

Forwarding Molecular Design of Heterogeneous Catalysts

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A new dual-atom catalyst for efficient water oxidation combines the benefits of homogeneous and heterogeneous catalysis.

Catalysis research has long been divided between homogeneous and heterogeneous catalysis. In homogeneous catalysis, reactivity arises from molecular catalysts in a homogeneous solution, while in heterogeneous catalysis reactivity comes from sites on a surface. The main advantage of homogeneous catalysis is the ability to design reaction sites within molecularly defined catalysts in order to achieve high catalytic activity, measured in the number of product molecules evolved per site per second (turnover frequency, TOF). However, homogeneous catalysis suffers from degradation of the molecular catalysts during the reaction, leading to a low number of total product molecules evolved (turnover number, TON). In comparison, heterogeneous catalysis has incredibly high TONs—so much so that discrete TONs are often impractical to report. A new, promising area of research is intended to combine the benefits of both homogeneous and heterogeneous catalysis by tethering the molecular catalyst onto a solid surface to achieve tunability, high TOFs, and high TONs. While there have been encouraging reports of heterogenized molecular catalysts, especially for the water oxidation reaction that evolves O_2 from H_2O ,^{1,2} defining and tailoring the molecular structure of composites has been a critical challenge. When studying a specific catalytic activity on composite surfaces, the important question to ask is how many reactive sites are tethered to a given surface site and in what geometry?

In this issue of ACS Central Science,³ the authors, building upon the previous breakthrough work, tether a dual-atom Ir molecular water oxidation catalyst to heterogeneous catalysts in various surface-bound geometries and demonstrate differences between these configurations (Figure 1). In particular, they found that dual-atom Ir catalysts bind either perpendicular (“end-on”) or parallel (“side-on”) to

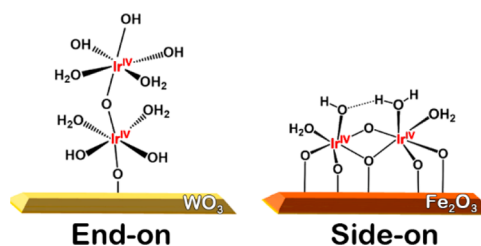


Figure 1. Ir dual-atom heterogenized catalyst (Ir-DHC) in “end-on” and “side-on” configurations. Reprinted with permission from ref 3. Copyright 2018, American Chemical Society.

the surfaces, depending on the surface type. The “end-on” binding leaves the reactive Ir site dangling from the surface, which led the authors to propose a mechanism explaining the changes in the resulting catalytic activity similar to the action of the water oxidation complex of photosystem II (with the highest reported TOFs).

The essential breakthrough of this work is the application of a characterization technique, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), to study composite surfaces.⁴ DRIFTS measures the infrared vibrational spectrum from surfaces by collecting the full sphere of reflected and scattered light, which is especially important for rough surfaces. Using this technique, the authors have distinguished between the following configurations of the catalysts: single-atom Ir catalysts (Ir-SAC), “side-on” bound dual-atom heterogenized catalysts (Ir-DHC), and “end-on” bound Ir-DHC; whereas the formation of aggregated Ir nanoparticles was ruled out. The Ir-SAC and “side-on” Ir-DHCs yield a pair of singlet peaks in DRIFTS spectra for symmetric and asymmetric CO stretches within the Ir-complexes. The CO stretches become doublet peaks for the “end-on” Ir-DHCs, with the lower frequency doublet attributed to the dangling top Ir-site and the higher frequency to the bottom Ir-site. The ability to differentiate between these configurations by their vibrational spectra was suitably corroborated by density functional theory

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calculations of their expected frequencies and the manifestation of the doublet peaks in the “end-on” Ir-DHCs. The electronic structure of “side-on” Ir-DHC, which does not exhibit a doublet peak despite containing two Ir atoms, should be similar to two separate Ir-SACs. Therefore, identifying the “end-on” configuration provides a more explicit metric of dual-atom catalysts and especially the ones that can behave differently from single-atom catalysts. While the DRIFTS data constitute fairly convincing evidence of the existence of “end-on” Ir-DHCs, the authors utilized a complementary technique, high annular dark-field scanning transmission electron microscopy, to distinguish between Ir-DHCs and Ir-SACs by revealing differences in intensity from neighboring undecorated surface atoms. Although this method is not as accurate for reporting molecular geometries as the DRIFTS is, it could be used advantageously to approximate the surface density of Ir-DHCs and Ir-SACs. It would be nice to see such quantification in future work.

The strategy to synthesize preferentially “end-on” over “side-on” Ir-DHCs is pleasantly straightforward and derives from their respective surface geometries. The research team screened several heterogeneous oxide catalysts with known activity for water oxidation: Fe_2O_3 , TiO_2 , CeO_2 , and WO_3 . They found that the “end-on” Ir-DHC forms only on WO_3 , for which the distance between neighboring surface sites is larger than the two Ir atoms in the Ir molecular precursor. Based on the doublet peaks in the DRIFTS spectra, the authors conclude that “end-on” configurations appear selectively on WO_3 with undetectable levels of “side-on” configurations. Therefore, if only “side-on” configurations are desired, an oxide such as Fe_2O_3 should be chosen as a heterogeneous catalyst, whereas for “end-on” configurations only, WO_3 should be used. The combination of direct molecular characterization with a straightforward synthesis of one geometry versus another is indeed a promising result for the field of heterogenized molecular catalysts.

The question that the authors attempt to address is identifying the differences in the nature of the catalytic activity of the “end-on” Ir-DHCs, Ir-SACs, and bare oxide surfaces for O_2 evolution reaction. They found that while the overall efficiency and speed for converting H_2O to

products do not change appreciably, tethering molecular catalysts does modify the selectivity for O_2 over a peroxide (e.g., H_2O_2) product. Selectivity for O_2 evolution is the highest on the special “end-on” Ir-DHC surfaces. Based on a calculation of a proposed mechanism, the authors suggest that changes in the product selectivity arise from the site-based catalytic activity of the molecular catalysts. However, at this stage it is not clear whether changes to the catalytic activity arise from the molecular catalysts themselves or from their effect on the undecorated surface sites of the bare catalyst, which are also highly active for both O_2 and peroxide evolution. Surface sites decorated by molecular catalysts should constitute a small fraction of all the potentially active sites on the heterogeneous surface (Figure 2). Conversely, if

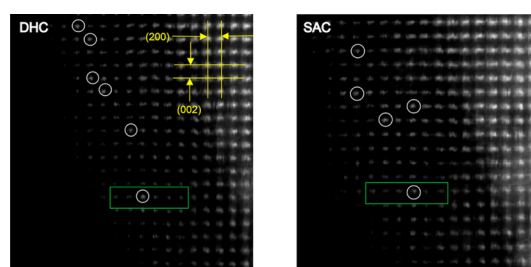


Figure 2. Atomic structure of “end-on” Ir dual-atom catalysts, Ir-DHCs (left), and Ir single-atom catalysts, Ir-SACs (right), on the surface of WO_3 . Reprinted with permission from ref 3. Copyright 2018 American Chemical Society.

one views the tethered catalysts as surface dangling bonds or defect centers, a small fraction of tethered catalysts could markedly change the electronic properties of the collective surface.^{5–7} Indeed, the promise of combining heterogeneous and homogeneous catalysts in one system should lie in how they affect each other in unexpected and synergistic ways. Overall, the authors have made a great step forward by demonstrating the ability to detect and tailor the molecular structure of homogeneous catalysts on heterogeneous surfaces, with important effects on the resulting catalytic activity.

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