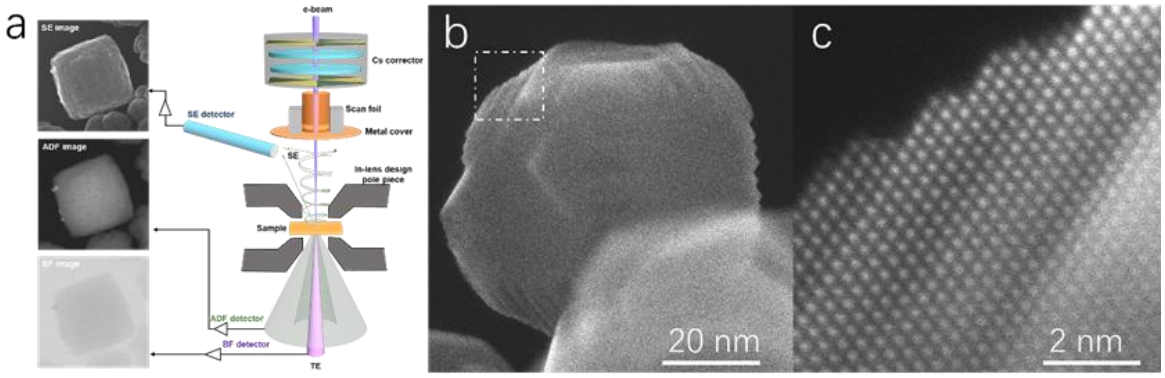

Fig. 1a) Simultaneous acquisition of bright field (BF), annular dark field (ADF), and secondary electron (SE) images in STEM; b) SE image of CeO_2 NPs; c) Atomic-resolved SE image of the stepped region marked by the dashed line in b).

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SA-IL-02

Precise Engineering of Atomic Photocarrier Acceptors for Selective C1 Conversion

Xiyi Li1 , Junwang Tang* 2 , Yang Lan* 1

1 Department of Chemical Engineering, University College London, London WC1E 7JE, United Kingdom.
2 Industrial Catalysis Centre, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China
**Email: jwtang@tsinghua.edu.cn; yang.lan@ucl.ac.uk.*

ABSTRACT

Solar-driven direct conversion of C1 gases (CH4/CO2) offers significant potential for carbon neutrality and sustainable chemicals production1,2 . However, the high kinetic barriers associated with the activation of inert chemical bonds (C-H 439 kJ mol-1 and C-O 705 kJ mol-1) necessitate energetic photocarriers34 . This often leads to undesired side reactions, including overoxidation or overreduction, which compromise product selectivity. Herein, atomic photocarrier acceptors were precisely controlled to enhance the selectivity in CH4 oxidation and CO2 reduction while preserving high catalytic activity: 1. Atomic CuOx clusters, acting as photohole acceptors, were selectively deposited on oxidative sites of TiO2, lowering the oxidative potential and suppressing interactions between CH3 intermediates and superoxide radicals at reduction sites. This shifted product selectivity from ~65% CO2 to ~60% C2 products5 . 2. Ni single-atom photoelectron acceptors were coordinated with a three-dimensional, cage-like cucurbit[n]uril ligand, forming a hydrophobic microenvironment that inhibited competitive proton reduction from H2O, achieving an exceptional CO selectivity of ~98%2 . These findings highlight the power of the precise engineering of atomic photocarriers acceptors in steering reaction pathways and advancing selectivity control in C1 chemistry

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SA-IL-03

Rational Design of Novel Dual-atom Catalysts for Greenhouse Gas Abatement or Utilization

Pengfei Xie*[1]

[1]*College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, China*
**Email:pfxie@zju.edu.cn*

ABSTRACT

Single/dual catalysts exhibit excellent catalytic performance in the conversion of greenhouse gas molecules (CH_4 and CO_2). However, the elucidation of structure-activity relationships and reaction mechanisms remains a significant research challenge, which hinders the rational design of high-efficiency catalysts.
Our research group has developed a multi-dimensional paradigm integrating high-throughput computations, machine learning, and experimental validation to facilitate rational catalyst design. We have successfully developed a series of dual-atom catalysts,[1-6] including Cu_2/ZSM-5, Pd_1Rh_1@CeO_2, Cu_2@C_3N_4, and Ru_1In_1/NC. Through theoretical calculations combined with *in-situ* spectroscopic characterization techniques, we systematically investigated the physicochemical properties of dual-metal atomic sites, including valence states and coordination environments etc. By establishing correlations between these structural parameters and catalytic activity/rate-limiting step energy barriers, we revealed fundamental structure-performance relationships and derived essential scientific principles. This approach has enabled three major breakthroughs: 1) low-temperature methane combustion, 2) high-selectivity methane oxidation, and 3) highly efficient CO_2 reduction. Our work establishes novel strategies, methodologies, and systems for greenhouse gas mitigation under this new research paradigm.

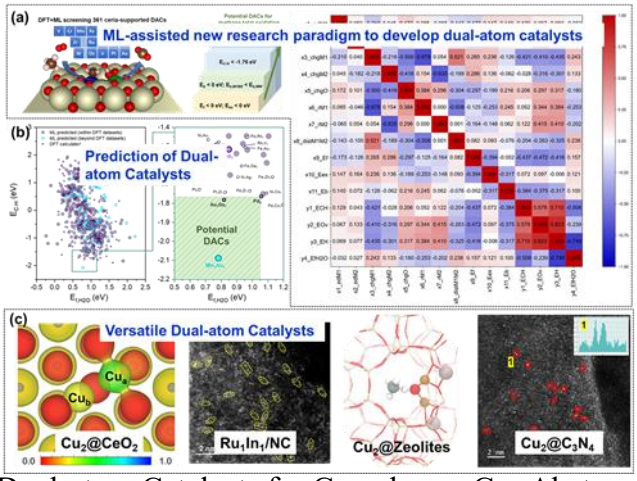

Figure 1. Novel Dual-atom Catalysts for Greenhouse Gas Abatement or Utilization

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SA-IL-04

Fe–P Catalytic Pairs Enable Efficient Activation of H2 and D2O for Reductive Amination and Deuteration Transformations

Haifeng Qi *

Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Translational Research Hub, Cardiff University, Maindy Road, Cardiff CF24 4HQ, UK
**Email: qih11@cardiff.ac.uk*

ABSTRACT

Deuterated amines serve as crucial building blocks in drug synthesis and in the identification of metabolites of new pharmaceuticals. The development of efficient and broadly applicable strategies for the selective synthesis of such deuterated compounds continues to garner considerable interest from both academic and industrial researchers worldwide. In previous studies, we reported a robust Ru1/NC single-atom catalyst for the highly efficient reductive amination of furfural1 , as well as a Ru1CoNP surface single-atom alloy catalyst that enabled a new transformation of furfural amination towards the synthesis of N-heterocyclic piperidines 2 . In the present work, we further report an Fe-P pair-site catalyst featuring highly dispersed and isolated phosphorus-coordinated Fe sites, which facilitates tandem reductive amination - deuteration sequences for the synthesis of deuterated amines3-4 .

We have successfully synthesized an optimal material Fe-P catalytic pair that enables a one-pot tandem process for reductive amination and deuteration, directly producing deuterated amines (**Fig. 1a**). Supported by DFT calculations and control experiments, we demonstrate that the Fe-P pair sites exhibit a moderate ability to activate D2O (**Fig. 1b**), while the Fe sites efficiently facilitate H2 activation (**Fig. 1c**), in which synergistic function of these sites enables effective tandem catalysis. This Fe-P catalytic pair exhibits outstanding performance in both reactivity and regioselectivity for a wide range of deuterated anilines, amines, bioactive complexes, and drugs (> 50 examples). Of particular interest is the deuterated modification of Kinetin, a compound widely used in cosmetic products for its anti-aging properties, which can be directly derived from bio-based furfural (**Fig. 1d**). This novel transformation not only broadens the spectrum of amination products accessible from furfural, but also opens a new avenue for the valorization of abundant bio-based platform molecules.

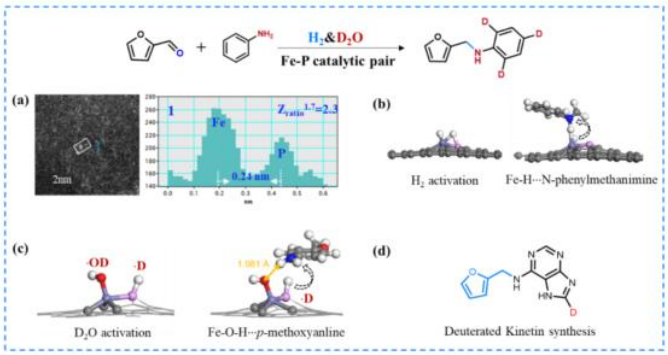

Fig. 1. (a) HRTEM image for Fe-P catalytic pairs; (b) H2 activation for reductive amination; (c) D2O activation for deuteration; (d) deuterated Kinetin synthesis from bio-based furfural.

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SA-IL-05

From Single Atoms to Nanoparticles: Atomically Defined Catalyst Design and Mechanistic study

Jingyi Yang* [1,2]

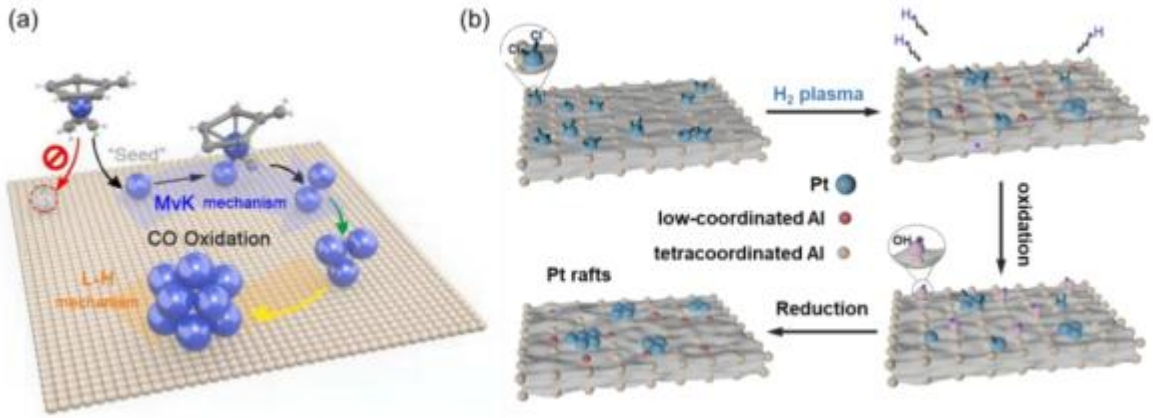
[1]*Department of Interface Science, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*
[2]*CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 116023, Dalian, P. R. China*

ABSTRACT

Single-atom catalysts (SACs) not only maximize noble metal utilization but also provide well-defined active sites that offer deep insights into catalytic mechanisms. Beyond improving metal efficiency, single-atom catalysis has advanced the field of nanocatalysis by enabling the design and understanding of catalysts at the atomic level. In particular, single atoms serve as ideal precursors for constructing uniform metal clusters/nanoparticles with atomically defined nuclearity. Their homogeneous molecular structure and strong interactions with the support can be preserved upon suitable activation, allowing precise control over active site formation at the subnanometer scale.

Here, we present two case studies that exemplify the transformation from single atoms to clusters/nanostructures and the associated catalytic implications. In the first case, we developed a controllable synthesis method to construct atomically defined Pt subnanometer clusters by growing them atom-by-atom from isolated Pt single atoms supported on Fe doped MgAl2O4 oxide (**Scheme 1a**). Mechanistic studies of CO oxidation reveal a transition in reaction pathway: from a Mars-van Krevelen mechanism on single atoms to a Langmuir-Hinshelwood mechanism facilitated by neighboring Pt atoms in clusters. In the second case, we explore the role of cold plasma treatment in directing the nanoparticle formation from single atoms on mechanically prepared α-Al2O3 (**Scheme 1b**). Especially the H2 plasma-assisted process creates a high density of hydroxyl, leading to slow aggregation and the formation of raft-like Pt agglomerations from SACs. The resulting catalyst exhibits enhanced activity in the propane dehydrogenation reaction while maintaining high selectivity.

These results demonstrate how single atoms can be used not only as active sites but also as building blocks for well-controlled nanostructures. Understanding their transformation offers a valuable strategy for tuning catalytic performance through precise structural design.



Scheme 1. (a) Atom-by-atom synthesis of Pt clusters via atomic layer deposition and the corresponding transition in the CO oxidation reaction pathway; (b) Effect of H2 plasma treatment on the aggregation of Pt single atoms into raft-like nanoparticles.

SA-IL-06

Design and Synthesis of Low-Loading Pt-Based Catalysts and Study of Their Catalytic Performance

Xiucheng Sun[1] , Runtian He[1] , Ying Li* [1]

[1] *Institute of Industrial Catalysis, State Key Laboratory of Green Chemical Synthesis and Conversion, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, China.*
**Email: liying@zjut.edu.cn*

ABSTRACT

Platinum group metal (PGM) catalysts exhibit outstanding catalytic performance in crucial reactions such as proton exchange membrane fuel cells, automotive exhaust purification, and the water-gas shift (WGS) reaction, owing to their unique electronic structures and excellent chemical stability. However, the scarcity and high cost of precious metals make the development of precious metal reduction technologies a perpetual focus in PGM catalyst research.

We are dedicated to the design and synthesis of low-loading precious metal catalysts. We have achieved Pt reduction through strategies including precise control of Pt particle size, modulation of the Pt coordination environment, and the construction of synergistic components such as FeOx nano-islands and hydroxyl-rich TiO_2 supports. (1) Controllably synthesized single-atom Pd1/FeOx catalyst with an ultra-low loading of 0.05 wt% exhibits a significantly higher turnover frequency (TOF) than commercial 1 wt% PGM catalysts. (2) Uniform sub-nanometer Pt clusters were controllably synthesized via an alcohol-alkali reduction method. For formaldehyde oxidation, Pt loading was reduced by an order of magnitude (< 0.1 wt%) while achieving complete formaldehyde conversion at room temperature. The activity far exceeds that of both single-atom Pt and nanoparticle Pt catalysts. (3) Precisely constructed OH coordination on Pt cluster surfaces enables complete CO conversion over a wide temperature window (20-200 °C) in the CO preferential oxidation (CO-PROX) reaction, even at a low Pt loading of 0.3 wt%. The OH ligands weaken CO adsorption, mitigating CO poisoning and facilitating O_2 adsorption and activation on the Pt clusters. (4) Constructing FeOx nano-islands on the support allows for the selective anchoring of Pt1 single atoms onto them. In CO-PROX, CO is adsorbed and activated on Pt1, while FeOx activates O_2, enabling synergistic catalysis between Pt1 and FeOx. (5) Utilizing hydroxylated supports promotes Pt dispersion as single atoms and enhances their stability during the high-temperature RWGS reaction. Surface OH groups participate in the RWGS reaction, facilitating CO_2 adsorption and activation, while the single-atom Pt weakens CO adsorption, improving reaction selectivity.

These researches provide valuable insights for developing highly efficient and cost-effective catalysts and offers theoretical guidance for understanding the catalytic mechanisms of platinum group metals.

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SA-IL-07

Functionalized Carbon as a Platform for Rational Design of Low-Nuclearity Metal Catalysts

Mengqi Yang[1], jingyi Chen[1],Tongtong Feng[1],Xiaoling Mou[1], Yunjie Ding[1,2,3], Ronghe Lin*[1]

[1]*Hangzhou Institute of Advanced Studies, Zhejiang Normal University, 1108 Gengwen Road, Hangzhou 311231, China*
[2]*Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China*
[3]*The State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China*
*Email: catalysis.lin@zjnu.edu.cn

ABSTRACT

The rational design of heterogeneous catalysts with precisely tailored metal active sites is pivotal for unraveling structure-performance relationships and reaction mechanisms. However, conventional synthesis methods often yield non-uniform metal sites, complicating the establishment of such correlations. Nitrogen-doped carbons (NC), with their tunable defect configurations and strong interactions with metals, offer a versatile platform to engineer low-nuclearity metal catalysts with well-defined coordination environments. This talk highlights three strategies to modulate metal speciation on NC for enhanced catalytic performance: i) **Defect Engineering via Controlled Pre-Oxidation**[1]: A universal synthetic approach enables precise tuning of nitrogen speciation (e.g., pyridinic, pyrrolic, quaternary) in carbon frameworks through polymer pre-oxidation and pyrolysis will be introduced. This method boosts nitrogen content (up to 22 wt.%) and enhances catalytic activity in lithium-ion batteries and selective oxidations, demonstrating the critical role of pyridinic-N in optimizing active sites. ii) **Single-Atom Au Catalysts with Tailored Coordination**[2]: By controlling activation temperatures, single Au atoms anchored on NC exhibit tunable oxidation states (Au^0 to Au^{3+}) and coordination environments (Cl, N, or O ligands) can be constructed. These atomic ensembles display substrate-dependent reactivity in alkyne semi-hydrogenation, mimicking molecular recognition patterns for α-OH-functionalized alkynols, underscoring the synergy between distinct Au sites and specific N-defects. iii) **Low-Nuclearity Pt-Mo Ensembles via Defect-Driven Assembly**[3]: Sequential metal deposition on NC with engineered N-defects generates Pt-Mo subnanoclusters (e.g., $Pt_3Mo_1N_3$). These ensembles achieve unprecedented activity (0.62 $molHCOOH\ molPt^{-1}\ s^{-1}$) and stability in gas-phase formic acid dehydrogenation, attributed to Pt-Mo synergy and defect-mediated stabilization. Collectively, these studies illustrate how functionalized carbons enable atomically precise control over metal active sites, bridging the gap between homogeneous and heterogeneous catalysis. Future efforts will focus on expanding this platform to diverse metal systems and reactions, advancing the development of high-performance catalysts through defect-driven nanostructuring and operando mechanistic insights.

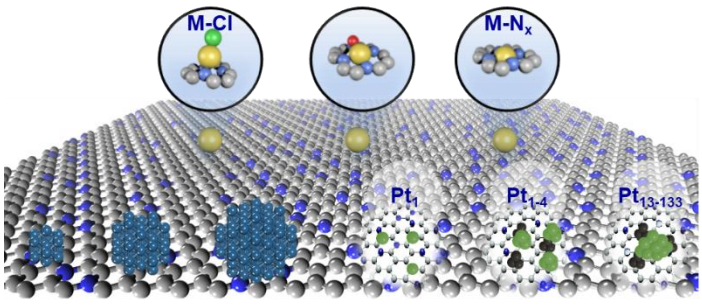

Fig. 1. N-doped carbon as platform to construct low-nuclearity metal catalysts.

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SA-IL-08

Zeolite-Confined Single-Atom Catalysts for Enhanced Performance in Valorization of Biomass-derived Platform molecule

Wenhao Luo*[1], Zhijie Wu[2]

[1]*College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot, China*
[2] *State Key Laboratory of Heavy Oil Processing and Key Laboratory of Catalysis of CNPC, China University of Petroleum, Beijing, China*
**Email: w.luo@imu.deu.cn*

ABSTRACT

Precisely tailoring confined metal single-atoms within zeolite scaffolds and understanding the origin of the unique behavior of such atomically dispersed catalysts are pivotal and challenge in chemistry and catalysis.[1] Non-edible biomass is one prime, renewable and abundant carbon-based alternative. The exploration and development of biomass for energy production and the manufacturing of value-added chemicals, can be a promising option for the sustainable and green chemistry. Herein, we have successfully fabricated Ni single-atoms within BEA zeolite (Ni_1@Beta) through a facile *in situ* two-step hydrothermal strategy, notably without using any chelating agent for stabilizing Ni species. The as-obtained Ni_1@Beta exhibits a superior performance in terms of activity (with a turnover frequency value up to 114.1 h^{-1}) and stability (for 5 consecutive runs) in the selective hydrogenation of furfural, surpassing those of Ni nanoparticle analogues and previously reported Ni-based heterogeneous catalysts.[2] Additionally, Ru/La_1-Y, with atomically dispersed La species stabilized confined proximity between metal and acid sites, significantly boosts hydrodeoxygenation (HDO) performance in terms of activity, selectivity towards pentanoic biofuels and stability in the direct, one-pot HDO of neat ethyl levulinate. Isolated La species, upholds the confined proximity by preventing zeolite lattice deconstruction during catalysis.[3] With the aid of advanced characterization techniques and combined with theoretical calculations, the nature and impact of single-atom species, have been identified. Our findings provide efficient strategies for the fabrication of single-atoms within zeolites, which could be of great help for the design of metal-zeolite combinations in the chemoselective reactions involved in biomass conversion and beyond.

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SA-IL-09

Asymmetric Mo-Ni sulfur vacancies drive sustainable methanol heterogeneous carbonylation

Qiao Yuan[1,2], Xiangen Song*[2], Yunjie Ding*[2], Roland A. Fischer*[1]

[1]*TUM School of Natural Sciences, Department of Chemistry, Chair of Inorganic and Metal-Organic Chemistry and Catalysis Research Center, Technical University of Munich, Garching, Germany*
[2]*Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China*
**Email: xiangensong@dicp.ac.cn; dyj@dicp.ac.cn; roland.fischer@tum.de*

ABSTRACT

Methanol carbonylation is of great importance in industry but remains a challenge to abandon the usage of the halide additives and noble metals. Methanol carbonylation involves two important but difficult steps including the activation of C−O bond of methanol and the coupling of C−C with CO. In the Monsanto process, the hydrogen iodide (HI) generated during the reaction cycle could activate methanol by breaking the C−O bond in classic Rh−I system.[1] The oxidative addition of regenerated CH_3I is far easier than that of CH_3OH because the C−I bond energy (239 kJ/mol) is much lower than C−O bond energy (385 kJ/mol).[2]

Herein, we report the realization of direct methanol heterogeneous carbonylation to carbonyl-containing chemicals, with a remarkable space-time-yield (STY) of 4.74 $mol_{acetyl}/kg_{cat.}/h$ and a durable stability as long as 100 h on Ni@MoS_2 catalyst (**Figure 1**).[3] Mechanistic analysis reveals that the asymmetric Mo−Ni sulfur vacancies localized at edge site of Ni@MoS_2 exhibit distinct charge density, which strongly activate CH_3OH to break its C−O bond and non-dissociatively activate CO. Density functional theory calculations further suggest that the low charge density in Mo−Ni, the Ni site, could significantly lower the barrier for CO migration and nucleophilic attack of methoxy species, and finally leads to the rapid formation of acetyl products. Ni@MoS_2 catalyst could also effectively realize the carbonylation of ethanol, n-propanol and n-butanol to their acyl products, which may demonstrate its universal application for alcohols carbonylation.

This work offers a new perspective in rational design of catalyst and mechanism understanding in methanol heterogeneous carbonylation.

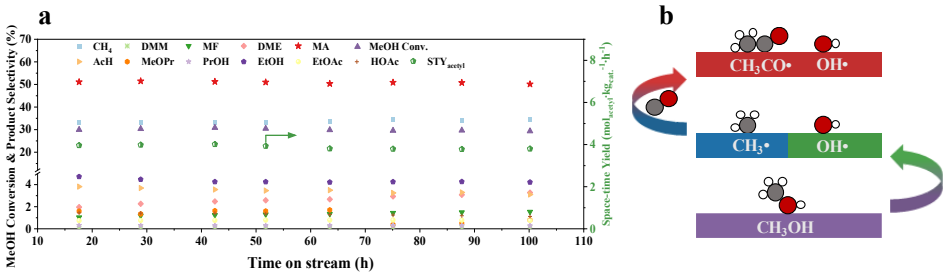

Figure 1. (a) Stability test of Ni@MoS_2 catalyst in methanol carbonylation reaction. (b) Schematic diagram of the catalytic reaction mechanism of methanol carbonylation

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SA-IL-10

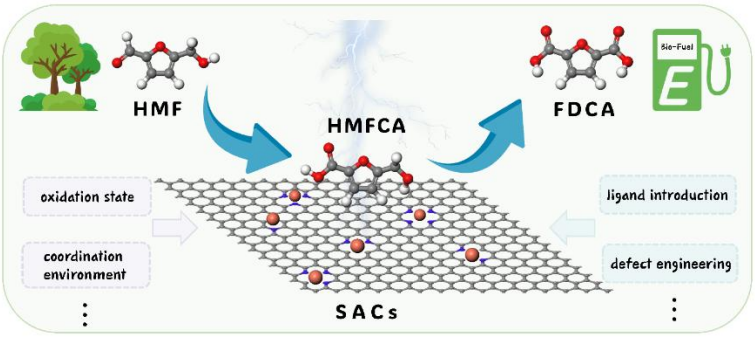
Electrochemical HMF conversion to high-added product on Single-atom catalysts

Song Liu[1*]

[1] *College of Chemistry, Chemical Engineering and Resource Utilization, Northeast Forestry University, Harbin 150040, China*
**Email: carlosliusong@nefu.edu.cn*

ABSTRACT

Electrocatalytic technology enables the conversion of 5-hydroxymethylfurfural (HMF), a pivotal platform molecule bridging biomass feedstocks to bio-based chemicals, providing a dual-functional measure to simultaneously address global energy and environmental challenges.[1] The application of single-atom catalysts (SACs) into this process is highly promising due to their maximized atomic utilization and abundant accessible active sites. However, studies on HMF conversion catalyzed by SACs primarily focus on favorable activity and selectivity, whereas mechanistic insights remain limited. Our recent work has revealed the dominant role of oxygen intermediates adsorption on metal-doped amorphous NiFe alloys in the electrochemical oxidation of HMF. Building on this finding, we implement multiple strategies—including modulating the oxidation state of active sites, introducing defect engineering, and incorporating diverse ligands—to precisely regulate oxygen intermediates adsorption, thereby elucidating how this governs HMF conversion performance in SACs. Furthermore, by coupling *in situ* characterization techniques with density functional theory (DFT) calculations, we identify the key electronic properties of SACs active sites that critically influence electrochemical behavior. These findings not only establish a rational design framework for SACs in the conversion of HMF under mild conditions but also reveal the inherent mechanism by which oxygen intermediates adsorption regulates HMF electrochemical performance.



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SA-IL-11

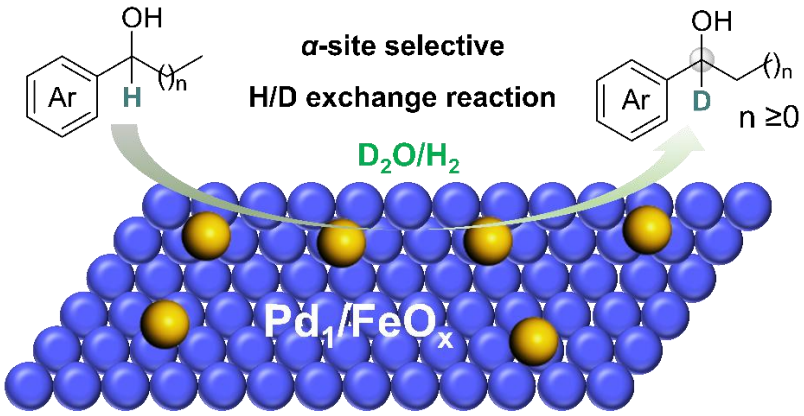
Catalytic α-Site-Selective Hydrogen-Deuterium Exchange of Benzylic Alcohols by Palladium Single-Atom Catalyst

Xiang-Ting Min,[1] Shu-Xian Li,[1], [2] Botao Qiao*, [1]

[1]*CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Dalian 116023, China.*
[2]*School of Light Industry & Chemical Engineering, Dalian Polytechnic University. Dalian 116034, China.*
**Email: bqiao@dicp.ac.cn*

ABSTRACT

Catalytic hydrogen-deuterium exchange (HDE) has emerged as a valuable tool for achieving site-selective deuteration and the precision labeling of bioactive molecules. Incorporation of deuterium at metabolically labile positions, enabled by such methods, can potentially improve drug efficacy through the kinetic isotope effect[1-5]. However, achieving precise, site-selective incorporation of deuterium at specific molecular positions remains challenging[2-5]. Herein, we report a highly efficient α-site-selective HDE of benzylic alcohols via a palladium single-atom catalyst (Pd SAC). By using the Pd SAC, exceptional activity and selectivity in HDE reactions were achieved, delivering up to 95% deuterium incorporation (D-inc.) at the α-position while effectively suppressing undesired pathways (e.g., α,β-multisite deuteration). Mechanistic investigations reveal that the Pd SAC promotes site-selective HDE through two distinct surface pathways: (i) a previously unreported direct C─H bond activation and (ii) a modified borrowing hydrogen process in which high-pressure hydrogen inhibits the keto enol tautomerization, thereby largely circumvents α,β-multisite deuteration. The catalyst exhibits robust stability, reusability, and broad substrate compatibility, underscoring its potential for practical applications. This work marks a significant advance in heterogeneous single-atom catalytic methodologies for site-selective deuteration, offering a complementary solution to longstanding challenges in catalytic organic synthesis.



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SA-IL-12

Process Intensification of Surface Reactions in Hydrophobic Single-Atom Catalysts

Wengang Liu* [1] , Yudi Zhao[1] , Huiling Feng[1]

[1] *College of Material Science and Engineering, Qingdao University of Science and Technology, Qingdao, China*
**Email:liuwengang@qust.edu.cn*

ABSTRACT

Diffusion-reaction coupling is a cornerstone of chemical engineering, yet in single-atom catalysis, the critical role of mass transfer at the catalyst interface is often overlooked. Inspired by the hydrophobic environments found in highly efficient enzymatic reactions, this work focuses on intensifying this coupling by constructing hydrophobic single-atom catalysts to unlock their full catalytic potential. We demonstrate that a hydrophobic microenvironment significantly boosts mass transfer, improves reaction kinetics, and enhances product selectivity. The core of this improvement lies in a unique "capture-release" mass transfer mechanism at the interface (Figure 1). This mechanism utilizes stronger van der Waals interactions to selectively "capture" reactant molecules (e.g., O2) while simultaneously weakening electrostatic interactions with product molecules (e.g., H2O2) to facilitate their "release," thus accelerating reaction kinetics and preventing product decomposition. Experimentally, a hydrophobic Fe-N-C catalyst, prepared via silanization, exhibited more than a twofold enhancement in catalytic activity for the selective oxidation of ethylbenzene C-H bonds. Furthermore, a hydrophobic Zn single-atom catalyst enabled the highly efficient photocatalytic synthesis of high-concentration H2O2. This research confirms that constructing a hydrophobic microenvironment is a key strategy for optimizing mass transfer, thereby unleashing and enhancing the intrinsic performance of single-atom catalysts.

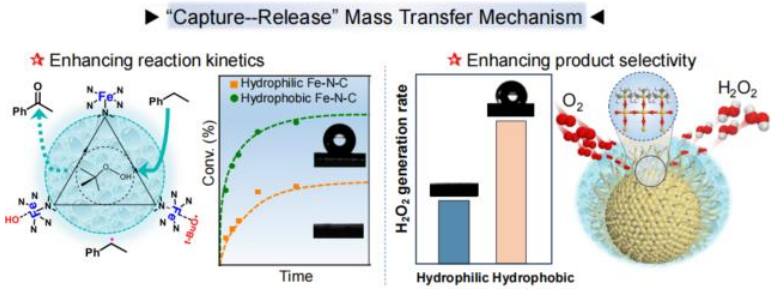

Figure 1: Capture-Release Mass Transfer Diagram.

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SA-IL-13

Photo-thermo Catalysis for Propane Dehydrogenation on Single-Atom Catalysts under Mild Conditions

Leilei Kang[1], Yanan Xing[1,2], Xiao Yan Liu*[1], Aiqin Wang[1,3], Tao Zhang[2,3]

[1]CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China
[2] University of Chinese Academy of Sciences, Beijing, China
[3]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China
**Email: xyliu2003@dicp.ac.cn*

ABSTRACT

The propane dehydrogenation reaction requires high operating temperatures (600 ~ 800 °C), which often leads to catalyst sintering or coking, resulting in deactivation and necessitating frequent regeneration. To address these challenges, the following strategies can be adopted from a fundamental research perspective: First, designing and synthesizing thermally stable catalysts, such as alloyed single-atom catalysts and intermetallic compounds, can prolong catalyst lifespan and maintain regeneration activity for propane direct dehydrogenation. Second, introducing oxidants (e.g., O_2, CO_2) for oxidative dehydrogenation of propane can moderately reduce reaction temperature, improve propylene equilibrium yield, and lower carbon emissions, though the activation temperature remains relatively high (> 500°C). Third, utilizing solar energy can enable photo-thermo catalytic dehydrogenation under mild conditions. Based on our previous work on photo-thermo synergistic catalysis for propane oxidation[1,2], our group has achieved low-temperature (<100 °C) propane dehydrogenation to propylene using single-atom catalysts under solar irradiation[3] and further explored new reaction routes by introducing other gases.

Using self-designed and constructed fixed-bed and batch photo-thermo catalytic reaction systems, we evaluates the performance of the synthesized catalysts and optimized reaction conditions, including light intensity, temperature, gas composition, and flow rate. We discover that single-atom catalysts supported on semiconductor TiO_2 can facilitate propane dehydrogenation to propylene at low temperatures under various conditions. Advanced characterization techniques, such as aberration-corrected electron microscopy, *in situ* IR spectroscopy, EPR, and so on, will be employed to analyze the dispersion of single atoms and the adsorption of reactants, intermediates, and products on the catalyst surface. Combined with isotopic labeling experiments and theoretical calculations, plausible reaction mechanisms will be proposed. These findings will pave new ways to realize catalytic activation of C-H bonds in alkanes under mild conditions.

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SA-IL-14

Electron-Relay Catalysis in Bi-functional Single-Atom Catalysts for Efficient Water Purification

Man Yang* [1] , Yujing Ren [2] , Shaodong Sun[1]

1School of Materials Science and Engineering, Xi'an University of Technology, Xi'an, 710048, China
2Interdisciplinary Research Center of Biology & Catalysis, School of Life Sciences, Northwestern Polytechnical University, Xi'an, 710072, China
**Email: myang@xaut.edu.cn*

ABSTRACT

The limitation of single isolated site in the multistep or multifunctional catalytic process is inevitable, thus prompting the exploration of building multifunctionality of single-atom catalysts (SACs). Inspired by the enzyme catalytic mechanism in the biological respiratory chain (Figure 1a), this work achieves "electron-relay catalysis" by designing and constructing bi-functional SACs, promising the extent application and enhanced intrinsic activity for SACs. The electron-relay catalysis process is triggered by a molecule acting as an electron donor. The obtained electron will be further delivered by SACs to the reactant, resulting in the enhanced electron transfer kinetics on SACs. In advanced oxidation processes (AOPs), a Co_1-OV/WOX catalyst, featuring with neighbor Co single atom and oxygen vacancy (Co_1-OV) dual sites on tungsten oxide, achieves a exceptional performance by synergistic generation of $^1O_2$ reactive oxygen species from both peroxymonosulfate (PMS) and oxygen molecule (O_2) activation via single-electron relay process (Figure 1b). In detail, the introduction of PMS donates an electron to Co_1, which is then rapidly transferred to OV. This transfer directly activates O_2, adsorbed on OV, to further produce $^1O_2$. This research provides a key strategy of fabrication bi-functional SACs to drive electron-relay catalysis for improving catalytic oxidation performance of SACs, and potentially advances the applications in extensive oxidation reactions.

Figure 1 (a) O_2 activation behavior of natural enzyme system in respiratory chain. (b) O_2 activation behavior of SA-OV dual site imitating natural enzyme system.

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SA-IL-15

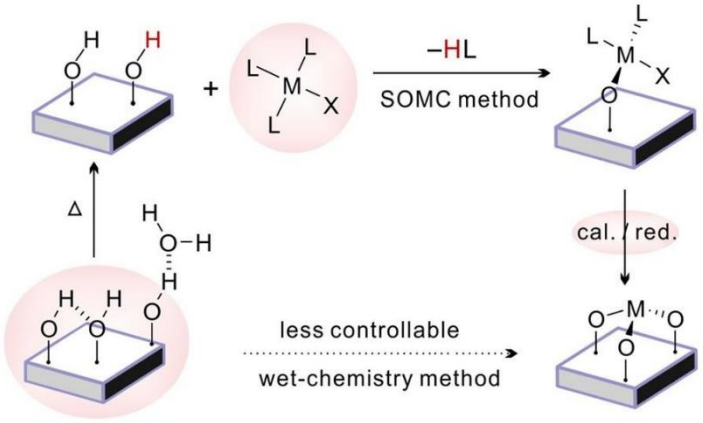
Model Catalysis by 2D Metal Oxide-supported Single Atom Catalysts

Pengxin Liu* [1,2]

[1]*School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, People's Republic of China*
[2]*Shanghai Key Laboratory of High-Resolution Electron Microscopy, Shanghai 201210, People's Republic of China*
**Email: liupx@shanghaitech.edu.cn*

ABSTRACT

The design, synthesis and characterization of model catalytic systems are important methods to study the molecular mechanism of heterogeneous catalytic reactions. Single-atom catalysts are regarded as one type of these model systems. However, based on the existing synthesis methods of single-atom catalysts, it is difficult to obtain a model system with uniform structured active sites, especially with a highly uniform coordination structure. Although this status quo has little impact on the studies on the catalytic performances of single-atom catalysts, it shows great impact on the clear identification of the active structure, the precise establishment of structure-activity relationship, and the atomic-level cognition of the microscopic mechanism of catalytic reactions, which are the main factors hindering single-atom catalysts as an ideal model catalytic system. Based on several examples of the design, synthesis, characterization and molecular mechanism studies, this report introduces the research progress from two aspects: the synthesis methods of two-dimensional crystalline supports and single-atom catalysts.



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SA-IL-16

Design of novel single-atom-modified Ti-MOF catalysts for CO2 photoreduction to value-added chemicals

Xiaowa Nie*[1] , Shuang Wang[1] , Shunshan Song[2] , Xinwen Guo* [1]

[1] *State Key Laboratory of Fine Chemicals, Frontier Science Center for Smart Materials, School of Chemical Engineering, Dalian University of Technology, Dalian, China*
[2] *Department of Chemistry, Faculty of Science, The Chinese University of Hong Kong, Shatin, NT, Hong Kong, China*
**Email: niexiaowa@dlut.edu.cn; guoxw@dlut.edu.cn*

ABSTRACT

CO_2 conversion to value-added chemicals using light energy has important application prospects in renewable energy utilization and greenhouse effect alleviation. In this work, single-atom Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Ru, Rh, Pd, Ag, Hf, Ta, Os, Ir, and Pt were chosen as modifiers to be anchored onto the ligand of Ti-BPDC (BPDC=2,2 '-bipyridine-5,5'-dicarboxylic acid) to construct the single-atom-modified Ti-MOF photocatalysts. DFT calculations were performed to study the reaction mechanism and catalytic performance of these candidate catalysts for CO_2 reduction to C1 chemicals. Key descriptors were correlated with the limiting free energy change of the overall reaction to identify the structure-activity relationships. The calculation results revealed that Fe/Ti-BPDC, Ag/Ti-BPDC, and Cr/Ti-BPDC are catalytically active and selective toward the HCOOH generation, while Pd/Ti-BPDC is more promising for CH3OH generation[1]. The computational results were verified by experiments. Based on the proposed design strategy, a series of bimetallic single-atom Cu-M modified Ti-MOF photocatalysts (M=Sc, Mn, Fe, Cu, Nb, Ru, Rh, Pd, Pt, Os, Ir, In, Sn, and Bi) were designed and screened by DFT calculations for their application in CO2 reduction to C_2 chemicals. The calculation results revealed that Cu-In/Ti-BPDC exhibits the highest activity and selectivity for C_2H_4 generation, with a limiting free energy change of 1.37 eV, and the reaction of *CO2-*COOH → *COOH- *COOH is identified as the rate-determining step[2]. This work provides important basis and directional guidance for the rational design and synthesis of high-efficient single-atom-based photocatalysts for CO2 conversion to value-added chemicals.

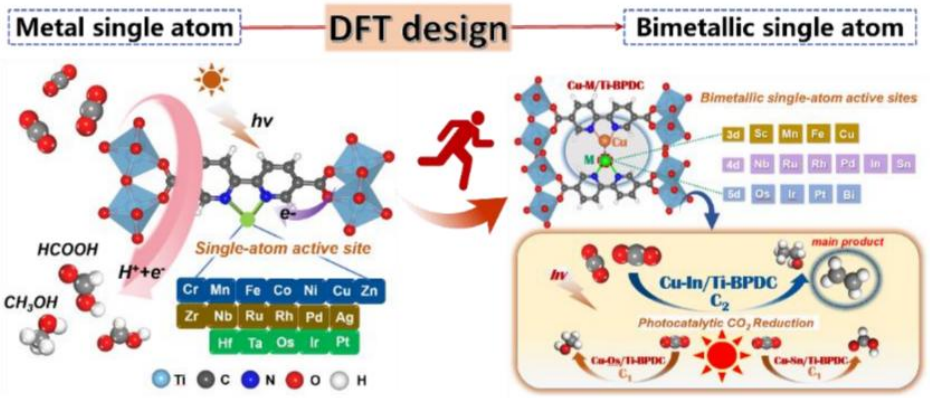

Figure 1. Design of single-atom-modified Ti-MOF catalysts for CO2 photoreduction to value-added chemicals.

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SA-IL-17

Dynamic coordination environments regulation for single-atom catalysts

Qingqing Gu[1] , Aiqin Wang[1] , Bing Yang* [1]

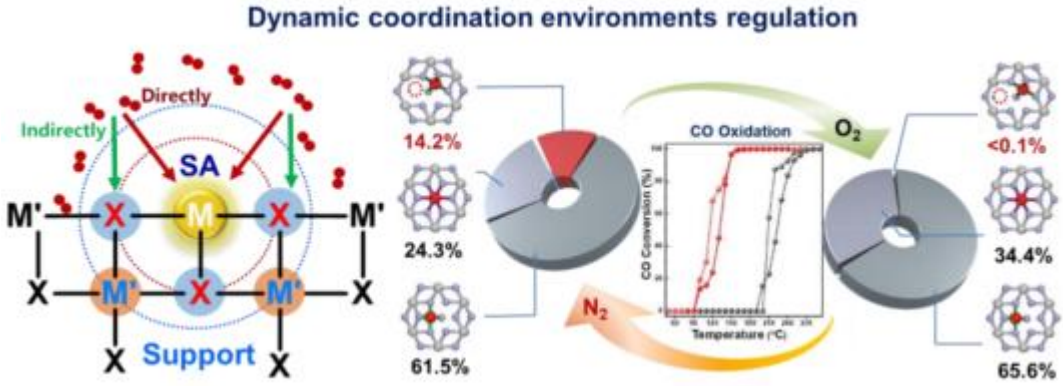
[1]*CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China*
**Email: byang@dicp.ac.cn*

ABSTRACT

Single-atom catalysts (SACs) have attracted enormous interest due to their maximization of atom utilization and specific reactivity, which have developed as one of the most active frontiers in heterogeneous catalysis. The manipulation of the coordination environment surrounding the single-atom active site is a well-established strategy for tuning SAC activity. Beyond the static perspective, the coordination environment and the catalytic performance of single-atom catalytic centers could be further modulated by reactive atmospheres under reaction conditions. Thus, understanding how the local coordination environment of single-atom sites dynamically responds to the atmosphere is essential for establishing intrinsic structure-activity relationships from dynamic perspective.

In this work, we regulated the coordination environment of Pt_1/MOx SACs by using oxidative and nonoxidative atmosphere, which resulted in distinct Pt single-atom species distributions. Combining Raman spectroscopy with computational studies, we semi-quantitatively revealled the distribution of diverse Pt_1 On– Ceδ+ species within each specific SAC. Remarkably, the minority species of Pt_1O_4–Ce^{3+}–Ov, which formed preferentially under nonoxidative atmosphere and accounted for only 14.2%, exhibited the highest site-specific reactivity for low-temperature CO oxidation, outperforming the more abundant Pt_1O_4–Ce^{4+} and Pt_1O_6–Ce^{4+} species. Furthermore, *in situ* characterizations revealed that these Pt single-atom species undergo further transformation during the CO oxidation reaction.

This work provides fundamental insights into the dynamic evolution of coordination environments around single-atom sites under varying atmospheres and quantitatively elucidates the distribution of distinct single-atom species within a given SAC material.



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SA-IL-18

Correlation between coordination number of Pt single atoms and activity of perhydro-dibenzyltoluene dehydrogenation

Kuo Liu*[1], Ligang Zhang[1,2], Tao Zhang[2,3]

[1]*Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China*
[2]*University of Chinese Academy of Sciences, Beijing, China*
[3]*Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China*
**Email: kuoliu@ipe.ac.cn*

ABSTRACT

Hydrogen (H_2) is considered as a clean and renewable secondary energy, and is promising for replacement of fossil fuel. Nevertheless, H_2 is inclined to leak during transportation, increasing the possibility of explosion due to its broad explosion limit range. Consequently, it is imperative to find a safe way to transport H_2. H_2 storage using liquid organic hydrogen carries (LOHCs) could transport H_2 at ambient conditions and is safe for H_2 storage and transportation. Among different LOHCs, dibenzyltoluene (DBT) with a H_2 storage capacity of 6.2 wt% is safer or more economical than other LOHCs, e.g., toluene, carbazoles[1,2]. However, the dehydrogenation of perhydro-dibenzyltoluene (H18-DBT) always uses the precious metal Pt as the active component[3]. Application of single-atom catalysts (SACs) with high Pt utilization is an effective way of reducing the cost of the catalyst[4-6]. However, until now, application of SACs in H_2 storage/release using DBT/H18-DBT is still lacking. In this study, Pt single atoms with different coordination numbers were prepared by finely tuning the densities of Pt on CeO_2 (Pt_1/CeO_2), and were applied in H18-DBT dehydrogenation. The dehydrogenation activity on Pt SACs far exceeded those on Pt nanoparticle catalysts reported previously. Pt_1/CeO_2 with a lower coordination number exhibited a better activity of H18-DBT dehydrogenation than those with higher coordination numbers. Pt_1/CeO_2 with a lower coordination number exhibited a new dehydrogenation mechanism involving preferential dehydrogenation of the middle ring of H18-DBT, leading to its high dehydrogenation performance. The coordination environment of Pt single atoms correlated closely with the activity of H18-DBT dehydrogenation.

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Oral

SA-Oral-01

2D Conductive Ni-HAB as a Catalyst for the Electrochemical Oxygen Reduction Reaction

Zhihua Chen*[1,2]

Department of Chemical Engineering, Stanford University, Stanford, California 94305, USA

ABSTRACT

Catalytic systems whose properties can be systematically tuned via changes in synthesis conditions are highly desirable for next generation catalyst design and optimization. Herein, we present a 2D conductive metal–organic framework (c-MOF) consisting of M-N4 units (M = Ni, Cu) and a hexaaminobenzene (HAB) linker as a catalyst for the oxygen reduction reaction (ORR). By varying synthetic conditions, we prepared two Ni-HAB catalysts with different crystallinities, resulting in catalytic systems with different electrical conductivities, electrochemical activity, and stability. We show that crystallinity has a positive impact on conductivity and demonstrate that this improved crystallinity/conductivity improves the ORR performance of our model system. Additionally, density functional theory (DFT) simulations were performed to probe the origin of M-HAB's catalytic activity, and they suggest that M-HAB's organic linker acts as the active site for the ORR, with the role of the metal being to modulate the linker sites' binding strength.

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SA-Oral-02

Single Pt Atoms in MOFs to Construct Single-site Catalysts with Diversified Coordination Environments

Liu Shaoxiong[1], Wang Tiefeng*[1]

[1] *Beijing Key Laboratory of Green Reaction Engineering and Technology (Chemical engineering, Tsinghua University, Beijing, China)*
**Email: wangtf@tsinghua.edu.cn*

ABSTRACT

Researchers have long pursued the optimization of single-atom active site synthesis and the understanding of their structure–catalytic performance relationships. However, due to the inherent heterogeneity of catalyst supports, most single-atom catalysts (SACs) feature non-uniform coordination environments, with limited means for precise control or differentiation. To bridge the gap between experimental studies and theoretical calculations, model materials with uniformly coordinated "unit-site catalysts" are highly desirable.

Here, we report a one-pot strategy to anchor zero-valent platinum (Pt) single atoms onto UiO-66–X (X = H, NH_2, Br, I) metal–organic frameworks (MOFs), creating uniform coordination environments. We systematically examined how ligand environments influence the catalytic performance and thermal stability of Pt sites. An optimized solvothermal synthesis with mechanical stirring ensured high Pt dispersion within MOF pores, preventing nanoparticle formation. XPS and EXAFS analyses confirmed bidentate coordination between Pt and ligand atoms (C, N, Br, I). The Pt sites displayed distinct catalytic activities, showing a volcano-like trend with their Bader charges.

Moreover, the four catalysts exhibited differing sintering resistances under hydrogen. Notably, Pt_1@UiO-66–Br retained atomic dispersion after 300 °C hydrogen treatment. DFT calculations revealed this stability results from the combined thermodynamic and kinetic factors of hydrogen adsorption. Based on this, a migration model for "Pt–hydrogen" species within MOF pores is proposed.

This strategy is extendable to other noble metals (Rh, Pd, Au) and various MOFs (IRMOF-3, MIL-101–NH_2), offering a general approach for designing stable, tunable SACs.

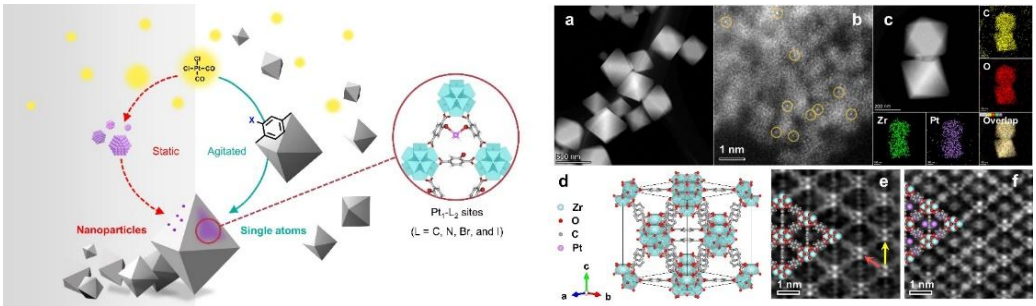

Figure 1. Schematic illustration of the synthesis mechanism of Pt single-atom-loaded UiO-66–X, the structure of the active sites, and the corresponding STEM images.

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SA-Oral-03

Single Atom Catalysts-Enabled Catalytic Ammonia Combustion at 1100°C

Yankun Du[1], Bingqing Yao[1], Ning Yan*[2], Qian He*[1]

1. Department of Material Science and Engineering, College of Design and Engineering, National University of Singapore, Singapore

2. Department of Chemical and Biomolecular Engineering, College of Design and Engineering, National University of Singapore, Singapore

**Email: Ning Yan ning.yan@nus.edu.sg; Qian He: heqian@nus.edu.sg*

Background: Ammonia (NH_3), a carbon-free fuel produced from air, water, and renewable energy, offers high energy density (12.7 MJ/L) and scalable infrastructure, making it a promising energy carrier. However, its combustion faces challenges, including a narrow flammability range, high ignition temperature, slow flame speed, and significant NO_x emissions.[1,2] A promising approach is catalytic ammonia combustion (CAC),[3] which leverages surface-mediated reactions to enhance combustion efficiency while suppressing NO_x emissions, benefiting from NH_3's inherent role as a reductant in SCR/SNCR processes. However, thermal efficiency limitations restrict the applicability of high-temperature CAC (HT-CAC). HT-CAC is a difficult task due to (i) demanding stability requirements for catalysts and (ii) potentially high NO_x emissions.

Methods: Supporting active metals on various metal oxides and then testing their HT-CAC performance in a fixed-bed reactor. Choosing the potential catalyst for HT-CAC according to ignition temperature, NO_x emissions, and good thermal stability.

Results: The as-prepared single atoms catalyst ignites NH_3 combustion just above 200 ºC and has excellent stability when operated at 1100 ºC. The presence of the catalyst also reduces the NO_x emission to around 50 ppm without detectable NH_3 slip.

Discussion and Conclusion: HT-CAC offers an alternative and complementary approach that can serve as a standalone solution for high-grade heat applications or be integrated into broader combustion systems—as a pre-burner, flame stabilizer, or NO_x control module. The emergence of thermally robust catalysts, combined with advances in characterization, offers exciting possibilities for enabling catalytic combustion in regimes previously inaccessible by conventional catalysts.

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SA-Oral-04

Selective Oxidation of Ethane and Derivatives over Rhodium Single-Atom Catalysts

Bin Li[1], Jiali Mu[2], Siquan Feng[2], Xiangen Song*[1], Li Yan*[1], Yunjie Ding*[1,2]

[1]*Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China*
[2]*State Key Laboratory of catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China*
**Email: Yunjie Ding (dyj@dicp.ac.cn); Li Yan (yanli@dicp.ac.cn); Xiangen Song (xiangensong@dicp.ac.cn).*

ABSTRACT

Light alkanes are the primary components of natural gas, shale gas, and gas hydrates. In recent years, the conversion of low-carbon alkanes has gained significant attention, with increasing demand for upgrading ethane to high-value-added products[1]. However, due to the high C-H bond dissociation energy of ethane, the activation of low-carbon alkanes typically requires high temperatures, resulting in substantial energy consumption. Therefore, achieving low-temperature direct catalytic conversion of low-carbon alkanes is of great importance.
We report a Rh-based single-atom catalyst supported on activated carbon with S, N, and I synergistic coordination. Comprehensive characterization results indicate that the coordination environment of Rh is modulated by functional groups within the activated carbon. Among them, Rh_1/AC-SNI exhibits the highest turnover rate (TOR) for selective oxidation of ethane at low temperature, reaching 158.5 mol/(mol_{Rh}•h), with acetaldehyde being the predominant oxygenated product. The formation mechanisms of acetaldehyde and ethanol follow two distinct pathways, which are verified by ^{18}O isotope labeling experiments: the oxygen sources for ethanol and acetaldehyde are derived from O_2 and H_2O, respectively. In situ FEL-TOF/MS was employed to capture these key intermediates. Additionally, we report the application of this catalyst in the direct oxidation of ethanol. Rh_1/AC-SNI, in the presence of I_2, efficiently catalyzes the direct oxidation of ethanol to glycolic acid, establishing a sustainable regeneration-driven oxygen shuttle cycle mediated by water.

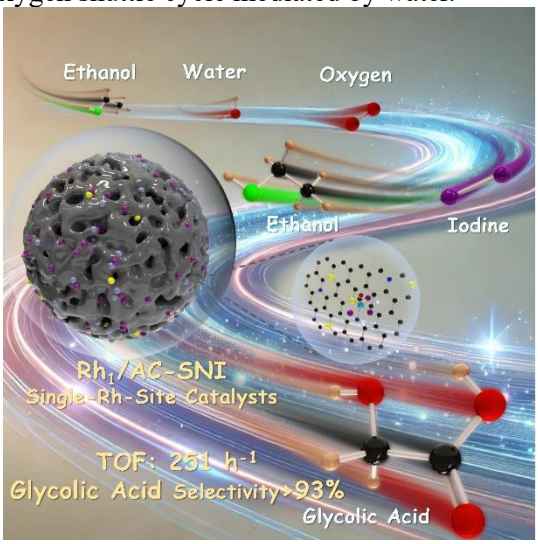

Figure 1. Spatially resolved in-situ STXM mapping of reversible metal dynamics in Ni–Co spinel catalysts.

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SA-Oral-05

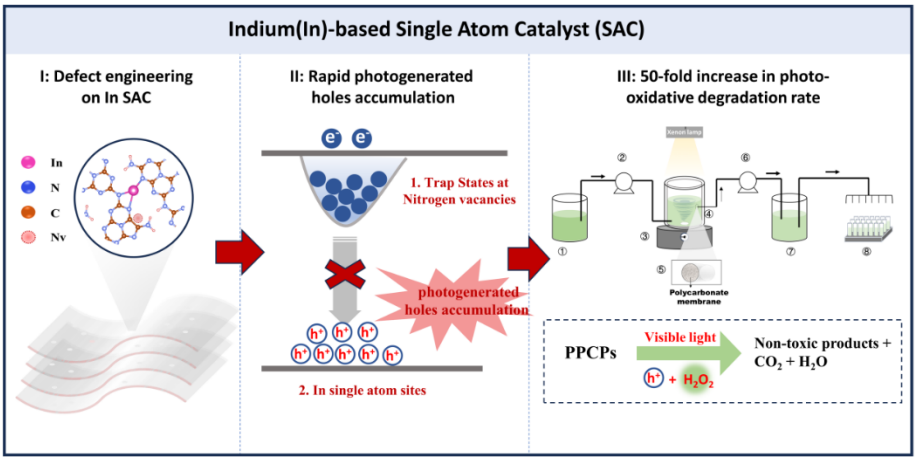
Defect-Engineered Indium Single-Atom Photocatalysts for Efficient PPCP Degradation via Hole Accumulation

Jingjing Zhang, Xuan Yang, Rajasekhar Balasubramania

Department of Civil & Environmental Engineering, National University of Singapore, Singapore
**Email: jjz@nus.edu.sg*

ABSTRACT

This research presents a novel approach employing defect-engineered indium (In) single-atom photocatalysts with nitrogen vacancy (Nv) defects dispersed in carbon nitride foam (In-Nv-CNF) to increase the concentration of photogenerated holes, thus leading to enhanced photocatalytic performance towards PPCPs degradation. The In-Nv-CNF photocatalysts were synthesized through a straightforward one-step calcination method. The defect-engineered In-Nv-CNF demonstrates a significant improvement in photocatalytic performance, with a 50-fold increase in the photo-oxidative degradation rate of antibiotics such as tetracycline and ciprofloxacin under visible light compared to pristine carbon nitride. In a continuous flow reactor, the efficiency of In-Nv-CNF shows efficient the continuous removal of a pharmaceutical mixture (tetracycline and ciprofloxacin) reaching 94% and 85%, respectively, under a short hydraulic retention time of 30 minutes. Mechanism analysis reveals that the enhanced performance is attributed to nitrogen vacancies, which create defect states within the bandgap, serving as electron traps that facilitate the accumulation of long-lived holes at the single indium atom sites. This study provides a promising strategy to enhance the efficiency of photocatalytic processes, focusing on the critical role of photogenerated holes in driving oxidation reactions [1].



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Poster

SA-Poster-116

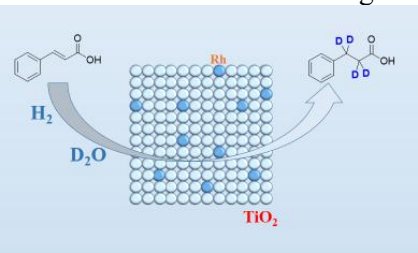
Reductive Deuteration of Cinnamic Acid Catalyzed by Heterogeneous Atomically Dispersed Rhodium

Fatima Asif,[1, 2,] Shu-Xian Li,[1, 3,] Wen-Ting Zhang, [1, 2] Xiang-Ting Min,[1, *] Botao Qiao[1, 2, *]

[1] *CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.*
[2] *University of Chinese Academy of Sciences, Beijing 100049, China.*
[3] *Dalian University of Technology, Dalian 116023, China.*
* *Corresponding authors E-mail: bqiao@dicp.ac.cn, minxiangting@dicp.ac.cn*

ABSTRACT

Deuterium (D) labelling has extensive applications in numerous areas as there is a growing interest in developing methodologies for the deuteration of organic molecules. [1] Reductive deuteration has emerged as a powerful tool in pharmaceutical and chemical synthesis, since it is capable of selective incorporation of deuterium into organic molecules. Here, we disclose a breakthrough method for the reductive deuteration of cinnamic acid catalyzed by heterogeneous atomically dispersed rhodium (Rh_1/TiO_2). Our catalyst exhibits superior activity compared to traditional heterogeneous catalysts. Under optimized conditions, Rh_1/TiO_2 achieves 99% deuteration efficiency of cinnamic acid within 6 hours. The mild conditions, high efficiency, and selectivity of our method make it an attractive strategy for the synthesis of deuterated pharmaceuticals and fine chemicals. Mechanistic investigations suggest a concerted catalytic pathway involving hydrogen gas activation, isotopic exchange, and ultimately reductive deuteration of the substrate. The present methodology aligns with advances in heterogeneous catalysis for deuteration reactions and highlights the versatility of atomically dispersed metal catalysts. This work not only demonstrates the potential of atomically dispersed Rh catalysts in precise isotopic labeling but also offers a scalable and environmentally friendly alternative to traditional homogeneous deuteration protocols.



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SA-Poster-117

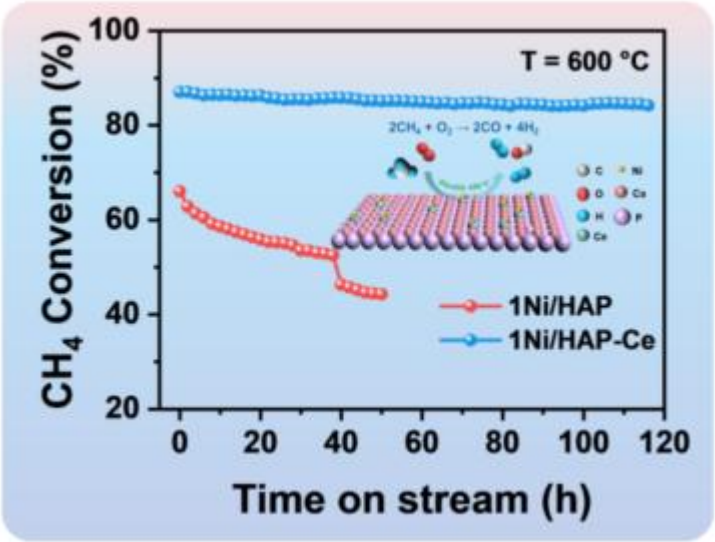
Ce-Doped HAP Stabilized Single-Atom Nickel Catalyst for Active and Durable Partial Oxidation of Methane to Syngas

Yunxia Liu1 , Botao Qiao 1,*

[1] *CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*
**Email: bqiao@dicp.ac.cn*

ABSTRACT

The catalytic partial oxidation of methane (POM) to syngas presents a promising route for efficient methane utilization. However, catalyst durability remains a critical challenge due to the high operating temperatures typically exceeding 600 °C. Nickel, the most commonly used active metal in POM, suffers from significant deactivation caused by oxidation and sintering of its metallic sites under reaction condition. Herein, we demonstrate that Ce-doping into hydroxyapatite (HAP) effectively stabilizessingle-atom Ni species, delivering outstanding POM performance with over 98% CH4 conversion and 86% syngas selectivity at 700 °C. Furthermore, the 1Ni/HAP-Ce catalyst (Ni normal loading 1 wt%) exhibits excellent stability during continuous testing at 600 °C for 115 h without obvious deactivation, which significantly exceeds that of corresponding 1Ni/HAP catalysts (methane conversion dropped 22% after 50 h). The H2-TPR analysis reveals that Ni spices in 1Ni/HAP-Ce catalyst show a higher reduction temperature, indicating the enhanced Ni-Ce interaction and enhanced oxidation resistance of Ni under POM conditions. These findings highlight the critical role of support engineering in the development of robust single-atom catalysts for high-temperature applications such as POM.



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SA-Poster-118

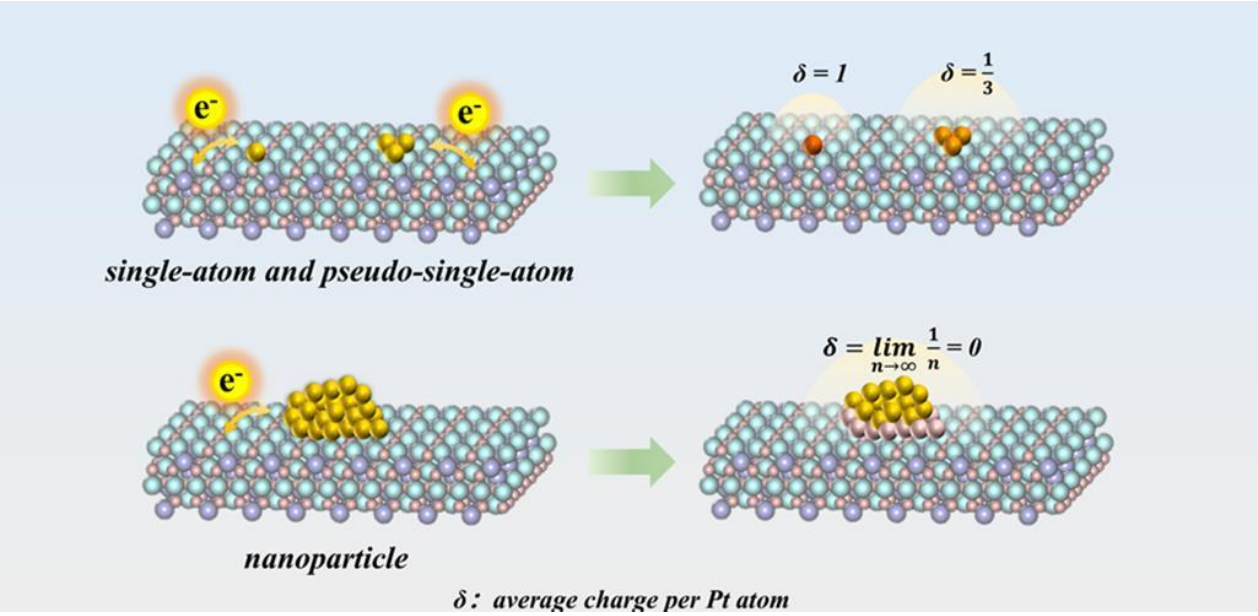
Size-dependent strong metal-support interaction modulation of Pt/CoFe2O4 catalysts

Yangyang Li [1,2] , Jingyi Yang [3,*], Botao Qiao [1,4,*], Tao Zhang [2,4]

[1] *CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*
[2] *University of Chinese Academy of Sciences, Beijing 100049, China*
[3] *Fritz Haber Institute of the Max Planck Society, Berlin 14195, Germany*
[4] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*

ABSTRACT

Supported metal catalysts are the backbone of heterogeneous catalysis, playing a crucial role in the modern chemical industry. Metal-support interactions (MSIs) are known important in determining the catalytic performance of supported metal supported catalysts. This is particularly true for single-atom catalysts (SACs) and pseudo-single-atom catalysts (pseudo-SACs), where all metal atoms are dispersed on, and interact directly with the support. Consequently, the MSI of SACs and pseudo-SACs are theoretically more sensitive to modulation compared to that of traditional nanoparticle catalysts. In this work, we experimentally demonstrated this hypothesis by an observed size-dependent MSI modulation. We fabricated CoFe2O4 supported Pt pseudo-SACs and nanoparticle catalysts, followed by a straightforward water treatment process. It was found that the covalent strong metal support interaction (CMSI) in pseudo-SACs can be weakened, leading to a significant activity improvement in methane combustion reaction. This finding aligns with our recent observation of CoFe2O4 supported Pt SACs. By contrast, the MSI in Pt nanoparticle catalyst was barely affected by the water treatment, giving rise to almost unchanged catalytic performance. This work highlights the critical role of metal size in determining the MSI modulation, offering a novel strategy for tuning the catalytic performance of SACs and pseudo-SACs by fine-tuning their MSIs.



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SA-Poster-119

Influence of Na Promoter in Tuning Catalytic Properties of Rh/TiO2 in Hydrogenation Reactions

Munam Jung[1] , Maxim Park Dickieson[1] , Qian He[2] , Yawen Zhang[3] , Kyungho Lee[4*], Ning Yan[1*]

[1]*Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585, Singapore*
[2]*Department of Materials Science and Engineering, National University of Singapore, 9 Engineering, Drive 1, Singapore 117575, Singapore*
[3]*School of Chemical and Molecular Engineering, Peking University, 202 Chengfu Road, Yanyuan Street, Haidian District, Beijing, China, 100871*
[4]*Clean Fuel Research Laboratory, Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea*
**Email: khlee9@kier.co.kr , ning.yan@nus.edu.sg*

ABSTRACT

Alkali metals are commonly employed as promoters in heterogeneous metal catalysts to enhance catalytic activity, product selectivity, and stability. However, their precise mechanistic role remains elusive due to the intricate combination of geometric and electronic influences, dynamic surface transformations, and their context-dependent behavior based on the support material and reaction environment. In this study, we offer a comprehensive perspective on the multifaceted function of alkali metal promoters in hydrogenation reactions, using Na-modified Rh/TiO_2 as a representative system. We systematically investigate the interactions within the Rh–Na–TiO_2 ternary system under hydrogen atmosphere and trace the behaviors of activated hydrogen using a suite of advanced characterization techniques such as high-angle annular dark-field imaging scanning transmission electron microscopy (HAADF-STEM), temperature programmed reduction (TPR), temperature programmed desorption (TPD), H2-D2 exchange, quasi in situ x-ray photoelectron spectroscopy(XPS), and diffuse reflectance infrared fourier transform spectroscopy (DRIFTS). The Na addition does not alter the textural property significantly. On the other hand, Basic Na species near the Rh preferentially scavenges the acidic H+ enriching the Rh surface to be more electron rich and simultaneously suppressing the hydrogen spillover from Rh to the support. Additionally, Na incorporation exhibits bond-specific effects on the hydrogenation of C=C, C=O, N=O and CO2. Furthermore, alkali metal doping in CO2 hydrogenation reaction changes the selectivity drastically, shifting the dominant product from methane to carbon monoxide.

SA-Poster-120

Density effect of rhenium single-atom catalysts for aldehyde hydrogenation

Xunzhu Jiang[1] , Xiangting Min,[1] Bo Zhang,[1] Wengang Liu, [2] * Botao Qiao* [1]

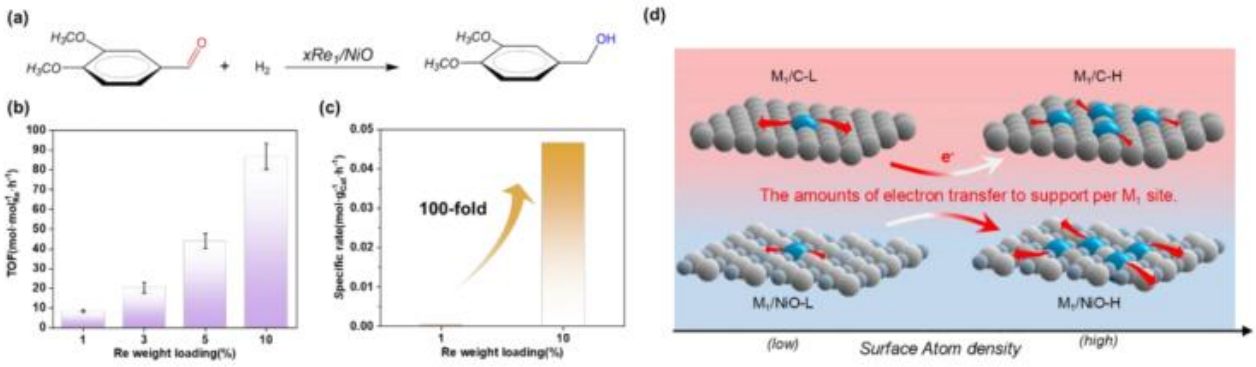
[1]*CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China*

[2]*Department College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China*

**Email: bqiao@dicp.ac.cn ; liuwengang@qust.edu.cn*

ABSTRACT

In recent years, high-metal-loading single-atom catalysts (SACs) have gained attention for their exceptional catalytic properties across various heterogeneous catalysis applications. Different from the isolated sites in low-density SACs, metal atoms in high-density SACs positioned closer together, offering potential long-range interactions. Such interactions may substantially modulate the electronic structure of individual metal centers via electron transfer, spin coupling, or charge redistribution and, consequently, thereby altering their intrinsic activity. However, due to the challenge of fabricating oxide-supported SACs with high metal loading, previous studies on the atomic density effect have focused primarily on carbon-based supports[1,2] . In this work, we synthesized NiO-supported Re SACs through a simple ball-milling method, and successfully modulated the surface atomic density by adjusting the Re precursor-to-NiO ratio, obtaining Re1/NiO SACs with Re loading of 1, 3, 5, and 10 wt%. Catalytic performance tests in the veratraldehyde hydrogenation demonstrated that increasing Re atomic density enhanced intrinsic catalytic activity (turnover frequency, TOF) by up to 10 times in terms of every Re atoms, resulting in an overall 100-fold improvement in the specific catalytic rate based on catalyst weight. Characterization and theoretical calculations revealed that increasing the atomic density of Re single atoms led to a rise in their oxidation state, opposite to the observations on carbon material-supported SACs. The more electron-deficient Re single-atom sites facilitated the adsorption and activation of aldehyde groups, significantly boosting the intrinsic catalytic activity. These findings underscore the crucial role of atomic-density modulation in optimizing catalytic performance.



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SA-Poster-121

Electrothermal Water-Gas Shift Reaction with a Silicomolybdate-Based Palladium Single-Atom Catalyst

Jinquan Chang[1], Chen Chen[1], Xinbing Ma*[2], Ning Yan*[1,2]

[1*] *Department of Chemical and Biomolecular Engineering, National University of Singapore, 117585, Singapore*
[2] *Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, Fuzhou, China*
**Email: xbma@tju.edu.cn , ning.yan@nus.edu.sg*

ABSTRACT

The water-gas shift (WGS) reaction is often conducted at elevated temperature and requires energy intensive separation of hydrogen (H_2) from methane (CH_4), carbon dioxide (CO_2), and residual carbon monoxide (CO). Designing processes to decouple CO oxidation and H_2 production provides an alternative strategy to obtain high-purity H_2 streams. We report an electrothermal WGS process combining thermal oxidation of CO on a silicomolybdic acid (SMA)-supported Pd single-atom catalyst (Pd_1/CsSMA) and electrocatalytic H_2 evolution. The two half-reactions are coupled through phosphomolybdic acid (PMA) as a redox mediator at a moderate anodic potential of 0.6V (versus Ag/AgCl). Under optimized conditions, our catalyst exhibited TOF of $1.2 s^{-1}$ with turnover numbers above 40000 mol_{CO2} mol Pd^{-1} achieving stable H_2 production with a purity consistently exceeding 99.99%.

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SA-Poster-122

"Suspended" Single Rhenium Atoms on Nickel Oxide for Efficient Electrochemical Oxidation of Glucose

Bo Zhang, Xunzhu Jiang, Aiqin Wang, Botao Qiao*, Tao Zhang

CAS Key Laboratory of Science and Technology on Applied Catalysis,
Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China
**Email: bqiao@dicp.ac.cn*

ABSTRACT

Well-defined single-atom catalysts (SACs) serve as ideal model systems for directly comparing experimental results with theoretical calculations, offering profound insights into heterogeneous catalytic processes.1-2 However, precisely designing and controllably synthesizing SACs remain challenging due to the unpredictable structure evolution of active sites and generation of embedded active sites, which may bring about steric hindrance during chemical reactions. Herein, we present the precious nonpyrolysis synthesis of Re SACs with a well-defined phenanthroline coordination supported by NiO (Re1-phen/NiO) (Fig.1). 3Multiple experimental characterizations together with theoretical calculations unravel the idea that the isolated Re atoms are suspended on the NiO surface, connected by phenanthroline ligands standing perpendicular to the surface. This unique structure provides the Re1-phen/NiO SAC with a strong capability to activate glucose molecules, enabling fully exposed Re=O double bonds in an open-ended reaction environment to simultaneously react with hydroxyl and aldehyde groups at both ends of the glucose molecule, rapidly forming glucaric acid.

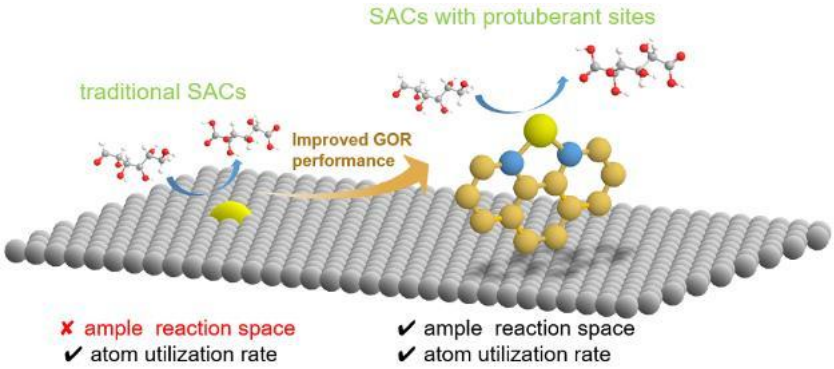

Fig. 1. "Suspended" Single Rhenium Atoms on Nickel Oxide for Electrochemical Oxidation of Glucose

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SA-Poster-123

Sulfite-Enforced, Reduced Phosphomolybdate Catalyzed Aerobic Methane Oxidation to Methanol

Tie Wang[1,2], Sikai Wang[1,2], Hua An[1,2], Max J. Hülsey[2], Hiroyuki Asakura[3,4], Qian He[5*], Ning Yan[1,2*]

[1]*Joint School of National University of Singapore and Tianjin University, Fuzhou 350207, China.*
[2]*Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore.*
[3] *Department of Applied Chemistry, Kindai University, Osaka, Japan.*
[4] *Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Kyoto, Japan.*
[5]*Department of Materials Science and Engineering, National University of Singapore, Singapore.*
**Email: heqian@nus.edu.sg, ning.yan@nus.edu.sg*

ABSTRACT

The direct oxidation of methane to methanol with molecular oxygen has been regarded as a promising pathway for methane conversion and methanol synthesis with high atomic efficiency. Considering the inertness of CH_4 and O_2, proper catalyst design has become a need for the aerobic methane conversion in aqueous media at ambient temperature. [1] Notably, H_2-reduced Mo sites in the palladium-phosphomolybdate system (Pd/CsPMA) achieved room-temperature aerobic methane conversion with methanol selectivity close to 100%. [2] However, the methanol productivity falls far below the thresholds for industrial application, partially due to the deactivation of the active sites. [3,4]
Inorganic ligands have been utilized as effective promoters to modulate the electronic structures of catalytic active sites for better performances. [5] In this work, the effect towards aqueous room-temperature partial oxidation of methane over Pd/CsPMA of a series of inorganic salts were screened and Na_2SO_3 was found to have superior promotion effect of 4.7-fold (Figure 1). The reductive reaction medium assisted maintaining the high productivity of methanol by supporting the reduced Mo sites against reoxidation, which was found to be one of the key root causes of catalyst deactivation. SO_3^{2-} was found to adsorb and coordinate to reduced Mo sites easily through spectroscopic investigations and theoretical studies. Specifically, the SO_3^{2-}-modified PMA exhibited excellent redox properties in cyclic voltammetry experiments with high intimacy with O_2, thus have greater chance to create more efficient active sites. These discoveries showcased a good example of active site modification with inorganic ligands, providing a catalyst development strategy with high potential applicability to other oxide-based systems.

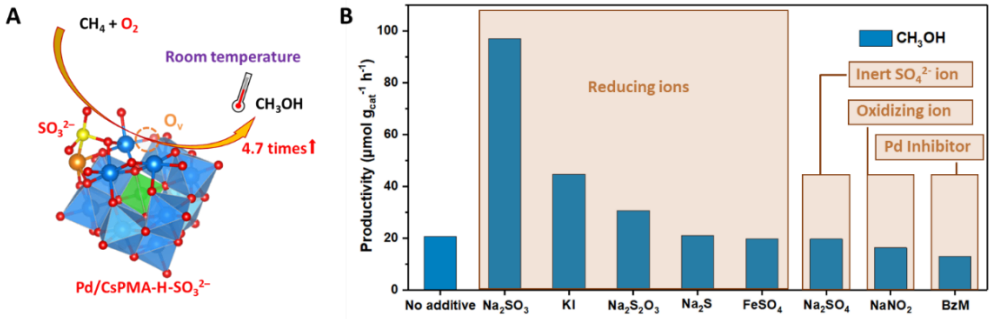

Figure 1 (A) Schematic illustration of SO_3^{2-} as a promoter for improved aerobic methane oxidation to methanol by modifying reduced Mo sites in PMA. (B) Room-tempeature methane oxidation performance of H_2-reduced Pd/CsPMA with different soluble inorganic salts added.

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SA-Poster-124

Cage-siloxane based porous supports functionalized with metal-reducing groups into the entire framework

Masuda Takumi[1], Takuya Hikino[2,3], Rei Umeda[1], Atsushi Shimojima[1,3], Yasushi Sekine *[1,3]

[1] *Department of Applied Chemistry, Faculty of Science and Engineering, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555, Japan*

[2] *Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan*

[3] *Kagami Memorial Research Institute for Materials Science and Technology, Waseda University, 2-8-26 Nishiwaseda, Shinjuku-ku, Tokyo 169-0051, Japan*

**Email: ysekine@waseda.jp*

ABSTRACT

Metal-supported catalysts are essential for large-scale chemical production. Their performance depends on properties such as shape, surface exposure, and dispersion. High dispersion of metal species increases the number of unsaturated sites, imparting unique properties distinct from bulk metals.[1] Silica is one of the most common supports, but it exhibits weaker interactions with metals compared to reducible oxides. Therefore, highly dispersed metals on silica tend to agglomerate under external factors such as heating. Confining metal species within porous materials is a promising approach to suppress agglomeration. Achieving confinement with high dispersion typically requires substituents that can interact with metal species.[2-3] However, post-synthetic introduction of such substituents onto porous silica is difficult to control sites in the framework.

In this study, novel nanoporous silica was synthesized using a building block approach, wherein hydrosilyl groups were introduced simultaneously during the support formation. Cage siloxanes composed of double n-membered ring structures offer high thermal and chemical stability as building blocks and can be easily cross-linked to form porous frameworks.[4] The incorporated hydrosilyl groups facilitate on-site reduction of noble metals. Specifically, a D4R-type cage siloxane ($[Si_8O_{12}][OH]_8$, Q8H8)[5] was cross-linked with triethoxysilane, yielding TESQ8H8. Then, TESQ8H8 was stirred with a $HAuCl_4$ solution to obtain Au/TESQ8H8. TEM images of Au/TESQ8H8 confirmed the presence of Au nanoparticles.[6] Au/TESQ8H8 exhibit resistance to sintering, as the average Au particle size remained almost unchanged after post-calcination. Furthermore, confinement effect of Au/TESQ8H8 was estimated to be enhanced after thermal treatment. This approach represents a promising strategy for designing controllable silica-based metal supports.

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SA-Poster-125

Defying the oxidative-addition prerequisite in cross-coupling through artful single-atom catalysts

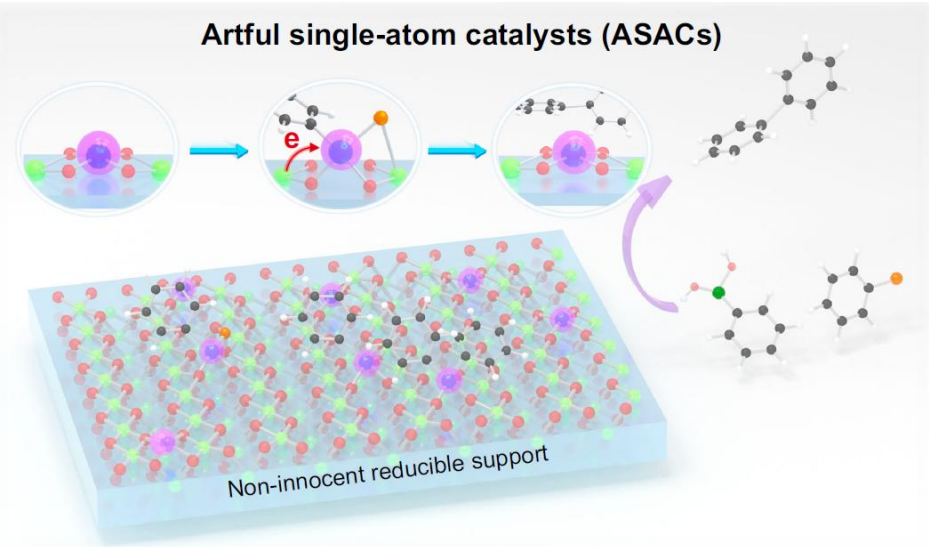
FU Xingjie[1], SHI Jiwei[1], LU Jiong*[1]

[1] *Department of Chemistry, National University of Singapore, Singapore, Singapore*

Email: fuxingjie@u.nus.edu

ABSTRACT

Heterogeneous single-atom catalysts (SACs) have gained significant attention for their maximized atom utilization and well-defined active sites, but they often strugglewithmulti-stage organic cross-coupling reactions due to limited coordination space and reactivity. Here, we report an "anchoring-borrowing" strategy combined facet engineering to develop artful single-atom catalysts (ASACs) through anchoring foreign single atoms onto specific facets of the non-innocent reducible carriers. ASACs exhibit adaptive coordination, effectively bypassing the oxidative-addition prerequisite for bivalent elevation at a single metal site in both homogenous and heterogeneous cross-couplings. For example, Pd1-CeO_2(110) ASAC exhibits unparalleled activity in coupling with more accessible aryl chlorides, and challenging heterocycles, outperforming traditional catalysts with a remarkable turnover number of 45,327,037. Mechanistic studies reveal that ASACs leverage dynamic structural changes, with reducible carriers acting as electron reservoirs, significantly lowering reaction barriers. Furthermore, ASACs enable efficient synthesis of biologically significant compounds, drug intermediates, and active pharmaceutical ingredients (APIs) through a scalable high-speed circulated flow synthesis, underscoring great potential for sustainable fine chemical manufacturing.



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SA-Poster-126

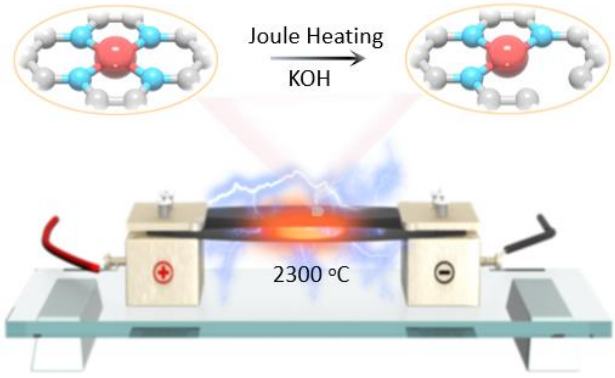
De-Saturation of Single-Atom Copper Catalysts for Accelerating Propargylic Substitution Reactions

Qilong Cai†, Yang Meng†, Chao Wu†, Wenjia Qu, Qiang Wang, Tan Li, Chengyi Liu, Jinxing Chen, Huihui, Lin, Qian He, Yafei Zhao*, Shibo Xi*, Jiong Lu*

[1] *Department of Chemistry, National University of Singapore, Singapore, Singapore.*
[2] *State Key Laboratory of Precision and Intelligent Chemistry, University of Science and Technology of China (USTC), Jinzhai Road 96, Hefei, Anhui 230026, P. R. China.*
*Email: yafeizhao@ustc.edu.cn , xi_shibo@partner.nus.edu.sg, chmluj@nus.edu.sg

ABSTRACT

Rational design of proximal coordination microenvironments surrounding catalytic sites to achieve optimal reaction kinetics represents a paramount pursuit in single-atom catalysts (SACs), yet continues to pose substantial synthetic challenges. Developing innovative strategies that simultaneously stabilize low-coordinated single-metal species on solid supports, while ensuring atomic precision and high activity, remains imperative. Herein, we demonstrated a de-saturation strategy for SACs (denoted as De-sat SACs) using a top-down approach based on a KOH-mediated Joule thermal shock to obtain under-coordinated and asymmetric SACs for efficient organic synthesis. Using copper-based SACs as a proof-of-concept, our de-saturation strategy effectively converts the CuN_4 to CuN_3 configuration. The De-sat Cu SACs exhibit remarkable catalytic activity in propargylic substitution reactions, tolerating a broad range of nucleophiles (N–, C– and O–), as well as diverse aryl, alkyl, tertiary and cyclic propargylic carbonates. The coordination reduction in these De-sat SACs not only breaks the structural symmetry to enhance site accessibility but also elevates the energy of the orbital of Cu atom, thereby facilitating the formation of copper–alkynyl intermediates and boosting their catalytic performance. Our findings establish a new platform for the rational design and synthesis of de-saturated yet stable SACs, facilitating challenging catalytic transformations toward sustainable chemical manufacturing.



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SA-Poster-127

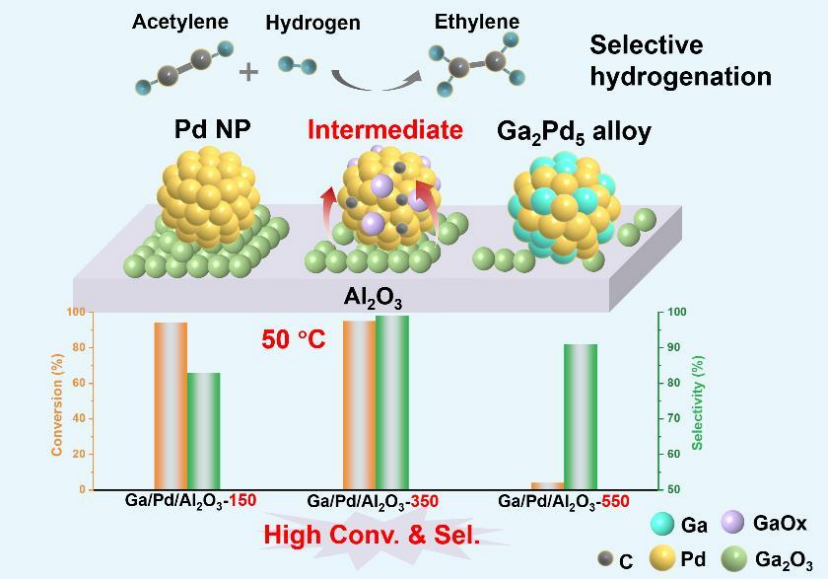
Partially reduced Ga-Modified Pd/Al_2O_3: Boosting Selectivity in Acetylene Semi-Hydrogenation at High Conversion

Rizheng Jing1,2 , Leilei Kang2 , Qingqing Gu2 , Aiqin Wang* 2 , Tao Zhang2

[1] *University of Chinese Academy of Sciences, Beijing 100049, China.*
[2] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.*
**Email: aqwang@dicp.ac.cn*

ABSTRACT

PdGa intermetallic compounds have been reported as highly selective catalysts for the semi-hydrogenation of acetylene.1 However, the formation of intermetallic compounds always requires a high reduction temperature, which leads to a relatively large particle size, low metal utilization as well as high reaction temperature. Herein, we report that partially reduced Ga in $Ga/Pd/Al_2O_3$ catalyst can boost the selectivity of ethylene without compromising the activity. Compared with Pd/Al_2O_3 catalyst, the selectivity of ethylene was increased from 55% to 99% at high acetylene conversion of 95%. Compared with PdGa intermetallic compound, the reaction temperature significantly decreased from 90 °C to 50 °C. A series of operando characterizations revealed that Ga existed in a partially reduced state between 0 to +3, presenting on the surface and sub-surface of Pd nanoparticles. Distinct from the PdGa intermetallic compounds, the partially reduced Ga species allows for the occurrence of carburization of Pd NPs in the early stage of the reaction, forming GaOx(x=0~1.5) decorated PdCx, which was believed as the real active site. Both Ga decoration and carbon infiltration contributed to the remarkable increase in ethylene selectivity at high acetylene conversion.



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SA-Poster-128

Water-mediated tuning of the selectivity in nitroarenes hydrogenation over a Pt/Fe_2O_3 catalyst

Anqi Li1,2 , Xiaofeng Yang*1 , Aiqin Wang* 1 ,Tao Zhang* 1

[1]*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China.*
2University of Chinese Academy of Sciences, Beijing 100049, China.
**Email: yangxf2003@dicp.ac.cn , aqwang@dicp.ac.cn , taozhang@dicp.ac.cn*

ABSTRACT

The selective hydrogenation of nitroarenes with multiple reducible groups to aromatic amines has attracted considerable interests in the field of single-atom catalysis[1] . Compared to the intensive efforts on the modification of catalysts, little attention has been paid to the effect of water although water is produced as a byproduct and often used as a solvent in this reaction. In this study, we have synthesized a well-defined PtNP/Fe2O3 catalyst featuring uniformly distributed Pt NPs on the (001) facet of Fe2O3 nanoplates, and investigated its catalytic performance in 3-nitrostyrene hydrogenation. Experimental results demonstrated that water content in the solvent had a significant effect on selectivity of 3-aminostyrene with the highest selectivity exceeding 98 % achieved at 10 vol% water content in the solvent. Through combined kinetic studies, in situ infrared spectroscopy, and density functional theory (DFT) calculations, it was revealed that the competitive adsorption of water molecules at active sites reduced the available sites for both the adsorption of -C=C group and H2 dissociation, meanwhile a new hydrogen-bonding adsorption site for the nitro (-NO2) group can be generated with the hydroxyl groups derived from water dissociation at the Pt-FeOx interface, thereby preferentially facilitating its hydrogenation and enhancing product selectivity. This work provides atomic-level insights into how the presence of water as a byproduct can modulate catalytic selectivity in nitroaromatic hydrogenation over a Pt/Fe2O3 catalyst.

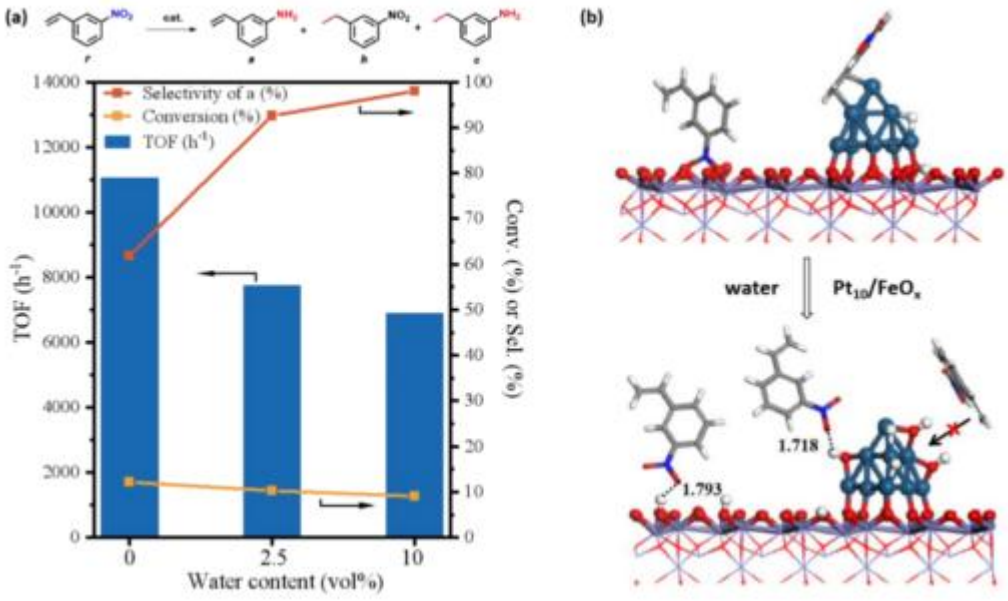

Figure 1. (a) Hydrogenation performance of 3-nitrostyrene with increasing amount of water. (b) Schematic diagram of water regulating the selectivity of hydrogenation reaction.

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SA-Poster-129

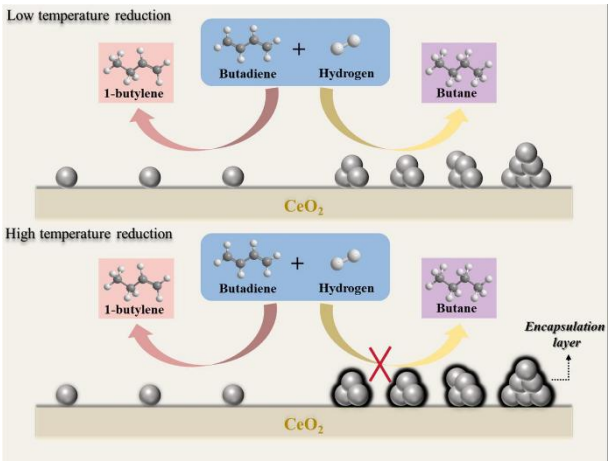
Palladium single-atom catalysts prepared via strong metal-support interaction for selective 1,3-butadiene hydrogenation

Yuan Gao 1,3 , Weihao Hua 1 , Cun Liu 1,* , Feng Hong 1 , Botao Qiao 1,2,*

[1]*CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 116023, Dalian, China*
[2] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 116023, Dalian, China*
[3] *University of Chinese Academy of Sciences, 100049, Beijing, China*

ABSTRACT

Selective hydrogenation of 1,3-budiatene to butenes is an effective way to eliminate the minor 1,3-budiatene impurities, which can cause intractable issues of catalyst deactivation in the C4 olefins upgrading processes. To this end, Pd single atom catalysts (SACs) exhibit remarkable selectivity to desired butene products due to the adsorption configuration of 1,3-budiatene in a mono-π mode. However, it is still a grand challenge to prepare thermal stable Pd SACs with conventional synthetic methods. Herein, we acquired Pd SACs via the selective encapsulation strategy exploiting classical strong metal-support interaction (SMSI), during which Pd nanoparticles are more prone to be encapsulated by oxide overlayer than Pd single atoms, thus Pd single atoms exclusively staying exposed to the catalytic environment. The as-obtained Pd/CeO2-H600 gives excellent catalytic performances in the selective hydrogenation of 1,3-budiatene with conversion of almost 100% and butenes selectivity of above 98% at 100 ℃. Moreover, the conversion of 99% and butenes selectivity of 97.5% can also remain nearly unchanged for 60 h at a weight hourly space velocity of 60,000 mL/gcat/h. This work illustrates the effectiveness of this selective encapsulation strategy to construct Pd SACs and may open up more opportunities to optimize the activity, selectivity, and durability in selective hydrogenation reactions.



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SA-Poster-130

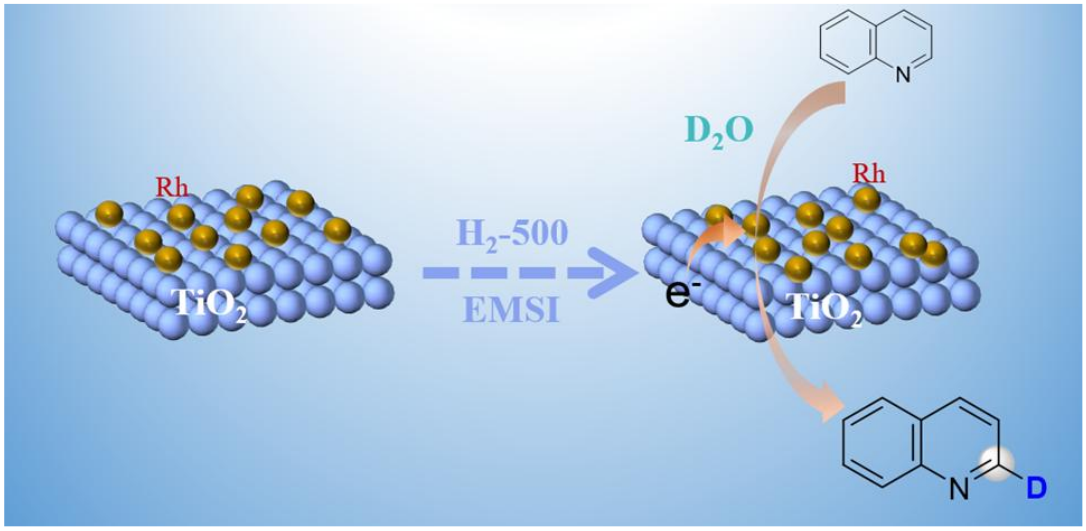
Mono-site selective deuteration of quinoline derivatives enabled by EMSI-tuned Rhodium single-atom catalysts

Wenting Zhang[1,2], Xunzhu Jiang[1,2], Xiang-Ting Min[1,*], Botao Qiao [1,2,*]

[1] *CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*
[2]*University of Chinese Academy of Sciences, Beijing 100049, China*
**Email: bqiao@dicp.ac.cn*

ABSTRACT

Deuterated drugs have emerged as a promising direction in new drug development due to their remarkable advantages in improving pharmacokinetics, reducing the formation of toxic metabolites, and inhibiting the stereoisomeric interconversion of chiral drugs.[1] Over 100 quinoline-based compounds have been approved for the treatment of various diseases, and their deuterated analogs are expected to exhibit improved pharmacokinetic profiles, enhanced safety, and therapeutic efficacy—thus facilitating structural optimization and clinical translation. However, traditional catalytic systems struggle to achieve high site-selectivity for C–H deuteration on the quinoline ring; for instance, Ru-based catalysts often require poisoning to suppress undesired hydrogenation byproducts.[2] To address this, we developed a tunable Rh/TiO_2 single-atom catalyst (SAC) and tuned via electronic metal–support interaction (EMSI) upon reduction at different temperatures. Experimental results revealed that Rh SACs treated at elevated temperatures triggered high level of EMSI, achieving highly site-selective monodeuteration of quinolines, with deuterium incorporation exceeding 90%. This work not only demonstrates the crucial role of EMSI in regulating the activity and selectivity of single-atom catalysts but also provides a new strategy for the development of highly selective deuterated pharmaceuticals.



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SA-Poster-131

H_2-reduced phosphomolybdate promotes room-temperature aerobic oxidation of methane to methanol

Sikai Wang[1,2], Victor Fung[3,4], Max J. Hülsey[2], Xiaocong Liang[5], Zhiyang Yu[5], Jinquan Chang[1,2], Andrea Folli[6], Richard J. Lewis[7], Graham J. Hutchings*[7], Qian He*[8], Ning Yan*[1,2,9]

[1]*Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117585, Singapore*
[2] *Joint School of National University of Singapore and Tianjin University, Fuzhou 350207, Fujian, China*
[3] *Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA.*
[4] *School of Computational Science and Engineering, Georgia Institute of Technology, Atlanta, GA, USA.*
[5] *State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou, China.*
[6] *Net Zero Innovation Institute, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, UK.*
[7] *Max Planck Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, UK.*
[8] *Department of Materials Science and Engineering, National University of Singapore, Singapore, Singapore.*
[9] *Centre for Hydrogen Innovations, National University of Singapore, Singapore, Singapore.*

Email: ning.yan@nus.edu.sg ; heqian@nus.edu.sg ; Hutch@cardiff.ac.uk

ABSTRACT

High-selectivity partial oxidation of methane to methanol with oxygen has remained a challenging research direction for decades, especially for low-temperature methane activation via the aerobic route. Here, our group reported a precipitated Pd-containing phosphomolybdate, which, after activation by hydrogen, converts methane and oxygen to methanol with nearly 100% selectivity at room temperature. The highest methanol productivity was 67.4 μmol/(gcat·h). Pd enables facile H_2 activation and hydrogen spillover to phosphomolybdate for Mo reduction, while subsequent O_2 and methane activation occur on the reduced Mo sites. Continuous production of methanol from methane was also achieved with simultaneous introduction of H_2, O_2 and methane into the system, where H_2 allows a moderately reduced state of phosphomolybdate to be maintained. Our group's work reveals the under-explored potential of a polyoxometalate-based catalyst for aerobic methane oxidation and underscores the importance of regulating the valence state to construct active sites for methane activation.

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SA-Poster-132

Electrothermal Conversion of Methane to Methanol at Room Temperature with Phosphotungstic Acid

Yilian D. Chen[1], Jinquan Chang[1], Ning Yan[1*]

[2]*Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore*.

ABSTRACT

Traditional methods for the aerobic oxidation of methane to methanol frequently require the use of noble metal catalysts or flammable H_2-O_2 mixtures. While electrochemical methods enhance safety and may avoid the use of noble metals, these processes suffer from low yields due to limited current density and/or low selectivity. Here, we design an electrothermal process to conduct aerobic oxidation of methane to methanol at room temperature using phosphotungstic acid (PTA) as a redox mediator. When electrochemically reduced, PTA activates methane with O_2 to produce methanol selectively. The optimum productivity reaches 29.45 $\mu mol\, g_{PTA}^{-1} h^{-1}$ with approximately 20.3% overall electron yield. Under continuous operation, we achieved 19.90 $\mu mol\, g_{PTA}^{-1} h^{-1}$ catalytic activity, over 74.3% methanol selectivity, and 10 hours durability. This approach leverages reduced PTA to initiate thermal catalysis in solution phase, addressing slow methane oxidation kinetics and preventing overoxidations on electrode surfaces. The current density towards methanol production increased over 40 times compared with direct electrochemical processes. The in-situ generated hydroxyl radical, from the reaction of reduced PTA and oxygen, plays an important role in the methane conversion. This study demonstrates reduced polyoxotungstate as a viable platform to integrate thermo- and electrochemical methane oxidation at ambient conditions.

SA-Poster-133

Oscillatory Strong Metal-Support Interaction in Pd/TiO_2 under Redox Conditions

Yuhui Chen[1], Ying Jiang*[1], Yong Wang*[1]

[1]*Center of Electron Microscopy and State Key Laboratory of Silicon and Advanced Semiconductor Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, China*
**Email: yjiang0209@zju.edu.cn; yongwang@zju.edu.cn*

ABSTRACT

Strong metal-support interaction (SMSI) plays a pivotal role in determining the activity, selectivity, and stability of heterogeneous catalysis. The encapsulation configuration of SMSI overlayers is highly dependent on the chemical environments. However, the dynamic behavior of SMSI under redox conditions remains insufficiently understood. In this presentation, I will present an oscillatory SMSI overlayer behavior and dynamic support responses of Pd/TiO_2 under the specific redox conditions. The configurations of SMSI overlayers in Pd/TiO_2 nanocatalysts were investigated under pure H_2, pure O_2, and a 5:1 O_2/H_2 mixture at 0.05 Pa and 650 °C at the atomic scale using environmental transmission electron microscopy (ETEM). In contrast to the stable SMSI encapsulations under pure O_2 and pure H_2 conditions, we reveal oscillatory SMSI overlayer behavior under the specific redox conditions. Specifically, the outer layer of the SMSI overlayer, characterized primarily by typical oxidative SMSI, undergoes oscillations between formation and retraction near the Pd-TiO_2 interface. Moreover, the SMSI oscillations locally modify the morphology of the TiO_2 support, with the SMSI overlayer serving as a temporary reservoir for Ti species to drive the tip-growth of the support protrusion. This process enables the tip-growth of support protrusions into nanowire morphology, without necessitating a well-defined crystalline relationship between Pd and TiO_2. The direct evidence presented in our work expands the understanding of the dynamic behavior of SMSI under reaction conditions and provides new insights into the solid-state growth mechanism.

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SA-Poster-134

Boosting C-O Bond Cleavage and Reverse Water-Gas Shift Activity via Enriched in-plane Sulfur Vacancies in Single-Layer Molybdenum Disulfide

Zhiyuan Zheng[1,2], Weijue Wang[1,2], Xiaofeng Yang[1], Xin Shang[*1], Xiong Su[*1], Yanqiang Huang[*1,2]

[1] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

[2] *University of Chinese Academy of Sciences, Beijing 100049, China*

**Email: suxiong@dicp.ac.cn, shangxin@dicp.ac.cn, yqhuang@dicp.ac.cn.*

ABSTRACT

The reduction of CO_2 to CO provides a promising approach to the production of valuable chemicals through CO_2 utilization.[1] However, challenges persist with the rapid deactivation and insufficient activity of catalysts.[2] Herein, we developed a soft-hard dual-template method to synthesize layered MoS_2 using inexpensive and scalable templates, enabling facile regulation of sulfur vacancies by controlling the number of layers. The concentration of in-plane vacancies keeps increasing with the reduction of MoS_2 layer number[3], contributing to 100% CO selectivity over single-layer MoS_2 and a stable performance over 300-hour reaction at 600 °C. The space-time-yield of CO reached 35.7 g_{CO} g_{cat}^{-1} h^{-1}, outperforming most current catalysts. Multiple characterizations and theoretical calculations revealed that in-plane sulfur vacancy sites endowed enhanced production of CO via direct dissociation of CO_2, showing an intrinsic activity of above 5.8 times higher than that of edge sulfur vacancy sites. The rate-limiting step was shifted from C-O cleavage in edge to sulfur vacancy regeneration in plane with a lower energy barrier. Our findings exemplified the specified design and synthesis of MoS_2 for high-temperature CO_2 reduction through the effective manipulation of distinct vacancy sites, shedding light on their potential industrial application.

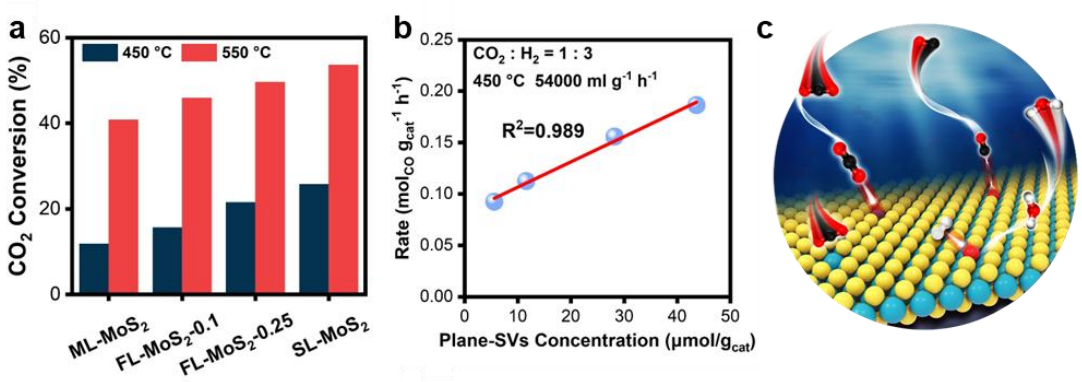

Figure 1. a) CO_2 conversion of MoS_2 samples under 450 °C and 550 °C. b) Correlation between the forward generation rate for CO and the concentration of in-plane S vacancies of MoS_2 catalysts. c) Schematic diagram of CO_2 activation and conversion at in-plane vacancies of MoS_2.

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SA-Poster-135

Three-Electron Uric Acid Oxidation via Interdistance-Dependent Switching Pathways in Correlated Single-Atom Catalysts for Boosting Sensing Signals

Bowen Jiang1 , Kuibo Yin* 1 , Litao Sun* 1

[1]*SEU-FEI Nano-Pico Center, Key Lab of MEMS of Ministry of Education, Southeast University, Nanjing 210096, P. R. China*

**E-mail: yinkuibo@seu.edu.cn; slt@seu.edu.cn*

ABSTRACT

The limited geometric and electronic complexity of conventional single-atom catalysts (SACs) constrains their sensing performance. To address this, correlated SACs (*c*-SACs) with precisely tuned single-atomic interdistance (SAD) were engineered to enhance uric acid (UA) oxidation for electrochemical sensing. Ru-based *c*-SACs with SADs of 9.3 Å, 7.0 Å, and 6.2 Å were synthesized via organometallic design and immobilized on carbon nanotubes. Electrochemical studies revealed that decreasing SAD to 6.2 Å drastically improved sensitivity (9.83 μA μM^{-1} cm^{-2}), outperforming most reported biosensors. This enhancement stemmed from a three-electron UA oxidation pathway, diverging from the conventional two-electron route, as confirmed by kinetic analyses, HPLC-MS, and density functional theory (DFT). The optimal 6.2 Å SAD enabled dual-site UA adsorption, lowering energy barriers and accelerating charge transfer. A flexible, portable biosensor integrating the 6.2 Å Ru *c*-SAC demonstrated real-time UA detection in human sweat, showing strong correlation with standard methods. This work highlights the critical role of atomic-scale SAD modulation in unlocking multi-electron processes and advancing high-performance SAC-based sensors, offering a blueprint for rational catalyst design in biosensing and healthcare applications.

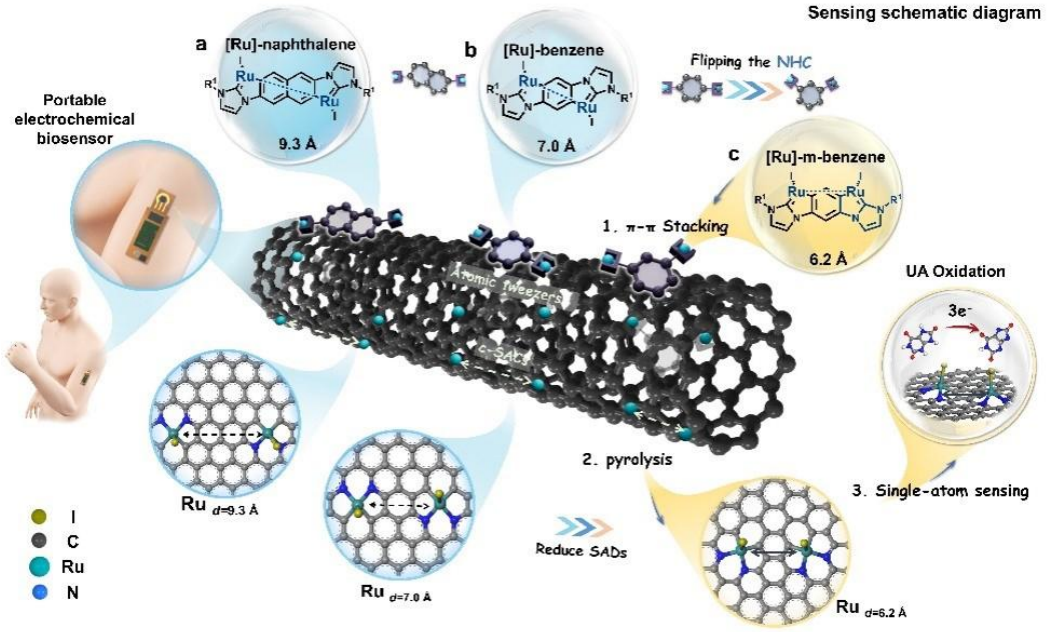

Figure 1. Sensing schematic diagram for the designed Ru based *c*-SACs of (a) Ru d=9.3Å, (b) Ru d=7.0Å and (c) Ru d=6.2Å, (R =n-octyl).

SA-Poster-136

DFT modeling of ceria-supported single-atom and few-atom gold species

Ivanova-Shor E.A.[*1,2], Nasluzov V.A.[1],Laletina S.S.[1], Shor A.M.[1]

[1]*Institute of Chemistry and Chemical Technology SB RAS, Krasnoyarsk, Russia*
[2]*Institute of Non-ferrous Metals and Materials, Siberian Federal University, Krasnoyarsk, Russia*
**Email: eshor1977@gmail.com*

ABSTRACT

Subnanometer gold species immobilized at oxide supports are well known to exhibit peculiar catalytic properties, particularly, in CO oxidation and water-gas shift reactions. The reducible oxide support such as ceria enhances the activity of metal particle due to the high mobility of its lattice oxygen and strong binding of the metal species. Being in a form of nanoparticle, the ceria substrate can tune the activity of metal species by variation of the nanoparticle size. To investigate the effect of ceria support on properties of gold species a theoretical DFT-GGA study of gold single atoms and few-atom species Au_n (n=2-4) anchored on a model ceria nanoparticles $Ce_{21}O_{42}$ and $Ce_{40}O_{80}$ has been performed.

Present study reports the structural features, electronic properties and energetic characteristics of ceria-supported gold systems. The influence of oxygen vacancies nearby metal moiety on properties of the gold moieties is presented. Relation of these features to activity of gold-ceria systems in CO oxidation is discussed. The data obtained for gold atoms are compared with those for palladium and silver species having from one to four atoms [1-3].

This study has been carried out under financial support of the Russian Science Foundation, grant № 25-23-20124 (https://rscf.ru/project/25-23-20124/) and grant of the Krasnoyarsk Regional Science Foundation. The authors thank the Supercomputing Center of the Institute of Computational Modeling SB RAS (Krasnoyarsk) for provided computational resources.

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SA-Poster-137

Unconventional phase 2D nanomaterial supported catalysts for highly efficient H_2 evolution

Zhenyu Shi[1], Anthony R. J. Kucernak[2]*, Hua Zhang[1]*

[1]*Department of Chemistry, City University of Hong Kong, Hong Kong, China;*
[2]*Department of Chemistry, Molecular Science Research Hub, Imperial College London, London, UK.*
Corresponding author: anthony@imperial.ac.uk; Hua.Zhang@cityu.edu.hk.

ABSTRACT

Crystal phase is a key parameter to determine the properties and functions of the two-dimensional (2D) transition-metal dichalcogenides (TMDs). The TMDs commonly serve as templates for growing metallic catalysts, which show great potential for various catalytic reactions. Although various noble metal/TMD hybrids have been prepared, the used TMD templates are normally in the thermodynamically stable 2H phase or mixed crystal phases. In addition, the effect of TMD crystal phase on the growth of the secondary material is poorly understood. For instance, when MoS_2 nanosheets (NSs) with mixed 1T and 2H phases were used to support Pt nanoparticles (PtNPs) as electrocatalysts for hydrogen evolution reaction (HER), ~65% of the PtNPs were epitaxially grown on this mixed-phase MoS_2 templates. In the meantime, the mixed-phase structure of the MoS_2 templates severely limits the further improvement of the noble metal/MoS_2 hybrids towards HER due to the poor conductivity of 2H phase of MoS_2. Therefore, constructing noble metal/MoS_2 hybrids based on metallic/semimetallic 1T/1T′ phase MoS_2 NSs with high phase purity is urgently desired to understand the phase-dependent growth of noble metals as well as to prepare highly efficient electrocatalysts.

In this work, we report the preparation of 1T′-MoS_2 and 2H-MoS_2 NSs with high phase purity, which are then used as templates to grow Pt. We found that the 2H-MoS_2 templates facilitate the epitaxial growth of PtNPs, while the 1T′-MoS_2 nanosheets support single-atomically dispersed Pt (s-Pt) under similar experimental conditions. Being used as an electrocatalyst for the HER in acidic media, the obtained s-Pt/1T′-MoS_2 possesses a mass activity of 85±23 A mg_{Pt}^{-1} at the overpotential of −50 mV and a mass-normalized exchange current density of 127 A mg_{Pt}^{-1} as revealed by high mass-transport floating electrode technique. Density functional theory (DFT) calculations indicate that the s-Pt adsorbed on the top site of Mo exhibits a hydrogen adsorption free energy close to zero, which could contribute to the efficient H_2 evolution of s-Pt/1T′-MoS_2. Importantly, the s-Pt/1T′-MoS_2 exhibits high stability during HER in both H-type cell and prototype proton exchange membrane electrolyser. Our work demonstrates that 1T′-TMDs can be ideal supports for catalysts used for various applications.

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SA-Poster-138

Selective Production of Acetylene from the C−C Coupling Reaction of CH_4 with CO_2 Mediated by $Ta_2O_2^+$ Cluster Cations

An Zhao 1,2,3 , Yan-Xia Zhao* 1,3 , Sheng-Gui He* 1,2,3

[1]*State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.*
[2]*University of Chinese Academy of Sciences, Beijing, China.*
[3]*Beijing National Laboratory for Molecular Sciences and CAS Research/Education Centre of Excellence in Molecular Sciences, Beijing 100190, China.*
**Email: chemzyx@iccas.ac.cn; shengguihe@iccas.ac.cn*

ABSTRACT

Co-conversion of methane and carbon dioxide to C2 hydrocarbons via the CCH_4−CCO_2 coupling reaction is of great significance to mitigate greenhouse effect and develop an alternative route for manufacture of important industrial feedstocks (e.g., C_2H_2), [1] however, it has not yet been achieved so far owing to the difficulty in breaking both of the C=O bonds in CO_2 as well as the precise control of sequential elementary reactions targeted for C_2 hydrocarbons. Herein, by using the tantalum oxide $Ta_2O_2^+$ as an active cluster, an unprecedented CCH_4−CCO_2 coupling reaction of CH_4 with CO2 to exclusively produce the C_2 hydrocarbon of C_2H_2 has been successfully realized even at room temperature by the state-of-the-art mass spectrometry. The in situ reconstruction from Ta−O−Ta cluster skeleton to tantalum carbide Ta−C−Ta experienced upon the pre-reaction with CH_4 is critical to delicately control the sequential elementary reactions targeted for C_2H_2 generation. [2] This finding not only leads to a breakthrough in the field of gas-phase and condensed-phase chemistry wherein the C_{2+} oxygenated compounds were the mainstream products for CCH_4−CCO_2 coupling of CH_4 with CO_2, but also explores a new active structure and a novel reaction mechanism beneficial for selective production of C_2 hydrocarbons from co-conversion of CH_4 and CO_2.

Keywords: Catalyst; Coal mines; Computational fluid dynamics; Monolith; Ventilation air methane.

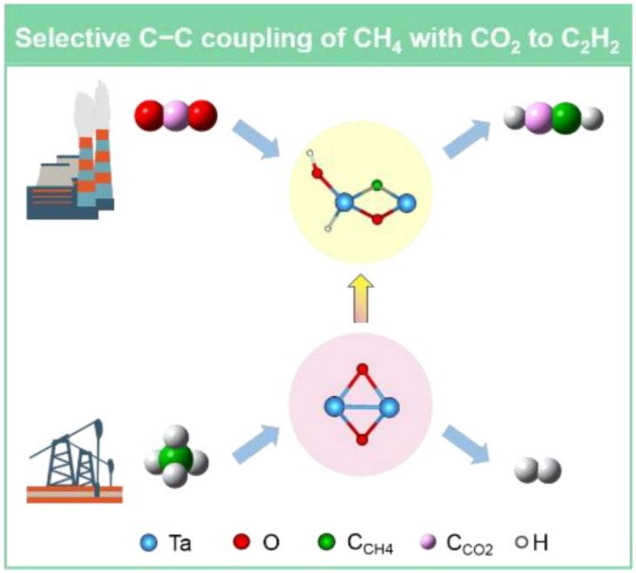

Figure 1. The C−C Coupling Reaction of CH4 with CO2 Mediated by Ta2O2+ Cluster Cations

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SA-Poster-139

Generation of Cyanonitrene Radicals from the Co-conversion of N_2 and CO_2 Mediated by Niobium Oxide Cluster Anions

Xiao-Xiao Liu[1,2,3], Zi-Yu Li*[1,3], Xi-Guan Zhao[1,3], Qing-Yu Liu[1,3], Sheng-Gui He *[1,2,3]

[1]*State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*
[2]*University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China*
[3]*Beijing National Laboratory for Molecular Sciences and CAS Research/Education Center of Excellence in Molecular Sciences, Beijing 100190, People's Republic of China*
**Email: liziyu2010@iccas.ac.cn; shengguihe@iccas.ac.cn*

ABSTRACT

Cyanonitrene radical, NCN, has been shown to play a crucial role in the formation of prompt-NO in combustion in the past decades.[1-2] The mechanism for the formation of NCN via the reaction CH + N_2 → NCN + H has been widely recognized.[3-5] In contrast, the contribution of other nitrogen or carbon sources to NCN generation remains uncharacterized. Herein, we successfully identify that a niobium oxide cluster anion can break the N–N bond in N_2 and two C–O bonds in CO_2 at room temperature, and simultaneously construct two C–N bonds for the formation of [NCN] unit. Furthermore, NCN radical is released upon the injection of external energy. Remarkably, the cluster transfers the unpaired spin density from the Nb active metal center to the two nitrogen atom during N_2 activation. In subsequent reaction with CO_2, the presence of highly reactive nitrogen radicals promotes the consecutive formation of two C−N bonds. Based on the flexible electron-donating capability of the metal sites and the robust binding strength between Nb and O, a series of complex reaction steps, including N–N bond cleavage, C–O bond cleavage, and C–N coupling, can proceed efficiently, which contributes greatly to the effective utilization of C and N atoms. This work presents an unprecedented pathway for the generation of NCN radical, and offer a novel reaction mechanism for the generation of NCN through C–N coupling by utilizing N_2 as a nitrogen source and CO_2 as a carbon source.

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SA-Poster-140

Biphenylene Network as Probe: Coordination-Activity Correlations in Non-Benzenoid Carbon-Supported SACs for CO_2RR

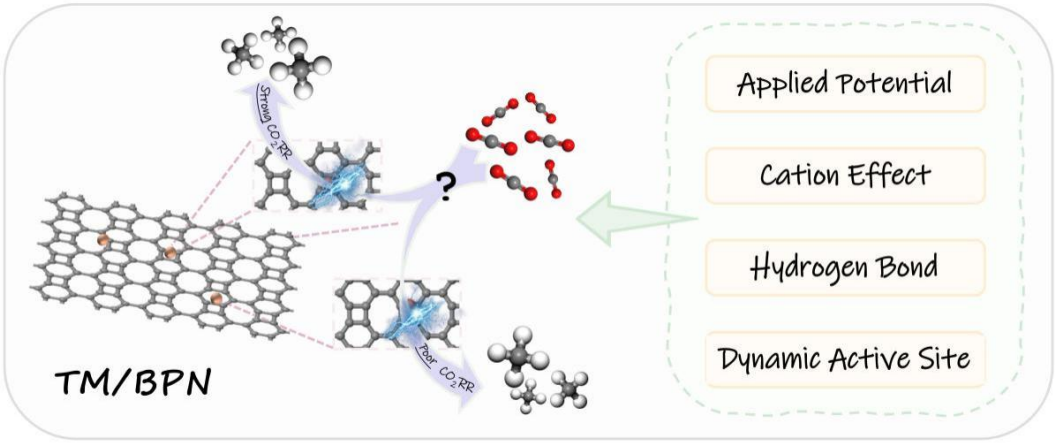
Yang Xu[1] , Chong Wang* [1] , Song Liu* [1]

[1]*College of Chemistry, Chemical Engineering and Resource Utilization, Northeast Forestry University, Harbin 150040, China*

**Email: wangchong@nefu.edu.cn (C. Wang), carlosliusong@nefu.edu.cn (S. Liu)*

ABSTRACT

Single-atom catalysts (SACs) have emerged as a promising class of catalysts for electrocatalytic CO2 reduction reaction (eCO2RR), offering the dual benefit of closing the carbon cycle and enabling renewable electricity storage.1,2 Density functional theory (DFT) calculations deliver atomic-scale descriptions, a powerful tool for gaining detailed mechanistic insights into reaction processes. Given the diverse modification strategies for SACs, elucidating the intrinsic structure-performance relationships is essential for efficiently screening high-performance candidates. However, research on these relationships remains limited by mechanistic complexity and dynamic interfacial environments under operational conditions. Biphenylene network (BPN), a novel non-benzenoid 2D carbon material, provides diverse coordination environments for doped transition metal (TM) atoms, enabling the formation of TM@BPN SACs to systematic structure-performance studies. We employed DFT calculation, *ab initio* molecular dynamics (AIMD), and solvation models to elucidate mechanistic insights governing the structure-performance relationships of TM/BPN for eCO2RR. Based on eCO2RR performance calculations, TM@BPNs with TMs occupying the four-membered ring center sites exhibit superior activity compared to other sites. This phenomenon may be triggered by solvation effects and dynamic structural evolution of active sites during eCO2RR. The universality of this mechanism is validated by extending to non-metallic active centers (e.g., B/N-doped) and alternative carbon substrates (e.g., graphdiyne, T-carbon). These findings elucidate the eCO2RR mechanisms of BPN-based SACs and accelerate the application of BPN as a promising substrate for SACs. The revealed structure-activity relationships offer rational perspectives for designing carbon-supported SACs with optimized eCO2RR performance.



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SA-Poster-141

Unprecedented Tetravalent Uranium Photocatalysts for Efficient C(sp^3)─C(sp^3) Bond Cleavage and Formation

Lian-Wei Ye[1], Han-Shi Hu[1], Congqing Zhu*[2], Jun Li*[1,3]

[1]*Department of Chemistry, Tsinghua University, Beijing 100084, China*
[2]*School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China*
[2]*Ganjiang Innovation Academy, Chinese Academy of Sciences, Ganzhou 341000, China*
**Email: zcq@nju.edu.cn; junli@tsinghua.edu.cn*

ABSTRACT

Photocatalysis is a pivotal area in synthetic chemistry. Despite extensive application potential in nuclear industry, uranium-based photocatalysts are historically limited to uranyl(VI/V) redox cycle. Here, we report the discovery of the first tetravalent uranium [U(IV)] photocatalyst that enables efficient C(sp^3)—C(sp^3) bond cleavage and formation under ideal visible light. The U(IV) alkoxy species mediates C—C bond cleavage in a wide range of cycloalkanols and promotes their coupling with electron-deficient alkenes, providing access to previously unattainable molecular architectures. These U(IV) alkoxy complexes, fully characterized by X-ray diffraction and magnetic studies, exhibit exceptional photocatalytic efficiency. Quantum chemical studies reveal that the energy barrier for C—C bond cleavage and formation is reduced to below 10 kcal · mol^{-1} under visible light excitation. This work introduces a new mechanistic paradigm for uranium-based photocatalysis and positions U(IV) alkoxy complexes as a versatile platform for bond activation and functionalization, expanding the potential applications of depleted uranium in synthetic chemistry.

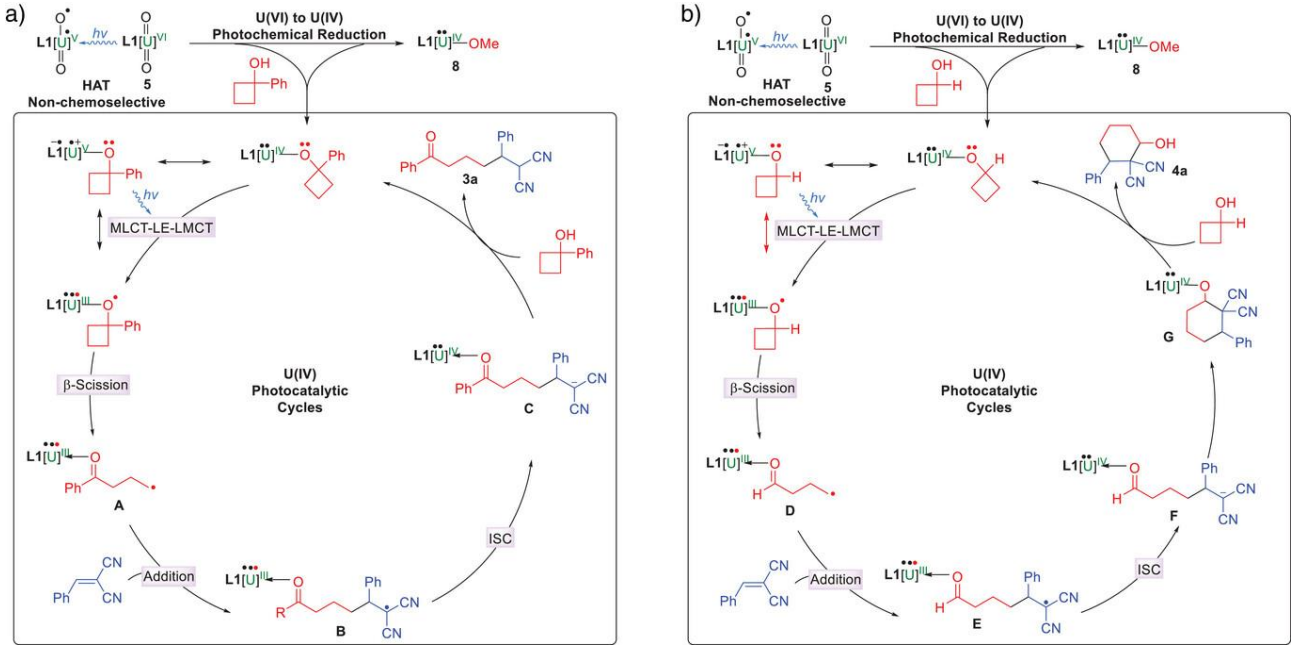

Figure. Proposed photocatalytic cycles. The non-chemoselective uranyl(VI) is initially photoreduced to generate a chemoselective U(IV) photocatalyst, which facilitates the conversion of α-substituted cyclobutanol or cyclobutanol to products 3a (a) and 4a (b), respectively.

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SA-Poster-142

Computational Screening of $Pt_1@Ti_3C_2T_2$ (T = O, S) MXene Catalysts for Water−Gas Shift Reaction

Yang Meng[1], Haiyan Wang[2], Jinxia Liang*[2], Chun Zhu*[2,3], Jun Li*[3,4]

[1]*National University of Singapore (Suzhou) Research Institute, Suzhou, 215123, China*
[2]*School of Chemistry and Chemical Engineering, Guizhou University, Guiyang 550025, China*
[3]*Department of Chemistry and Guangdong Provincial Key Laboratory of Catalytic Chemistry, Southern University of Science and Technology, Shenzhen 518055, China*
[4]*Department of Chemistry and Engineering Research Center of Advanced Rare-Earth Materials of Ministry of Education, Tsinghua University, Beijing 100084, China*

**Email:liangjx2009@163.com; czhu2014@163.com; junli@tsinghua.edu.cn*

ABSTRACT

Single-atom catalysts (SACs) provide an opportunity to elucidate the catalytic mechanism of complex reactions in heterogeneous catalysis. The low-temperature water−gas shift (WGS) reaction is an important industrial technology to obtain high purity hydrogen. Herein, we study the catalytic activity of $Pt_1@Ti_3C_2T_2$ (T = O, S) SACs, where one subsurface Ti atom with three T vacancies in the functionalized $Ti_3C_2T_2$ (T = O, S) MXene is substituted by one Pt atom, for the low-temperature WGS reaction, using density functional theory (DFT). The results show that $Pt_1@Ti_3C_2T_2$ provides an excellent platform for the WGS reaction by its bowl-shaped vacancy derived from the Pt_1 single atom and three T defects surrounding it. Especially, $Pt_1@Ti_3C_2S_2$ SAC has higher catalytic performance for the WGS reaction, due to the weaker electronegativity of the S atom than the O atom, which significantly reduces the energy barrier of H* migration in the WGS reaction, which is often the rate-determining step. In the most favorable redox mechanism of the WGS reaction on $Pt_1@Ti_3C_2S_2$, the rate-determining step is the dissociation of OH* into O* and H* with the energy barrier as low as 1.12 eV. These results demonstrate that $Pt_1@Ti_3C_2S_2$ is promising in the application of MXenes for low-temperature WGS reactions.

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SA-Poster-143

Porphyrin-triazine frameworks hosting palladium single atom for selective nitroarene reduction in aqueous media

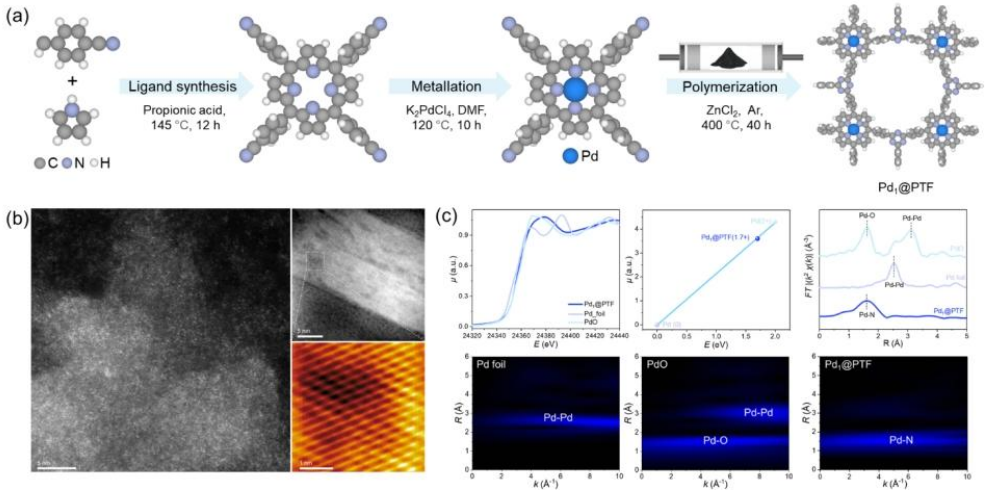
Jiachengjun. Luo[1], Gianvito Vilé*[1]

[1]*Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, Milano, 20133 Italy*
**Email: gianvito.vile@polimi.it*

ABSTRACT

Single-atom catalysts (SACs), the frontier in catalysis, optimizes atom utilization and exhibits unique properties that enhance reactivity and selectivity.[1] However, stabilizing single atoms on conventional supports remains challenging, as defects can alter metal coordination and compromise performance.[2] Covalent organic frameworks (COFs) offer a promising alternative, providing highly-defined structure, large surface areas, and robust stability.[3] While many COF-based SACs underperform due to the limited active site accessibility and inefficient catalytic activity.[4] Herein, we report a robust and efficient synthetic strategy for the preparation of structurally well-defined Pd-based SACs by anchoring Pd single atoms into a porphyrin-functionalized covalent organic framework. Our SACs demonstrate enhanced performance in the reduction of nitroarenes, bridging the gap between structural innovation and catalytic efficiency.

The procedure is mainly composed of two steps, the Por ligand synthesis and in situ growth generated SACs. After the synthesis of Pd_1@PTF SACs, the textural and physicochemical properties of Pd_1@PTFs were extensively analyzed. Comprehensive structural characterization, including AC-HAADF-STEM and XAS, confirms the atomically dispersed Pd species within a well-defined Pd-N_4 coordination environment of the COF network.[5] The resulting Pd_1@PTF catalyst exhibits outstanding thermal stability, a high surface area (901 $m^2\ g^{-1}$), and improved accessibility to catalytically active sites. Catalytic evaluation in the aqueous-phase hydrogenation of nitroarenes demonstrates remarkable activity and selectivity, with Pd_1@PTF catalyst achieving >95% conversion and selectivity in the reduction of nitrobenzene to aniline, and a turnover frequency (TOF) of 887 h^{-1}. Notably, the catalyst tolerated a broad substrate scope in an efficient manner and recyclability up to 4 cycles, reducing the range of substituted nitroarenes.



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SA-Poster-144

Investigation of the Synergistic Mechanism of Cu–Co Dual-Atom Catalysts

Chuanbin Wang[1], Jingnan Tian[2], Qian Tan*[1]

[1] School of Ecology, Environment and Resources, Guangdong University of Technology, Guangzhou, 510006, China
[2] School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China
Email: wangchuanbin6@163.com

ABSTRACT

Cobalt (Co) and copper (Cu) dual monatomic catalyst (NBC-Cu-Co) were prepared and the coordination structures of Co and Cu sites were determined as CoN_3 and CuN_3O_2. NBC-Cu-Co exhibited greater PMS activation capability than single metal doped biochar. Quenching experiments revealed that Co and Cu bimetallic doping could promote the generation of $SO_4^{\bullet-}$ and ·OH, but was detrimental to the production of $^1O_2$. DFT simulations demonstrated that the biochar loaded both CoN_3 and CuN_3O_2 sites had the largest PMS adsorption energy, the maximum O-O bond length, and the greatest number of electrons transferred, which contributed to the PMS activation to produce $SO_4^{\bullet-}$ and ·OH. Besides, the CuN_3O_2 site was an excellent active site for the $^1O_2$ generation due to its low reaction energy barrier. NBC-Cu-Co is an environmentally friendly catalyst towing to its ability in activating PMS to produce low-toxicity intermediates as well as reduce leaching of metal ions.

SA-Poster-145

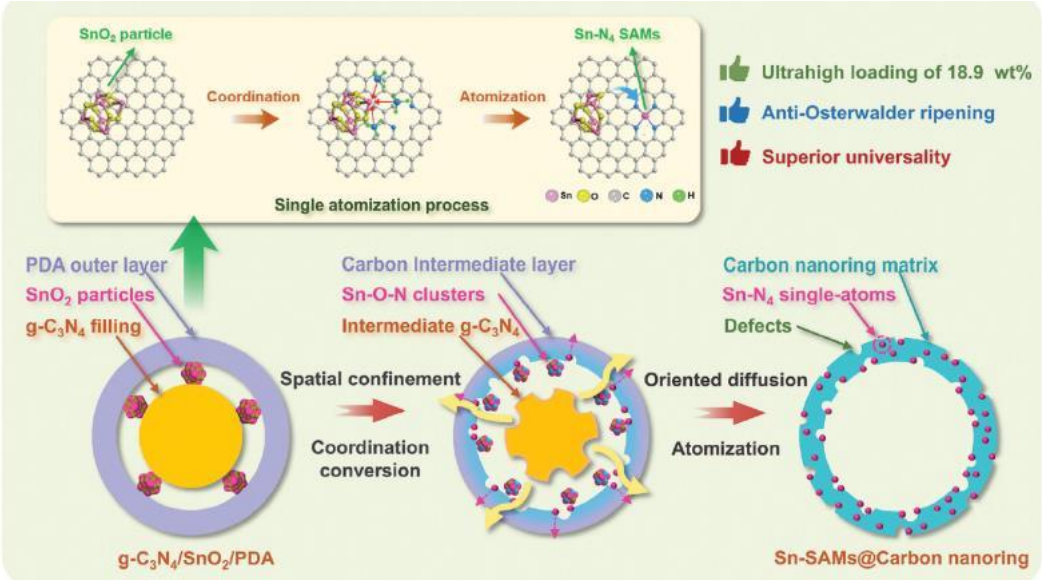
Fabrication of Ultrahigh-Density Metal Single Atoms Materials for High-Capacity Energy Storage

Lishen Ai, Zongbin Zhao*, Xuedan Song, Xuzhen Wang*, Jieshan Qiu*

[1]*School of Chemical Engineering, Liaoning Key Lab for Energy Materials and Chemical Engineering, Dalian University of Technology*
[2]*College of Chemical Engineering, State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology*
**Email: zbzhao@dlut.edu.cn (Z. Zhao)*
xzwang@dlut.edu.cn (X. Wang)
qiujs@mail.buct.edu.cn (J. Qiu)

ABSTRACT

Single-atom metals (SAMs) hold great promise for high-efficiency catalysis, biomedicine, and energy storage, however, their performance in various fields is often limited by low metal loading. Herein, for the first time, we report a top-down strategy to achieve ultrahigh-loading (18.9 wt%) Sn-SAMs on a carbon nanoring matrix (Sn-SAMs@CNR), derived from a ring-like nested g-C3N4@SnO2@polydopamine precursor (**Scheme 1**). It is demonstrated that the formation of Sn-SAMs involves a critical transition from oxygen-coordinated SnO2 to nitrogen-coordinated Sn-N4, coupled with spatial confinement-induced suppression of Ostwald ripening. Remarkably, N-containing gaseous intermediates from g-C3N4 dynamically drive the inside-out oriented diffusion of Sn atoms, enabling uniform ultrahigh loading across the entire carbon matrix. This strategy demonstrates broad applicability, as confirmed by its successful extension to other metals (Fe, Co, Ni, Cu, Sb). When employed as a sodium-ion battery anode, Sn-SAMs@CNR delivers exceptional performance, which experimental and theoretical analyses attribute to the high-density Sn-N4 sites optimizing electron density distribution and reaction kinetics. The material exhibits outstanding cycling stability, retaining 364 mA h g−1 at 1.0 A g−1 after 5000 cycles with an ultralow capacity decay rate of 0.00068% per cycle. This work pioneers a universal approach to achieve ultrahigh loading of single-atom metals on carbon matrices, opening new avenues for high-performance catalysis and energy storage applications.



Scheme 1. Schematic diagram of the evolution from g-C3N4/SnO2/PDA nested structure to Sn-SAMs@CNR (in cross-section).

References

1. Lishen Ai, Zongbin Zhao, Xuedan Song, Yongchao Tang, Yong Li, Xuzhen Wang, Honghui Bi, Yanbing Yuan, Jieshan Qiu. An Oriented Diffusion Strategy to Configure All-Region Ultrahigh-Density Metal Single

SA-Poster-146

Spectroscopic simulations and mechanistic study of dual-atom catalysts for water oxidation

Hengxin Cui[1] and Ke R. Yang*[1,2]

[1] *Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin, China 300071*
[2] *Frontier Science Center for New Organic Matter, Nankai University, Tianjin, China 300071*
**Email: ke.yang@nankai.edu.cn*

ABSTRACT

The oxidation of water is of fundamental importance in renewable energy technologies since it provides active electrons and protons for the production of hydrogen in water electrolysis and CO2 reduction in photosynthesis. The development of efficient water-oxidation catalysts is extremely important to facilitate this kinetically very challenging process and the key to achieve rational design of water-oxidation catalysts is through in-depth mechanistic understanding. Here, we present a theoretical study combining density functional theory (DFT) calculations with spectroscopic simulations to a recently developed dual-atom catalytic platform for water oxidation. Through comprehensive analysis of hydrogen-bonding networks and electronic configurations, we identified a structural model featuring (μ-OH)2 bridge in excellent agreement with experimental EXAFS data for the S1 state of a Ni,Fe dual-atom catalyst (DAC). We considered several possible catalytic pathways for water oxidation and the water nucleophilic attack (WNA) is the most like mechanism as suggested by both H/D kinetic isotope effect and free-energy profiles. In the WNA pathway, S1 is oxidized through two-step proton-coupled electron transfer, followed by an intramolecular proton transfer and electron transfer to form the active species [·O–NiIV …FeIII], which undergoes water nucleophilic attack via a low-barrier transition state (ΔG‡ = 0.58 eV), consistent with experimental kinetics. This work confirms the robustness of DFT+EXAFS protocol for characterizing active species at atomic level and demonstrates the cooperation between adjacent metal centers. Our study is currently being extended to other bimetallic systems (Co-Fe, Fe-Ni, Co-Ni) to gain fundamental insights for rational design of efficient water-oxidation catalysts for artificial photosynthetic systems.

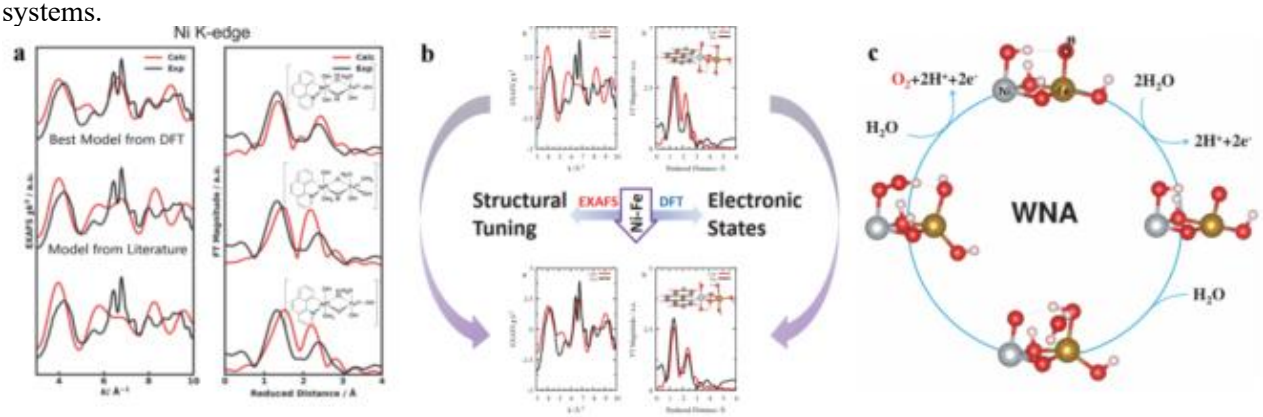


Figure 1. Theoretical investigation of dual-atom catalysts for water oxidation. (a) Experimental and simulation Ni K-edge EXAFS spectra, (b) Combining DFT and EXAFS simulation to characterize active species, (c) Catalytic cycle of the Ni-Fe DAC for water oxidation suggested by DFT calculations and experimental kinetics.

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