Unravelling The Mechanism of Basic Aqueous Methanol Dehydrogenation Catalyzed By Ru-PNP Pincer Complexes

Ruthenium PNP complex 1a (RuH(CO)Cl(HN(C2H4Pi-Pr2)2)) represents a state-of-the-art catalyst for low-temperature (<100 °C) aqueous methanol dehydrogenation to H2 and CO2. Herein, we describe an investigation that combines experiment, spectroscopy, and theory to provide a mechanistic rationale for this process. During catalysis, the presence of two anionic resting states was revealed, Ru–dihydride (3−) and Ru–monohydride (4−) that are deprotonated at nitrogen in the pincer ligand backbone. DFT calculations showed that O- and CH-coordination modes of methoxide to ruthenium compete, and form complexes 4− and 3−, respectively. Not only does the reaction rate increase with increasing KOH, but the ratio of 3−/4− increases, demonstrating that the “inner-sphere” C—H cleavage, via C—H coordination of methoxide to Ru, is promoted by base. Protonation of 3− liberates H2 gas and formaldehyde, the latter of which is rapidly consumed by KOH to give the corresponding gem-diolate and provides the overall driving force for the reaction. Full MeOH reforming is achieved through the corresponding steps that start from the gem-diolate and formate. Theoretical studies into the mechanism of the catalyst Me-1a (N-methylated 1a) revealed that C—H coordination to Ru sets-up C—H cleavage and hydride delivery; a process that is also promoted by base, as observed experimentally. However, in this case, Ru–dihydride Me-3 is much more stable to protonation and can even be observed under neutral conditions. The greater stability of Me-3 rationalizes the lower rates of Me-1a compared to 1a, and also explains why the reaction rate then drops with increasing KOH concentration.

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