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Integrating the Fields of Catalysis: Active site engineering in Metal Cluster, Metal Organic Framework and Metal Single Site

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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

near-edge structure (XANES) and extended X-ray adsorption fine structure (EXAFS) [14-15]. The development of high pressure scanning tunneling microscopy (STM) gives rise to dynamic studies of surface atoms under reaction conditions that could also be applied to catalysis [16-17].

As reviewed in the previous perspectives, catalysis research in our group combines the synthesis of nanoparticle catalysts, catalytic performance investigation, and characterization under reaction conditions [18]. The studied systems include (1) surface restructuring of metal single crystals induced by the adsorbate under reaction conditions by STM [19-21]; (2) size and shape dependence of nanoparticles (1-10 nm) on reactivity and selectivity [22-26]; (3) dendrimer-encapsulated metal clusters (DEMCs) for homogeneous catalytic reactions [27-30]; (4) strong metal support interaction (SMSI) of oxide-metal interfaces [31-32]. The successful heterogenizing homogenous catalyst (i.e., DEMCs) opens the door to investigate the chemical correlation of three fields of catalysis: heterogeneous, homogeneous, and enzymatic [18]. Research efforts were thus made to bridge these fields by constructing heterogeneous-homogenous, heterogeneous-enzyme hybrid catalysts, which could potentially combine the advantages of each field and leads to better catalytic performance [33].

Here in this paper, we summarized our latest research in unifying the three fields of catalysis via engineering the active sites. The catalytic performance of heterogeneous-homogenous hybrid catalysts was examined using supported DEMCs functionalized with surface ligands. Furthermore, we successfully synthesized a heterogeneous-enzyme hybrid catalyst by incorporating the enzyme-like active sites into metal organic frameworks (MOFs) for selective oxidation methane to methanol. We also included other two examples of engineering the active sites of MOFs for better catalytic performance. Finally, single site catalyst was regarded as a new type of heterogeneous-homogenous hybrid and used for the hydrogen production from methanol.

Heterogeneous-homogenous hybrid: DEMCs functionalizing with surface ligands

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

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 enantio-selectivity 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 CO_2 . 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-808 deactivates when reaction temperature is higher than 110°C due to the loss of adsorbed water molecules. Interestingly, the catalyst can be regenerated by feeding water vapor at 100°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.

benchmark Cu/ZnO/Al₂O₃ catalyst at different reaction temperatures. Adapted with permission from ref [39].
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Zr-MOFs could also function as catalyst support to promote the activity and selectivity of Cu catalyst via the strong metal support interaction (SMSI) between the guest copper nanocrystals (NCs) and the zirconium oxide secondary building units (SBUs) [39]. 18 nm Cu NCs were first synthesized by polyol process in the presence of polyvinylpyrrolidone (PVP) and then added into the MOF precursors solution to form a well-defined structure with a single Cu NC encapsulated inside a single UiO-66 crystal (denoted as Cu $\subset$ UiO-66). As a comparison, UiO-66 supported Cu NC (denoted as Cu/UiO-66) was synthesized by mixing the colloid solution of both Cu NCs and UiO-66 (Fig 3C, top). Methanol production from hydrogenation of CO₂ was then carried out using both Cu $\subset$ UiO-66 and Cu/UiO-66, together compared with the benchmark Cu/ZnO/Al₂O₃ catalyst. Interestingly, Cu $\subset$ UiO-66 shows an 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 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 Cu NCs could be explained by more contact points between Cu NCs surface and the zirconium oxide SBUs. Besides, the side reaction to form CO as a byproduct is thermodynamically more favored at higher reaction temperatures. More CO was detected on the benchmark Cu/ZnO/Al₂O₃ catalysts when reaction temperature increases to 200, 225 and 250 °C (Fig 3C, bottom). However, no CO was detected in Cu $\subset$ UiO-66 at all measured temperatures, showing the excellent methanol selectivity. As shown in Fig. 3C, the methanol formation over Cu $\subset$ UiO-66 is always higher than that of Cu/ZnO/Al₂O₃ at different temperatures, and exhibits a 8-fold increase at 175 °C. XPS results showed that Cu in Cu/UiO-66 was readily oxidized while the binding energy of Zr downshifted by 0.6 eV compared to the bare UiO-66, suggesting the interaction between Cu and zirconium oxide. We thus postulate the high TOF of methanol formation comes from the multiple oxidation states of copper and the SMSI between the guest Cu NCs and zirconium oxide SBUs of MOFs.

Oxide supported metal single-site for efficient hydrogen production

Metal single site catalysts, with supported atomically dispersed metal active sites, serve as a new frontier in heterogeneous catalysis in recent years. Due to the isolated single atom active site feature, SACs offer great advantages in maximizing the atomic efficiency to 100%, which is especially significant for noble metal catalysts. It is noteworthy that the strong metal-support interaction (SMSI) between supports and anchored metal atoms provides excellent thermal stability and modulation of electronic structures, endowing the extraordinary catalytic activity and selectivity. Hydrogen, the most abundant element in the universe, is regarded as an appealing energy resource due to its high energy density and only water production when used as a fuel. However, storage and transportation of pure hydrogen is practically challenging and unsafe. The concept of liquid organic hydrogen carriers (LOHC) provides an alternative solution for efficient hydrogen storage/generation process by transporting organic liquids and in situ generating hydrogen in the presence of catalyst. Our group recently proposed to use methanol as LOHC for hydrogen production due to its high gravimetric density and variety of production routes [40]. Using porous CeO₂ supported Pt single site catalyst (denoted as Pt₁/CeO₂, TEM was shown in Fig. 4a), methanol starts generating hydrogen gas and carbon

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 confirmed by continuous reacting at 300 °C for 120 h and over 90% of the best activity remained, as shown in Fig. 4c. Remarkably, the single site catalyst Pt₁/CeO₂ exhibits 40 times higher hydrogen production efficiency than that of 2.5 nm Pt/ CeO₂ and 800 times higher compared to 7 nm Pt/ CeO₂. The superior catalytic performance compared to traditional nanoparticle catalysts highlights the benefit of metal single site catalyst.

Fig.4 (a) Cs-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of Pt₁/CeO₂, the circled brighter dots are Pt single sites. (b) Turnover frequency (TOF) of Pt₁/CeO₂, 2.5 nm Pt/ CeO₂, and 7.0 nm Pt/ CeO₂ for hydrogen production in terms of methanol conversion per Pt site at different temperatures. (c) Stability test of single site catalyst Pt₁/CeO₂, 2.5 nm Pt/ CeO₂, and 7.0 nm Pt/ CeO₂ at 300 °C. Adapted with permission from Ref [40]. Copyright 2019 American Chemical Society.

Summary and outlook

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

Conflict of interest

The authors declare that they have no conflict of interest.

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