Mixed-Potential-Driven Catalysis: An Electrochemical Framework for Understanding Thermochemistry

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Heterogeneous catalysis is traditionally divided into “thermocatalysis” and “electrocatalysis”. However, the boundary between thermo- and electrocatalysis might not exist. There exists a type of heterogeneous catalysis that overall resembles “thermal” catalysis but proceeds via electrochemical mechanisms. The heterogeneous catalysis that occurs when the anodic and cathodic reactions are short-circuited in an appropriate electrolyte is conceptualized as mixed-potential-driven catalysis. We have established a theoretical framework[1] and provided experimental proof for mixed-potential-driven catalysis.[2–4]

By applying the Butler-Volmer equation, we determine the position of the mixed potential and the partitioning of overpotentials from the exchange currents. The catalytic activity of the catalyst components determines the direction of electron transfer between the components. Then, we verify the theoretical framework using glucose oxidation as a model, given its significance in generating high-value products and potential in fuel cell technology. By short-circuiting spatially separated electrodes we detect a short-circuit current in the absence of an external potential, providing direct evidence of the existence of mixed-potential-driven reaction mechanisms in glucose oxidation. Later, we show that the room-temperature CO oxidation with water over supported Au nanoparticles proceeds via the mixed-potential-driven mechanism. The overall CO oxidation process consists of the simultaneous electrochemical CO oxidation half-reaction and O_2 reduction half-reaction.

References

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