Theoretical Insights into Dioxomolybdenum Catalysis with Biomass-Derived Pinacol

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ABSTRACT

Density Functional Theory is used to unravel the mechanism of the nitrobenzene to aniline reduction, catalyzed by dioxomolybdenum (VI) dichloride [1]. The use of pinacol as an oxoaccepting reagent and the production of only acetone and water as byproducts, signals a novel and environmentally friendly way to add value to the oxygen-rich biomass-derived polyols [2]. The reaction proceeds through three consecutive cycles, each one responsible for one of the three reductive steps needed to yield aniline from nitrobenzene, with nitrosobenzene and hydroxylamine as intermediates. Each cycle regenerates the catalyst and releases one water and two acetone molecules. The mechanism involves singlet/triplet state crossings, a crucial feature in polyoxomolibdate catalyzed processes. The role of the Mo-coordinated water as the provider of the mysterious protons needed to reduce the nitro group, was revealed. The disclosure of this challenging mechanism and its rate limiting step can contribute to the design of more effective Mo(VI) catalysts.

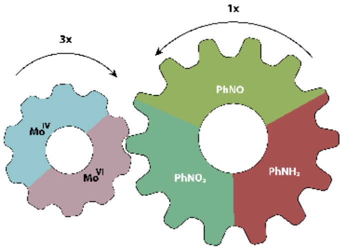

Figure 1: Three consecutive cycles of Mo^{VI}/Mo^{IV} reduction needed to reduce nitrobenzene to aniline, using pinacol as the oxoaccepting reagent.

References

[1] Kiriakidi, S. ; Silva-López, C. ; Sanz, R. ; Nieto-Faza, O ; Deciphering Nitroaromatics Reduction: Theoretical Insights into Dioxomolybdenum Catalysis with Biomass-Derived Pinacol, *ChemCatChem*, **2024**, e202301575.

[2] García, N.; García-García, P.; Fernández-Rodríguez, M. A.; Rubio, R.; Pedrosa, M. R.; Arnáiz, F. J.; Sanz R.; Pinacol as a new green reducing agent: molybdenum-catalyzed chemoselective reduction of sulfoxides and nitroaromatics, *Advanced Synthesis & Catalysis,* **2012**, 354, 321.