catalysts

Editorial

Editorial: Cobalt and Iron Catalysis

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Cobalt and iron have long history of importance in the field of catalysis that continues to this day. Currently, both are prevalent metals in a multitude of catalytic processes: the synthesis of ammonia [1], Fischer-Tropsch synthesis (FTS) [2–5], water gas shift [6–9], hydrotreating [10], olefin polymerization [11], hydrotreating [12,13], isomerization [14,15], alcohol synthesis [16–18], and photocatalysis [19–21]. One cannot underestimate the importance of hydrotreating. The U.S. Energy Information Administration (EIA) shows that crude demand for 2019 was ~100 million barrels per day [22]; this crude requires hydrotreating before it can be brought to market [23–25]. FTS is another example, as it is at the core of large-scale industrial processes in coal-to-liquid (CTL) [26–28] and gas-to-liquid (GTL) [23,24,29] processes, as well as futuristic research on biomass-to-liquid (BTL) [30,31] processes. It is responsible for the production of more than 300,000 barrels per day of synthetic fuels [32–35], with some examples being Sasol I and II in South Africa (160,000 BPD), Pearl GTL (140,000 BPD), Oryx GTL (34,000 BPD), Shenhua CTL (20,000 BPD), and Shell Bintulu Malaysia (12,000 BPD). Water gas shift and steam reforming, used as a precursor to many of the aforementioned processes for hydrogen production, is used to produce nearly 70 million metric tons of hydrogen per year (based on 2018 data) [36]. Trajectories of hydrogen are likely to rise provided that the current demand for "clean" energy continues, coupled with the fact that companies are still developing hydrogen-powered cars [36]. It is not clear at this time how such an economy may develop. For example, one possibility is onboard reforming of a chemical carrier of hydrogen (e.g., light alcohols) [37–41], while other options include steam reforming, partial oxidation, and the gasification of various natural resources carried out at centralized or decentralized locations. Furthermore, iron, which is central to the high temperature water–gas shift step in fuel processors for hydrogen production, also serves to catalyze water–gas shift concurrently with FTS when the H_2/CO ratio in syngas is low, as occurs with syngas derived from coal and biomass. In addition, the iron used in FTS helps to boost the selectivities of alcohols and olefins [16,42,43]. In fact, both iron and cobalt can be catalytically tuned to favor products for the oxygenate market or to provide feedstock to the olefin polymerization processes [16,17,44,45]. Plastics produced from the latter process serve as materials for packaging, healthcare, diagnostics, optics, electronics, and a host of other industries. Finally, the topic of CO_2 utilization is becoming increasingly important to alleviate greenhouse gas emissions and combat climate change. One key roadblock is having on-hand a renewable source of hydrogen. If these key metals have the ability to transform CO, there may be a path forward for developing them for CO_2 utilization; research in this area is already under way [46].

However, although many of the catalytic processes mentioned above are run at commercial scales, they are still implemented with a certain degree of "blackbox" thinking. There are good reasons for this; although we understand, in general terms, the catalyst formulations and process conditions involved that will result in a variety of product distributions of interest, we do not, as of yet, have a clear understanding of what precisely constitutes the "active site", which electronic and geometric effects are involved, how promoters and poisons influence the active site, and which elementary steps are involved in the complex surface reaction mechanisms [4,47–52]. A quick search from Google Scholar on the "Fischer Tropsch mechanism" resulted in over 6500 publications published in the past two years on this topic alone. The routes are not fully understood, and much more work is needed to bridge the gap between, on the one hand, density functional theory and microkinetic modeling, and, on the other hand, actual data (i.e., product workup, catalyst characterization) generated from the testing of industrially- and academically-relevant catalyst formulations. A multitude of unanswered questions come to the fore. (1) What is the rate limiting step of the mechanism and how can activity be improved? [53] (2) Which metals and promoters are most suitable for a specific process, and how do they work together to bring about the desired selectivity? [54–56] (3) Which specific reactor configurations and process conditions are superior for targeting specific product ranges? [57–60] (4) Which processes are involved in catalyst deactivation, which ones dominate, and how can they be managed? (5) What are the relationships between homogeneous and heterogeneous catalysts? [61].

Much of the importance of these metals lies in their ability to manage carbon, including the activation of carbon monoxide, the coupling of carbon with carbon, hydrogen, or oxygen [62], and the scission of the same, as well as their ability remove products, once formed [62]. The capacity for iron and cobalt to manage carbon creates an avenue for useful products to be constructed from much simpler molecules. This is a significant advantage over alternative approaches such as direct liquefaction and the upgrading of bio-oil produced from flash pyrolysis. For example, Fischer-Tropsch synthesis produce a plethora of paraffins, 1-olefins, and oxygenates from simply carbon monoxide and hydrogen. These products are then readily hydro-processed to produce alternative fuels (i.e., especially diesel and aviation fuels), as well as lubricants and waxes. The olefins and oxygenates produced can be used as feedstocks for various applications, including the manufacturing of plastics. Thus, deepening our understanding of how the properties of the catalyst and process conditions can be tuned will give rise to greater control of the product distribution [62].

This special series highlights the work of scientists and engineers from all over the world who embody the leading edge of catalyst research on cobalt and iron. This collection provides a broad overview of a multitude of processing routes. In addition to the aforementioned topics, global concerns also drive: environmentally-attractive catalysts through specific homogeneous asymmetric iron complexes [63], the development of consumer products (preservatives, cosmetics, and flavors) [64] and materials (inks, coating, and paints) [65], and effective waste water treatment [66]. Furthermore, environmental concerns necessitate not just the capture of CO_2, but also its utilization as a means of mitigation [46,57,67]. Yet, alternative means of energy, such as hydrogen, may help limit harmful emissions and could also pave the way for change. The importance of cobalt, as a less expensive metal relative to the precious metals, for light-driven water oxidation [68] and electrochemical processes for hydrogen production [69] further highlights the potential of harnessing these metals in a way that benefits society. Regarding current methods that utilize carbon, such as the FTS process, a series of studies included here examine the effect of reaction conditions and promoters [70], investigate the kinetics [53,59,60], and examine the reaction route through computational modeling [71], with the aim of tailoring new formulations in a scientifically-driven manner [55,56,72]. This offers the potential to more effectively utilize the routes that are already available. Our aim is to tune [54] catalysts to efficiently produce fuels and chemicals in a more environmentally-benign manner.

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