Control of Substrates Beyond the Catalyst Active Site

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Spatial control of incompatible elementary steps in a catalytic cycle enables conversion of methane into methanol.

Methane functionalization, directly into products such as methanol or longer chain functionalized hydrocarbons, would enable additional uses for methane feedstocks and facilitate transportation using existing infrastructure for liquid phases. The functionalization of all alkanes including methane is challenging for several reasons. The C–H bonds in alkanes have high bond energy and are hard to break and functionalize, and often the C–H bonds in the products are weaker and more reactive so that selectivity challenges arise. Efforts to cleanly employ O₂ as terminal oxidant in reaction chemistry generally are also needed to support developments in methane functionalization. The molecular and nanomaterial components that comprise the catalytic system for methanol oxidation, reported by Liu and co-workers, owe their performance to their spatial arrangement and positioning relative to each other in the catalytic ensemble. In this report, the geometry of a nanowire array is used to protect an O₂-sensitive rhodium catalyst that activates methane toward its ultimate conversion into methanol (Figure 1).

Following activation of methane by the rhodium catalyst, a series of elementary reaction steps propagates, and ultimately O₂ comes into play a key role in the oxidation chemistry leading to methanol. An electrochemical process—set at a distance from the O₂-intolerant Rh catalyst—destroys O₂ around the rhodium active site to protect that reactive center and enable its function in the methane activation step.

Catalyst design “beyond the active site” can be traced back to nature where metalloenzymes transport electrons via pathways incorporating iron–sulfur clusters, and protons are transported separately to active sites along amino acid residues such as histidine. Formate dehydrogenase is one example where the transition metal in the cofactor controls electron transfer reactions, and sulfur-derived ligands mediate delivery of protons so that everything can come together to mediate CO₂/HCOO⁻ interconversions. The separation of electron and proton transport pathways prevents side reactions such as formation of H₂ from electron and protons, or formation of CO from reaction of CO₂ with electrons (reduced metal centers).

The chemistry of enzyme active sites has inspired a wealth of inorganic chemistry over the past few decades, and this continues to date with the present report. Elegant synthetic inorganic chemistry has yielded structural and functional models of the iron–sulfur clusters involved in electron transport, and these synthetic mimics can now be used to probe bioinspired electron transfer chemistry and spectroscopic properties for comparison with the biological signatures.

Further synthetic inorganic chemistry has probed functional models of enzyme active sites so that knowledge of electron and proton transport properties on metals and ligands, respectively, can be understood at the molecular level. The effects of geometric positioning of catalyst components can also be manipulated by synthetic inorganic chemists and finely tuned using tricks such as a variation in solvent viscosity. As an example, work on functional molecular models of hydrogenase enzymes has

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shown that changes in solvent viscosity, such as using ionic liquids as a reaction medium, fine-tunes proton transport and enhances H₂ production rates by 3 orders of magnitude relative to catalysis in regular organic solvents.⁶

The chemistry of heterogeneous catalysis also relies heavily on the chemistry occurring beyond the active site, or on systems where multiple different “active sites” contribute in different roles to catalytic reaction outcomes. Elucidation of those reaction mechanisms can be more difficult than in molecular systems, but advances in operando and in situ techniques for probing reaction mechanisms of heterogeneous catalysts are advancing quickly. Catalysis using metal–organic frameworks, covalent organic frameworks, exchanged zeolites,⁷ and nanomaterial systems,⁸ continues to illustrate the importance of controlling geometry and the spatial arrangement of substrate transport relative to a catalyst active site. This chemistry of nanomaterials is where Liu and co-workers make a contribution with this report.¹

Liu and co-workers employ the known chemistry of (tetramesitylporphyrin)RhII, (TMP)RhII, in its reaction with half an equivalent of methane (CH₄) to give (TMP)RhII−H and (TMP)RhIII−CH₃.⁹,¹⁰ Protection of these highly air-sensitive reagents and products is achieved by positioning of (TMP)RhII inside a nanowire array. They also demonstrated that stoichiometric reaction of (TPP)-RhIII−CH₃ with organic peroxides gives methanol (MeOH) in the absence of the nanowire. When these stoichiometric reactions are combined cleverly in the nanowires array, overall electrochemical generation of MeOH was observed. This is successful because hydroperoxides are generated in situ electrochemically from O₂ and the applied electrochemical bias also serves to reduce the (TMP)Rh catalyst back to (TMP)RhII so that the catalytic cycle turns over. The structural importance of the nanowire array was emphasized by control experiments where a planar electrode led to a complete loss of catalytic activity.

The efforts of chemists to direct reaction pathways and ultimately optimize and control catalytic reaction outcomes take many forms and evolve with the needs of the chemical industry, the political climate, and the variation in availability of feedstock resources. Thus, the present work by Liu and co-workers also highlights renewed interest in catalysts that operate using electricity to provide the energy needed to drive a chemical reaction. The advent of cheap electricity derived from renewable sources has refocused ongoing efforts in chemistry and catalysis on processes where direct injection of electrons can drive product formation. Historically, catalysis on the industrial scale derived energy inputs thermally and often with high pressures, but many see an opportunity now to develop catalytic systems to input energy as electricity (electrons). Liu and co-workers build on a history of geometric and spatial control to tailor new reactions that harness electrical energy. Their strategy of using nanostructured materials to control substrate transport could find future application in industrially relevant multistep processes where reaction components of each step are incompatible.

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Notes
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