

Seminar

Selectivity in CO₂ Reduction

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The electrocatalytic CO₂ reduction reaction (CO₂RR) to generate fixed forms of carbons that have commercial value is a lucrative avenue to ameliorate the growing concerns about the detrimental effect of CO₂ emissions as well as to generate carbon-based feed chemicals, which are generally obtained from the petrochemical industry. The area of electrochemical CO₂RR has seen substantial activity in the past decade, and several good catalysts have been reported. While the focus was initially on the rate and overpotential of electrocatalysis, it is gradually shifting toward the more chemically challenging issue of selectivity. CO₂ can be partially reduced to produce several C₁ products like CO, HCOOH, CH₃OH, etc. before its complete 8e⁻/8H⁺ reduction to CH₄. In addition to that, the low-valent electron-rich metal centres deployed to activate CO₂, a Lewis acid, are prone to reduce protons, which are a substrate for CO₂RR, leading to competing hydrogen evolution reaction (HER). Similarly, the low-valent metal is prone to oxidation by atmospheric O₂ (i.e., it can catalyse the oxygen reduction reaction, ORR), necessitating strictly anaerobic conditions for CO₂RR. Not only is the requirement of O₂⁻ free reaction conditions impractical, but it also leads to the release of partially reduced O₂ species such as O₂⁻, H₂O₂, etc., which are reactive and result in oxidative degradation of the catalyst. In this presentation, mechanistic investigations of CO₂RR by detecting and, often, chemically trapping and characterising reaction intermediates are used to understand the factors that determine the selectivity in CO₂RR. The spectroscopic data obtained from different intermediates have been identified in different CO₂RR catalysts to develop an electronic structure selectivity relationship that is deemed to be important for deciding the selectivity of 2e⁻/2H⁺ CO₂RR. The roles played by the spin state, hydrogen bonding, and heterogenisation in determining the rate and selectivity of CO₂RR (producing only CO, only HCOOH, or only CH₄) are discussed using examples of both iron porphyrin and non-heme bioinspired artificial mimics. In addition, strategies are demonstrated where the competition between CO₂RR and HER as well as CO₂RR and ORR could be skewed overwhelmingly in favour of CO₂RR in both cases.

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4:00 PM (Tea / Coffee 03.45 PM)

Auditorium, TIFR-H