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Authors

Qi, Zhiyuan
Chen, Luning
Zhang, Shuchen
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Integrating the Fields of Catalysis: Active site engineering in Metal Cluster, Metal Organic Framework and Metal Single Site

Zhiyuan Qi¹, Luning Chen², Shuchen Zhang², Ji Su^{2,3}, Gabor A. Somorjai^{2,4}

¹ Chemical Sciences Division, ² Materials Sciences Division, ³ Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, United States

⁴Department of Chemistry, University of California-Berkeley, Berkeley, CA, 94720, United States

Corresponding Author

Gabor A. Somorjai: somorjai@berkeley.edu

Ji Su: jisu@lbl.gov

Abstract

Research evolved using nanoparticles synthesized and characterized under reaction conditions opened the door to study all three fields of catalysis: heterogeneous, homogenous, and enzyme. Fundamental studies of catalytic reactions ranging from hydrogenation to understand Fisher-Tropsch synthesis and isomerization ultimately led to the integration of three fields of catalysis. Our recent work on bridging heterogeneous, homogenous, and enzymatic catalysis was present including functionalization of dendrimer encapsulated metal clusters surface for lactonization, active site engineering in metal organic framework catalysts for methanol production and oligomerization, and single site catalyst for hydrogen production. We envision that the combination of active site engineering and unifying fields of catalysis could be applied to solve practical issues of science-based technology and develop new fields useful in energy research.

Keywords heterogeneous-homogenous hybrid, heterogeneous-enzyme hybrid, metal organic framework, metal support interaction, single site catalyst

Introduction

In the 1970s, using single crystal surfaces, mostly platinum and other transition metal surfaces as well, it was discovered that surface defects promote the bond breaking and reaction probabilities were correlated with undercoordinated surface sites (i.e. kinks and steps) [1-3]. Simultaneously, the evolution of low energy electron diffraction (LEED) surface crystallography revealed the surface reconstruction on Pt, NaCl, and ice crystals under different environments ranging from ultrahigh vacuum to high pressures when molecular adsorption happens [4-6]. The development of surface science opens up the evolution of surface instrumentations and further applications in tribology, bio-interfaces, microelectronics, energy conversion, nanoscience, and catalysis [7].

Research of model surfaces results in understanding the kinetics and thermodynamics of heterogeneous catalysis in which the catalysts occupy the different physical phase (solid, liquid or gas) from the reactants or products. The recycling of heterogeneous catalysts is easier compared to homogenous, but the optimization and characterization are more challenging. Therefore, advanced instrumentations were developed and applied for characterizing catalysts and in-situ catalytic studies, including sum frequency generation (SFG) vibrational spectroscopy [8-10], ambient pressure X-ray photoelectron spectroscopy (AP-XPS) [11-13], and synchrotron-based instruments such as X-ray adsorption

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4 near-edge structure (XANES) and extended X-ray adsorption fine structure (EXAFS) [14-15]. The development of
5 high pressure scanning tunneling microscopy (STM) gives rise to dynamic studies of surface atoms under reaction
6 conditions that could also be applied to catalysis [16-17].
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9 As reviewed in the previous perspectives, catalysis research in our group combines the synthesis of nanoparticle
10 catalysts, catalytic performance investigation, and characterization under reaction conditions [18]. The studied
11 systems include (1) surface restructuring of metal single crystals induced by the adsorbate under reaction conditions
12 by STM [19-21]; (2) size and shape dependence of nanoparticles (1-10 nm) on reactivity and selectivity [22-26]; (3)
13 dendrimer-encapsulated metal clusters (DEMCs) for homogeneous catalytic reactions [27-30]; (4) strong metal
14 support interaction (SMSI) of oxide-metal interfaces [31-32]. The successful heterogenizing homogenous catalyst (i.e.,
15 DEMCs) opens the door to investigate the chemical correlation of three fields of catalysis: heterogeneous,
16 homogeneous, and enzymatic [18]. Research efforts were thus made to bridge these fields by constructing
17 heterogeneous-homogenous, heterogeneous-enzyme hybrid catalysts, which could potentially combine the advantages
18 of each field and leads to better catalytic performance [33].
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22 Here in this paper, we summarized our latest research in unifying the three fields of catalysis via engineering the
23 active sites. The catalytic performance of heterogeneous-homogenous hybrid catalysts was examined using supported
24 DEMCs functionalized with surface ligands. Furthermore, we successfully synthesized a heterogeneous-enzyme
25 hybrid catalyst by incorporating the enzyme-like active sites into metal organic frameworks (MOFs) for selective
26 oxidation methane to methanol. We also included other two examples of engineering the active sites of MOFs for
27 better catalytic performance. Finally, single site catalyst was regarded as a new type of heterogeneous-homogenous
28 hybrid and used for the hydrogen production from methanol.
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36 **Heterogeneous-homogenous hybrid: DEMCs functionalizing with surface ligands**

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38 In the past ten years, our group has extensively studied the catalytic performance of Pt, Pd, Rh, Au DEMCs
39 supported on mesoporous silica (e.g., SBA-15), including hydrogenation, hydroalkoxylation, ring-opening, aldol
40 reaction, isomerization reaction [34]. Dendrimer with a radially symmetric branched molecular structure has been
41 proven as a reliable and versatile scaffold to synthesize and stabilize metal clusters (Fig. 1). The multivalent interaction
42 between dendrimer and metal clusters prevents the aggregation or leaching of metals. The deposition of dendrimer
43 encapsulated metal clusters (DEMCs) onto mesoporous silica supports provides the further thermal stability under
44 harsh reaction conditions (e.g. high temperature or pressure). Moreover, these supported DEMCs could be readily
45 modulated to combine the advantages of both heterogeneous and homogeneous catalysts: (1) DEMCs could catalyze
46 homogenous reactions while typical heterogeneous catalyst could not realize; (2) tunable selectivity and activity by
47 changing the dendrimer generation and terminal functional groups; (3) easy recyclability compared to homogeneous
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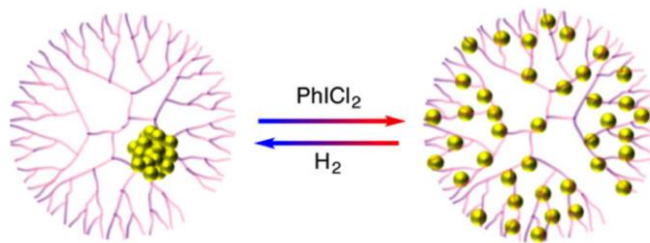


Fig.1 Schematic representation of the reversible oxidation by PhICl_2 and H_2 reduction of DEMCs. Adapted with permission from ref [34]. Copyright 2017 American Chemical Society. Further permissions related to the material excerpted should be directed to the ACS.

To introduce additional modulation of reactivity, enantio-, and chemo-selective, ancillary ligands N-heterocyclic carbenes (NHCs) was selected for surface functionalization [35]. By combining the concepts of supported DEMCs and NHC-ligated NPs, our group reported the first example of supported Au DEMCs functionalized by NHC ligands and extend NHC-ligated gold catalysis to a new reaction: lactonization of allene-carboxylic acids [36]. As shown in Fig. 2A, the formed lactone has an intramolecular cyclic structure, generated from the reaction between carboxylic group and allene (one carbon has two double bonds with the adjacent two carbon centers). A readily available NHC-Au(I)-Cl complex was selected as the precursor for the synthesis of Au NPs owing to its demonstrated high enantioselectivity and strong binding to metal. Au DEMCs synthesized in the presence of NHC (Au/G4OH-NP-1, *Cat-1*) and without NHC (Au/G4OH-NP-0, *Cat-0*) were both loaded onto SBA-15 (Fig. 2B). XPS measurement reveals that the oxidation state of surface gold in *Cat-0* was consistent with Au(0), while the Au $4f_{7/2}$ binding energy of *Cat-1* (84.9 eV) was 1.5 eV higher than *Cat-0*, and assigned to Au(I) species. However, XANES spectra of *Cat-1* and *Cat-0* were almost identical to gold foil, and linear combination analyses indicated over 95% Au in both *Cat-1* and *Cat-0* were metallic. We thus conclude that the surface of Au NPs in *Cat-1* is covered by a monolayer of Au(I) species, probably NHC-Au(I) complexes.

Intramolecular lactonization was selected to evaluate the effect of surface modification of Au DEMCs. *Cat-1* shows reactivity at room temperature in different deuterated solvents (i.e. CD_2Cl_2 , C_6D_6 , CDCl_3) and CD_2Cl_2 gave rise to the highest reaction rate. *Cat-1* achieved full conversion after 22 h at room temperature in CD_2Cl_2 , while no reaction was observed by *Cat-0* under the same reaction conditions. When toluene- d_8 was used as the solvent, *Cat-0* could achieve full conversion only at 100 °C. These results clearly demonstrated the enhancement of catalytic activity of Au DEMCs induced by the NHC complexes. Fig. 2D shows part of the follow-up catalyst scope. *Cat-2* to *Cat-4* with different functional groups were prepared. The increased ligand rigidity in *Cat-1* to *Cat-4* likely correlate with their increased activity, and the presence of hydroxyl group is critical in this reaction. Moreover, the ligand-derived enantioselectivity has been demonstrated with 16 ee.% achieved by *Cal-1*, which is, to the best of our knowledge, the first example of enantio-selectivity catalyzed by Au DEMCs.

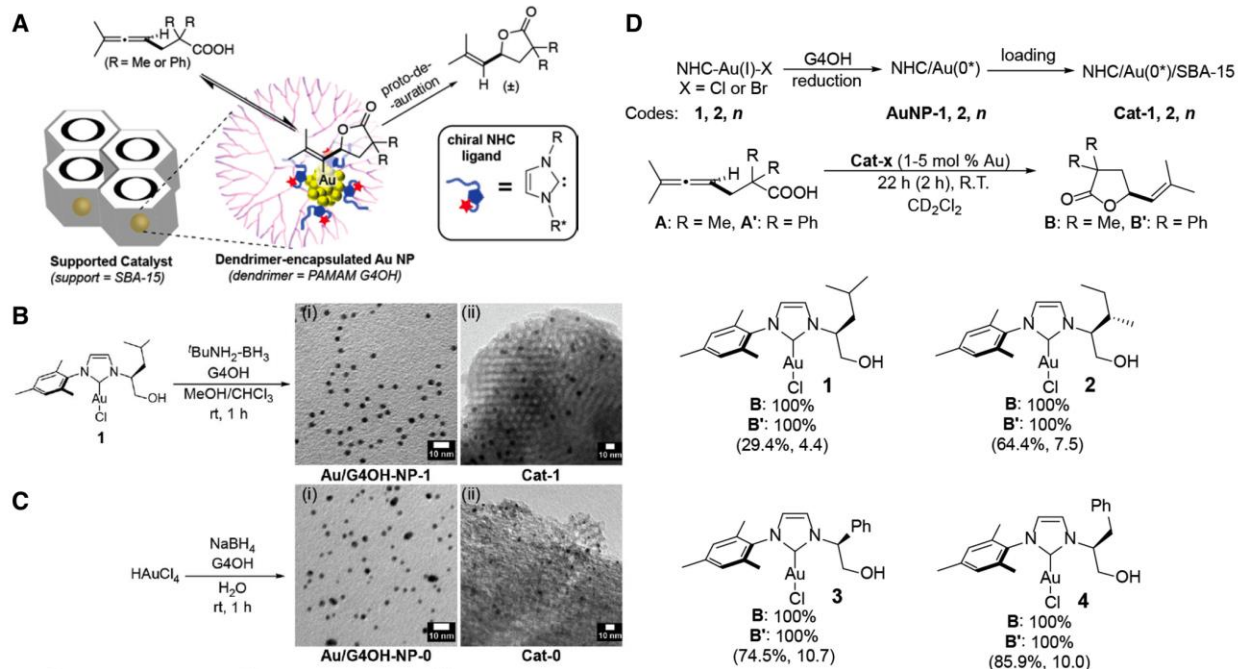


Fig. 2 (A) Scheme of supported dendrimer-encapsulated NHC-ligated Au NPs and the catalytic lactonization reaction pathway. The schematic representation of synthesis routes and TEM images of nanoparticles in (B) *Cat-1* and (C) *Cat-0*. (D) Schematics of the synthesis of the supported catalysts *Cat-n* (*n* is the sample code) with the different NHC structures. The yields of B and B' after 22 h reactions catalyzed by *Cat-n* are given below each structure. The yields of 2 h reactions and the corresponding TOF (h^{-1}) are listed in the parentheses. Adapted with permission from ref [35]. Copyright 2018 American Chemical Society.

Active site engineering in MOFs: heterogeneous-enzyme hybrid; Brønsted acid sites; and guest species

Metal organic frameworks (MOFs) are widely studied as heterogeneous catalysts due to their unique properties such as large surface area and porosity, high crystallinity, and ease of post-synthetic modification. The active sites in MOFs are usually undercoordinated metal ions/clusters, organic linkers with tunable substituents, and supported or encapsulated guest species. Recently, Somorjai group and Yaghi group have extended this active site category by incorporating enzyme-like active site into the MOF scaffold for selective oxidation methane to methanol [37]. Inspired by the enzyme catalyst named particulate methane monooxygenase (pMMO), the MOF-based catalyst was synthesized by installing biologically relevant imidazole moieties onto MOF followed by a sequential metalation to create the desired bis(μ -oxo) dicopper active sites, as shown in Fig 3A. Three ligands were incorporated into the MOF-808 including histidine (His), 4-imidazoleacrylic acid (Iza), and 5-benzimidazolecarboxylic acid (Bzz). The resultant MOF catalysts after metalation were denoted as MOF-808-His-Cu, MOF-808-Iza-Cu, and MOF-808-Bzz-Cu respectively. Methane oxidation to only methanol and water was observed at 150 °C for all three catalysts while a further increase in temperature will lead to the formation of CO₂. MOF-808-Bzz-Cu exhibited the highest methanol productivity at 150 °C among the three catalysts probably due to the higher number of copper-oxygen sites. Although the catalysts deactivate after the first cycle as a result of water molecules strongly bonded to the active sites, MOF-808-Bzz-Cu

shows the highest reported selective methanol productivity of $71.8 \mu\text{mol g}^{-1}$ at this temperature. We hope the successful incorporation of only enzyme active site will open a new avenue to synthesize heterogenized enzyme catalyst for board catalytic applications.

Strong Brønsted acidity could be achieved by simply treating MOF-808 with sulfuric acid (denoted as S-MOF-808) and the active site was identified as a motif consisting of a molecular water-adsorbed zirconium atom with a sulfate-chelated adjacent zirconium atom (Fig. 3B). The water molecule forms a hydrogen bond with the sulfate and thus gives rise to a strongly acidic proton. Oligomerization of light olefins (C3-C6) was then studied over S-MOF-808 [38]. Isobutene and cyclopentene preferred to form dimers, while other tested olefins including 1-butene, 2-methyl-1-butene, 2-methyl-2-butene and 3-methyl-1-butene favored isomerization. S-MOF-88 deactivates when reaction temperature is higher than $110 \text{ }^\circ\text{C}$ due to the loss of adsorbed water molecules. Interestingly, the catalyst can be regenerated by feeding water vapor at $100 \text{ }^\circ\text{C}$, and the reactivity could be completely restored.

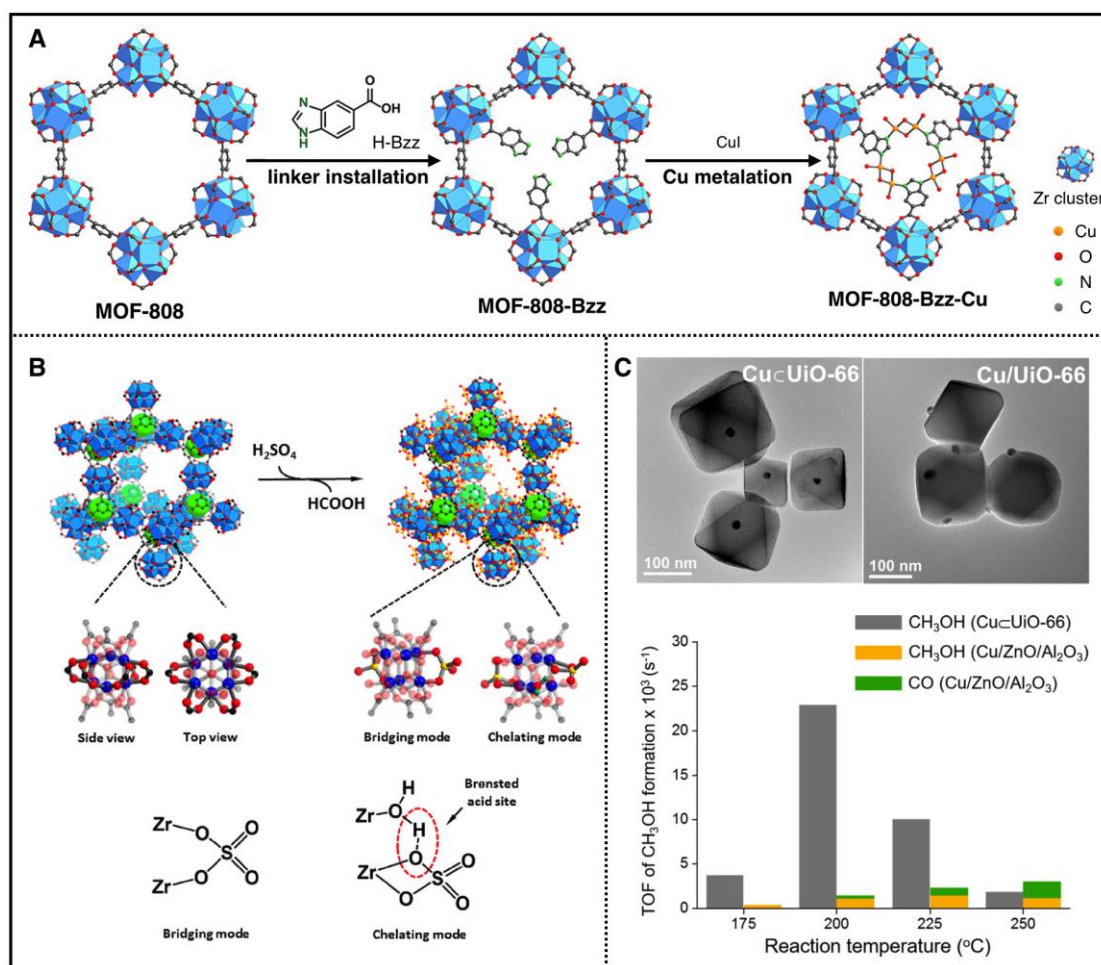


Fig. 3 (A) Post-synthetic modification to replace formate with ligands with imidazole, followed by Cu metalation. H atoms are omitted for clarity. Adapted with permission from ref [37]. Copyright 2018 American Chemical Society. (B) Structure of pristine MOF-808, sulfated S-MOF-808, and schematic representation of the two modes of sulfate ligands coordinated to zirconia clusters. Reprinted with permission from ref [38]. Copyright 2019 American Chemical Society. (C) TEM images of Cu@UiO-66 and Cu/UiO-66, and TOFs of product formation over Cu@UiO-66 and Cu/ZnO/Al₂O₃.

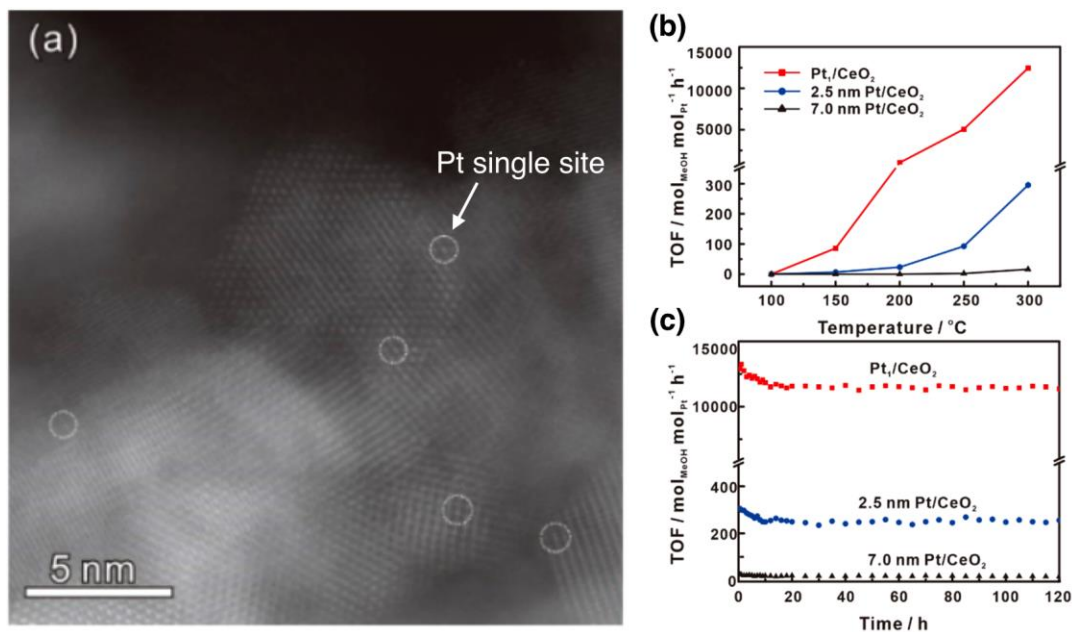
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4 benchmark Cu/ZnO/Al₂O₃ catalyst at different reaction temperatures. Adapted with permission from ref [39].
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6 Copyright 2016 American Chemical Society.
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9 Zr-MOFs could also function as catalyst support to promote the activity and selectivity of Cu catalyst via the strong
10 metal support interaction (SMSI) between the guest copper nanocrystals (NCs) and the zirconium oxide secondary
11 building units (SBUs) [39]. 18 nm Cu NCs were first synthesized by polyol process in the presence of
12 polyvinylpyrrolidone (PVP) and then added into the MOF precursors solution to form a well-defined structure with a
13 single Cu NC encapsulated inside a single UiO-66 crystal (denoted as Cu⊂UiO-66). As a comparison, UiO-66
14 supported Cu NC (denoted as Cu/UiO-66) was synthesized by mixing the colloid solution of both Cu NCs and UiO-
15 66 (Fig 3C, top). Methanol production from hydrogenation of CO₂ was then carried out using both Cu⊂UiO-66 and
16 Cu/UiO-66, together compared with the benchmark Cu/ZnO/Al₂O₃ catalyst. Interestingly, Cu⊂UiO-66 shows an
17 initial turnover frequency (TOF) of methanol formation of $3.7 \times 10^{-3} \text{ s}^{-1}$ at 175 °C under 10 bar of reaction gas (CO₂ and
18 H₂ = 1:3), which is 2 times higher than that of Cu/UiO-66. This two-fold increase in activity caused by the location of
19 Cu NCs could be explained by more contact points between Cu NCs surface and the zirconium oxide SBUs. Besides,
20 the side reaction to form CO as a byproduct is thermodynamically more favored at higher reaction temperatures. More
21 CO was detected on the benchmark Cu/ZnO/Al₂O₃ catalysts when reaction temperature increases to 200, 225 and 250
22 °C (Fig 3C, bottom). However, no CO was detected in Cu⊂UiO-66 at all measured temperatures, showing the
23 excellent methanol selectivity. As shown in Fig. 3C, the methanol formation over Cu⊂UiO-66 is always higher than
24 that of Cu/ZnO/Al₂O₃ at different temperatures, and exhibits a 8-fold increase at 175 °C. XPS results showed that Cu
25 in Cu/UiO-66 was readily oxidized while the binding energy of Zr downshifted by 0.6 eV compared to the bare UiO-
26 66, suggesting the interaction between Cu and zirconium oxide. We thus postulate the high TOF of methanol formation
27 comes from the multiple oxidation states of copper and the SMSI between the guest Cu NCs and zirconium oxide
28 SBUs of MOFs.
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42 **Oxide supported metal single-site for efficient hydrogen production**

43 Metal single site catalysts, with supported atomically dispersed metal active sites, serve as a new frontier in
44 heterogeneous catalysis in recent years. Due to the isolated single atom active site feature, SACs offer great advantages
45 in maximizing the atomic efficiency to 100%, which is especially significant for noble metal catalysts. It is noteworthy
46 that the strong metal-support interaction (SMSI) between supports and anchored metal atoms provides excellent
47 thermal stability and modulation of electronic structures, endowing the extraordinary catalytic activity and selectivity.
48 Hydrogen, the most abundant element in the universe, is regarded as an appealing energy resource due to its high
49 energy density and only water production when used as a fuel. However, storage and transportation of pure hydrogen
50 is practically challenging and unsafe. The concept of liquid organic hydrogen carriers (LOHC) provides an alternative
51 solution for efficient hydrogen storage/generation process by transporting organic liquids and in situ generating
52 hydrogen in the presence of catalyst. Our group recently proposed to use methanol as LOHC for hydrogen production
53 due to its high gravimetric density and variety of production routes [40]. Using porous CeO₂ supported Pt single site
54 catalyst (denoted as Pt₁/CeO₂, TEM was shown in Fig. 4a), methanol starts generating hydrogen gas and carbon
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4 monoxide as a byproduct at 150 °C, and achieved a TOF of 12500 h⁻¹ at 300 °C (Fig. 4b). The great stability was also
5 confirmed by continuous reacting at 300 °C for 120 h and over 90% of the best activity remained, as shown in Fig. 4c.
6 Remarkably, the single site catalyst Pt₁/CeO₂ exhibits 40 times higher hydrogen production efficiency than that of 2.5
7 nm Pt/ CeO₂ and 800 times higher compared to 7 nm Pt/ CeO₂. The superior catalytic performance compared to
8 traditional nanoparticle catalysts highlights the benefit of metal single site catalyst.
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33 **Fig.4** (a) Cs-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)
34 images of Pt₁/CeO₂, the circled brighter dots are Pt single sites. (b) Turnover frequency (TOF) of Pt₁/CeO₂, 2.5 nm Pt/
35 CeO₂, and 7.0 nm Pt/ CeO₂ for hydrogen production in terms of methanol conversion per Pt site at different
36 temperatures. (c) Stability test of single site catalyst Pt₁/CeO₂, 2.5 nm Pt/ CeO₂, and 7.0 nm Pt/ CeO₂ at 300 °C.
37 Adapted with permission from Ref [40]. Copyright 2019 American Chemical Society.
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41 42 **Summary and outlook**

43 We showed the successful examples of unifying different fields of catalysts using hybrid catalyst with engineered
44 active sites. Au DEMCs could achieve both great activity and enantio-selectivity of lactonization reaction via surface
45 ligands functionalization. Selective methane oxidation to methanol could be realized by incorporating only enzyme
46 active site onto MOF catalysts. Moreover, MOF catalysis could also be enhanced by introducing strong Brønsted
47 acidity and guest species. Besides the nanoparticles and cluster catalysts, it is planned to further study the catalytic
48 properties of single site catalysts with different loaded metal atoms and supports. The research will focus on enhancing
49 the reaction selectivity and use single site catalyst as a new example to bridge homogenous and heterogeneous catalysis.
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56 **Conflict of interest**

57 The authors declare that they have no conflict of interest.
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4 **Acknowledgement**

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16 **Reference**

- 17
18 1. Somorjai GA (1972) The Surface Structure of and Catalysis by Platinum Single Crystal Surfaces. *Catal Rev* 7:
19 87
20
21 2. West LA, Somorjai GA (1971) Effects of Surface Disorder, Various Surface Structures of Chemisorbed Gases
22 and Carbon on Helium Atomic Beam Scattering from the (100) Surface of Platinum. *J Chem Phys.* 54: 2864
23
24 3. Goodman RM, Somorjai GA (1970) LEED Studies of Liquid Lead, Bismuth, and Tin Surfaces. *J Chem Phys*
25 52(12): 6331-6335
26
27 4. Davy JG, Somorjai GA (1971) Studies of the Vaporization Mechanism of Ice Single Crystals. *J Chem Phys* 55:
28 3624
29
30 5. Bernasek SL, Siekhaus WJ, Somorjai GA (1973) Molecular Beam Study of Hydrogen-Deuterium Exchange on
31 Low- and High- Miller Index Platinum Single Crystal Surfaces. *Phys Rev Lett* 30(24): 1202-1204
32
33 6. Bernasek SL, Somorjai GA (1975) Small Molecule Reactions on Stepped Single Crystal Platinum Surfaces. *Surf*
34 *Sci* 48: 204
35
36 7. Somorjai GA (1976) Reactions on Single Crystal Surfaces. *Accts of Chem Res* 9: 248
37
38 8. Holinga GJ, York RL, Onorato RM, Thompson CM, Webb NE, Yoon AP, Somorjai GA (2011) An SFG study
39 of interfacial amino acids at the hydrophilic SiO₂ and hydrophobic deuterated polystyrene surfaces. *J Am Chem*
40 *Soc* 133(16):6243–6253
41
42 9. McCrea KR, Somorjai GA (2000) SFG-surface vibrational spectroscopy studies of structure sensitivity and
43 insensitivity in catalytic reactions: Cyclohexene dehydrogenation and ethylene hydrogenation on Pt (111) and Pt
44 (100) crystal surfaces. *J Mol Catal Chem* 163(1–2):43–53
45
46 10. Shen Y (1989) Surface properties probed by second-harmonic and sum-frequency generation. *Nature* 337:519–
47 525
48
49 11. Alayoglu S, Krier JM, Michalak WD, Zhu Z, Gross E, Somorjai GA (2012) In situ surface and reaction probe
50 studies with model nanoparticle catalysts. *ACS Catal* 2(11):2250–2258
51
52 12. Salmeron M, Schlögl R (2008) Ambient pressure photoelectron spectroscopy: A new tool for surface science and
53 nanotechnology. *Surf Sci Rep* 63(4):169–199
54
55 13. Bluhm H, Hävecker M, Knop-Gericke A, Kiskinöva M, Schlogl R, Salmeron M (2007) In situ X-ray
56 photoelectron spectroscopy studies of gas-solid interfaces at near-ambient conditions. *MRS Bull* 32(12):1022–
57 1030
58
59
60
61
62
63
64
65

14. Velasco-Velez J-J, Wu CH, Pascal TA, Wan LF, Guo J, Prendergast D, Salmeron M. (2014) Interfacial water: The structure of interfacial water on gold electrodes studied by x-ray absorption spectroscopy. *Science* 346(6211):831–834
15. Li Y, Liu J, Witham C, Hunag W, Marcus MA, Fakra SC, Alayoglu P, Zhu Z, Thompson CM, Arjun A, Lee K, Gross E, Toste FD, Somorjai GA (2011) A Pt-Cluster-Based Heterogeneous Catalyst for Homogeneous Catalytic Reactions: X-ray Absorption Spectroscopy and Reaction Kinetic Studies of Their Activity and Stability against Leaching. *J Am Chem Soc* 133 (34):13527-13533
16. Gross E, Shu XZ, Alayoglu S, Bechtel HA, Martin MC, Toste FD, Somorjai GA (2014) In situ IR and X-ray high spatial-resolution microspectroscopy measurements of multistep organic transformation in flow microreactor catalyzed by Au nanoclusters. *J Am Chem Soc* 136(9):3624–3629
17. Zhu Z, Melaet G, Axnanda S, Alayoglu S, Liu Z, Salmeron M, Somorjai GA (2013) Structure and chemical state of the Pt(557) surface during hydrogen oxidation reaction studied by in situ scanning tunneling microscopy and X-ray photoelectron spectroscopy. *J Am Chem Soc* 135(34):12560–12563
18. Ye R, Hurlburt TJ, Sabyrov K, Alayoglu S, Somorjai GA (2016) Molecular catalysis science: Perspective on unifying the fields of catalysis. *Proc Natl Acad Sci USA*. 113(19): 5159-5166
19. Zhu Z, Tao F, Zheng F, Chang R, Li Y, Heinke L, Liu Z, Salmeron M, Somorjai GA (2012) Formation of Nanometer-sized Surface Platinum Oxide Clusters on a stepped Pt(557) Single Crystal Surface Induced by Oxygen: A High-Pressure STM and Ambient-pressure XPS Study. *Nano Letters* 12, 1491-1497
20. Tao F, Dag S, Wang L, Liu Z, Butcehr DR, Bluhm H, Salmeron M, Somorjai GA (2010) Break-up of Stepped Platinum Catalyst Surfaces by High CO Coverage. *Science* 327: 850.
21. Eren B, Zherebetskyy D, Patera LL, Wu C, Bluhm H, Africh C, Wang L, Somorjai GA (2016) Activation of Cu(111) Surface by Decomposition into Nanoclusters driven by CO Adsorption. *Science*, 351: 475-478
22. Joo S, Park J, Renzas JR, Butcehr DR, Huang W, Somorjai GA (2010) Size Effect of Ruthenium Nanoparticles in Catalytic Carbon Monoxide Oxidation. *Nano Lett* 10: 2709-2713
23. An K, Somorjai GA (2012) Size and Shape Control of Metal Nanoparticles for Reaction Selectivity in Catalysis. *ChemCatChem* 4:1512-1524
24. Alayoglu S, Aliaga C, Sprung C, Somorjai GA (2011) Size and Shape Dependence of Pt Nanoparticles over Methylcyclopentane/Hydrogen Ring Opening / Ring Enlargement Reaction. *Cat Lett* 141: 914-924
25. Pushkarev VV, Musselwhite N, An K, Alayoglu S, Somorjai GA (2012) High Structure Sensitivity of Vapor-Phase Furfural Decarbonylation/Hydrogenation Reaction Network as a Function of Size and Shape of Pt Nanoparticles. *Nano Lett* 12, 5196-5201
26. Wang H, Wang Y, Zhu Z, Sapi A, An K, Criffin K, Michalak WD, Somorjai GA (2013) Influence of Size-Induced Oxidation State of Platinum Nanoparticles on Selectivity and Activity in Catalytic Methanol Oxidation in the Gas Phase. *Nano Lett* 13: 2976-2979
27. Borodko Y, Thompson CM, Huang W, Yildiz HB, Frei H, Somorjai GA (2011) Spectroscopic Study of Platinum and Rhodium Dendrimer (PAMAM G4OH) Compounds, Structure and Stability. *J Phys Chem C* 115: 4757-4767

- 1
2
3
4 28. Deraedt C, Melaet G, Ralston W, Ye R, Somorjai GA (2017) Platinum and Other Transition Metal Nanoclusters
5 (Pd, Rh) Stabilized by PAMAM Dendrimer as Excellent Heterogeneous Catalysts: Application to the
6 MethylCycloPentane (MCP) Hydrogenative Isomerization. *Nano Lett* 17: 1853-1862
7
8 29. Deraedt C, Ye R, Ralston WT, Toste FD, Somorjai GA (2017) Dendrimer Stabilized Metal Nanoparticles as
9 Efficient Catalysts for Reversible Dehydrogenation/Hydrogenation of N-Heterocycles. *J Am Chem Soc* 139, 49:
10 18084-18092
11
12 30. Li Y, Huang W, Witham C, Liu J, Zhu Z, Thompson C, Arjun A, Lee K, Marcus M, Toste DF, Somorjai GA
13 (2011) A Pt-Cluster-Based Heterogeneous Catalyst for Homogeneous Catalytic Reactions: X-ray Adsorption
14 Spectroscopy and Reaction Kinetic Studies of Their Activity and Stability against Leaching. *J Am Chem Soc* 133:
15 13527-13533
16
17 31. Baker LR, Kennedy G, Spronsen MV, Hervier A, Cai X, Chen S, Wang L, Somorjai GA (2012) Furfuraldehyde
18 Hydrogenation on Titanium Oxide-Supported Platinum Nanoparticles Studied by Sum Frequency Generation
19 Vibrational Spectroscopy: Acid-base Catalysis Explains the Molecular Origin of Strong Metal-Support
20 Interactions. *J Am Chem Soc* 134: 14208-14216
21
22 32. Wang L, An K, Sapi A, Liu F, Somorjai GA (2014) Effects of Nanoparticle Size and Metal/Support Interactions
23 in Pt-Catalyzed Methanol Oxidation Reactions in Gas and Liquid Phases. *Cat Lett* 144: 1930-1938
24
25 33. Ye R, Zhao J, Wickemeyer BB, Toste FD, Somorjai GA (2018) Foundations and strategies of the construction of
26 hybrid catalysts for optimized performances. *Nature Catalysis* 1: 318-325
27
28 34. Ye R, Zhukhovitskiy AV, Deraedt CV, Toste FD, Somorjai GA (2017) Supported Dendrimer-Encapsulated Metal
29 Clusters: Toward Heterogenizing Homogenous Catalysts.
30 <https://pubs.acs.org/doi/full/10.1021/acs.accounts.7b00232> *Acc Chem Res* 50:1894-1901
31
32 35. Ye R, Zhukhovitskiy AV, Kazantsev RV, Fakra SC, Wickemeyer BB, Toste FD, Somorjai GA (2018) Supported
33 Au Nanoparticles with N-Heterocyclic Carbene Ligands as Active and Stable Heterogeneous Catalysts for
34 Lactonization. *J Am Chem Soc* 140: 4144-4149
35
36 36. Shu X, Nguyen SC, He Y, Oba F, Zhang Q, Canlas C, Somorjai GA, Alivisatos, AP, Toste FD (2015) Silica-
37 Supported Cationic Gold(I) Complexes as Heterogeneous Catalysts for Regio- and Enantioselective Lactonization
38 Reactions. *J Am Chem Soc* 137, 7083-7086
39
40 37. Baek J, Rungtaweevoranit B, Pei X, Park M, Fakra SC, Liu Y, Matheu R, Alshimri SA, Alshehri S, Trickett
41 CA, Somorjai GA, Yaghi OM (2018) Bioinspired Metal-Organic Framework Catalysts for Selective Methane
42 Oxidation to Methanol. *J Am Chem Soc* 140, 51:18208-18216
43
44 38. Liu P, Redekop E, Gao X, Liu W, Olsbye U, Somorjai GA (2019) Oligomerization of Light Olefins Catalyzed by
45 Brønsted-Acidic Metal-Organic Framework-808. *J Am Chem Soc* 141, 29: 11557-11564
46
47 39. Rungtaweevoranit B, Baek J, Araujo JR, Archanjo BS, Choi KM, Yaghi OM, Somorjai GA (2016) Copper
48 Nanocrystals Encapsulated in Zr-based Metal-Organic Framework for Highly Selective CO₂ Hydrogenation to
49 Methanol. *Nano Lett* 16, 12, 7645-7649
50
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65

40. Chen, L, Hou K, Liu Y, Qi Z, Zheng Q, Lu Y, Chen J, Chen J, Pao C, Wang S, Li Y, Xie S, Liu F, Predergast D, Klebanoff L, Stavila V, Allendorf MD, Guo J, Zheng L, Somorjai GA (2019) Efficient hydrogen Production from Methanol Using a Single-Site Pt₁/CeO₂ catalyst. *J Am Chem Soc* 141, 45, 17995-17999