Computational Study of Substituents Effect on Pincer Ligands for CO_2 Hydrogenation Reaction

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ABSTRACT

PNP-type pincer ligands have attracted significant attention for their ability to support highly active catalysts through various transformations. [1] Therefore this study aims to investigate the use of a MACHO-Ru catalyst for CO_2 hydrogenation using DFT calculations.

During this investigation, a total of 9 substituents were applied (SiH_3, OH, OMe, Me, H, Ph, CF_3, CN, NO_2) to the pincer ligand focusing on exploring their electronic effects on the catalyst's activity.

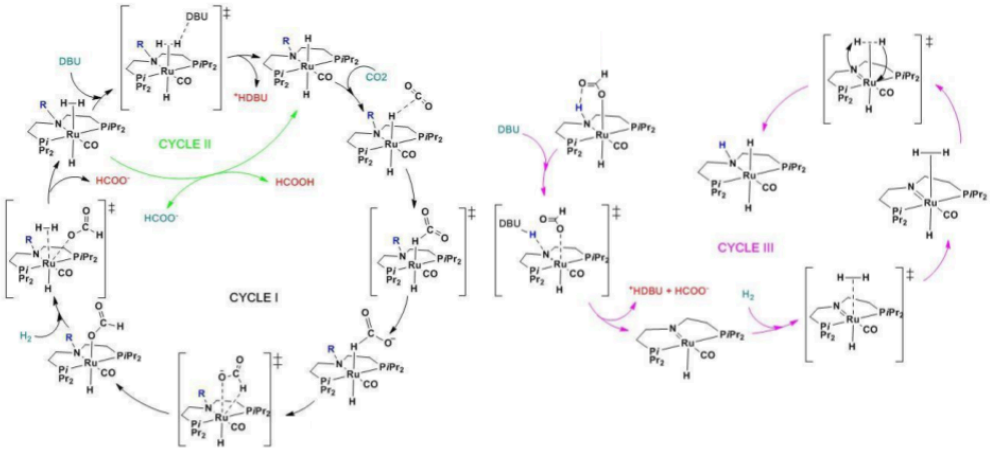

Figure 1: Proposed Carbon Dioxide Reduction Reaction to Formate.

After the proposed mechanisms and analyzing the energy profiles, we can conclude that the MACHO-Ru molecule is an eligible catalyst for the CO_2 reduction reaction to formate and it can be better tuned by simply changing the nitrogen substituents. Electron Donating Groups (EDG) in syn position better the catalytic activity (SiH_3 displayed the best performance). Meanwhile, we could also observe 2 types of catalysts (Noyori and Milstein) depending on the substituent of the N atom, and they offer different reaction mechanisms.

References

[1] Kuriyama, W., et. al, Catalytic Hydrogenation of Esters. Development of an Efficient Catalyst and Processes for Synthesising (R)-1,2-Propanediol and 2-(l-Menthoxy)ethanol. Org. Process Res. Dev. 2012, 16, 166−171.