

Modelling a Non-Electrochemical System Electrochemically: Mechanism of Hydrogen Peroxide Direct Synthesis on Palladium Catalysts

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The mechanism of catalytic non-electrochemical hydrogen peroxide direct synthesis (HPDS) from hydrogen and oxygen is conventionally considered as a Langmuir-Hinshelwood (LH) mechanism. A recent experimental study show that the conventional LH mechanism may not be true even on the most proto-typical HPDS catalyst: palladium (Pd) catalysts. In fact, it is proposed that the "non-electrochemical" HPDS is actually a heterolytic redox reaction of H_2 and O_2 forming H_2O_2 with proton-electron transfer on Pd surfaces. In this presentation, we provide a DFT model with accurate kinetics for the HPDS on Pd catalysts. We show that even with a more comprehensive model including solvation and free energy corrections, the LH mechanism fails to explain the experimental observations of HPDS. We then model the heterolytic mechanism by combining the Butler-Volmer equation with the electrochemical constant-potential DFT to compare the kinetics of HPDS with the side reaction, H_2O production. We prove that the heterolytic mechanism indeed explains experimental observations better than the LH mechanism, and that HPDS is kinetically favored than water production.