

Getting Down to Earth: The Renaissance of Catalysis with Abundant Metals

Guest Editorial for the *Accounts of Chemical Research* special issue on “*Earth Abundant Metals in Homogeneous Catalysis*”

Although organometallic chemistry can trace its origins to molecules like ferrocene and $\text{Mn}_2(\text{CO})_8$, the application of earth-abundant 3d transition metals to homogeneous catalysis has lagged behind the tremendous advances made with precious metals. Recently there has been renewed interest in the challenge of matching or surpassing the high activity and selectivity of well-established palladium, rhodium, or ruthenium catalysts by finding ligands and conditions to tame the capricious nature of base metals. This thematic issue in *Accounts of Chemical Research* is a timely account of recent developments across this emerging and diverse field of research. The 3d metals are known to undergo facile one electron oxidation state changes often with associated spin state complexity (see articles in this issue by Bedford and Holland), uncontrolled reactions with dioxygen (see article by Stahl), and facile ligand redistribution. By contrast 50 years of research on precious metal homogeneous catalysis has established predictable chemistry, usually based on two electron changes between diamagnetic oxidation states. The impact of precious metal catalysis is illustrated by the widespread use of palladium catalysis in the manufacture of pharmaceuticals and electronic materials and was recognized by the Nobel prize in 2010. This recognition, coupled with the 2001 and 2005 Prizes for asymmetric hydrogenation and olefin metathesis, respectively, clearly demonstrates the essential role second and third row transition metals have played in homogeneous catalysis and chemical synthesis.

The potential benefits to society and rewards to the researcher for studying catalysts with the earth abundant metals are many. The elements discussed in this special issue—titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper—are some of the most abundant in the earth's crust. They are much less expensive ($\text{Pd}(\text{OAc})_2$ is approximately \$75/gram, while $\text{Ni}(\text{OAc})_2$ is approximately \$10/g), and globally available to obtain than rare elements like palladium, platinum, and rhodium. The nearly unlimited supply of iron would allow reactions on the enormous scale of the Haber–Bosch ammonia synthesis to be implemented for hydrogen fuel production and utilization (see the articles by Bullock and Guan) or carbon dioxide hydrogenation (see article by Milstein). They are essential to life (except titanium, which is nevertheless usually biocompatible, and nickel, which is essential to bacteria but not humans) and thus often have less health and environmental impact than the precious metals. The promise of discovery of new mechanisms, reactivity principles, varieties of reactions, and substrate scope not seen with the 4d and 5d metals is perhaps the most exciting.

Nickel, cobalt, and iron catalysts have been investigated in parallel with the better known palladium ones for carbon–carbon bond formation in organic synthesis. This issue reports recent progress in the discovery of nickel- and iron-based cross coupling reactions that either avoid or make use of odd electron chemistry depending on the ligands and conditions (articles by Jarvo, Weix, Tobisu and Chantai, Shi, and Bedford). When

supported by appropriate ligands, nickel and cobalt enable efficient coupling reactions entailing the formal addition of carbon–hydrogen bonds to unsaturated compounds (Jamison and co-workers, Montgomery and co-workers, Ogoshi and co-workers, and Louie) and [2 + 2] and [2 + 2 + 2] cycloadditions (Cheng).

Iminopyridine ligands are emerging as privileged ligands in iron catalysis. This was identified early on for olefin polymerization catalysis (Small). The ligand's redox noninnocence was recognized and exploited for olefin hydrogenation (Chirik) and for carbon–carbon and carbon–heteroatom bond formation (McNeill and Ritter). β -Diketiminato ligands allow the synthesis of low coordinate iron and cobalt complexes allowing reactions with multiple intersecting spin states (Holland). By contrast, elements with mixed oxygen and nitrogen donors are optimum for the titanium and vanadium groups (Ryken and Schafer and Klosin and co-workers).

Enzymes activated by vanadium, manganese, iron, and copper are ubiquitous and provide inspiration to catalytic chemists. Metals supported by porphyrin and other macrocyclic ligands are common in nature, and these construction principles have been exploited by chemists to make selective oxidation and carbon–fluorine bond-forming catalysts (Groves). Reactions of non-heme iron oxygenases have been adapted to the chemistry of synthetic iron complexes to oxidize substrates with high regio- and stereoselectivity (Oloo and Que). The ultimate challenge has been to utilize air as the oxidant, and there has been progress in the development of copper catalysts that use dioxygen for selective alcohol oxidation and carbon–heteroatom bond formation (McCann and Stahl) and vanadium catalysts for biomass conversion (Hanson).

Finally there have been exciting developments in iron catalysis with the discovery of ligands that allow bifunctional catalysis. These are mixed phosphorus and nitrogen polydentate ligands that store a proton that is used in the catalytic cycle. Several of these ligands have already been used effectively in ruthenium catalysis. They are very effective at activating iron for hydrogenation, asymmetric hydrogenation, and dehydrogenation reactions (Milstein, Gao, Guan, and Morris).

Paul Chirik, Guest Editor

Princeton University

Robert Morris, Guest Editor

University of Toronto

■ AUTHOR INFORMATION

Notes

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