

Investigação Computacional do Efeito de Substituintes em Ligantes Pinça na Hidrogenação Catalítica do CO₂

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RESUMO – A conversão de CO₂ em compostos de maior valor agregado, como moléculas oxigenadas (álcoois, ácidos carboxílicos e ésteres), é de significativo interesse financeiro, industrial e ambiental, além de representar um desafio para a catálise. A maior dificuldade é a integração ótima das funcionalidades catalíticas para a ativação do hidrogênio molecular e a redução do CO₂, ligadas à estabilidade do catalisador. Os ligantes pinça do tipo PNP têm atraído atenção por sua capacidade de suportar catalisadores altamente ativos em uma ampla variedade de transformações. Assim, esta pesquisa tem como objetivo propor um estudo computacional, utilizando DFT, para elucidar os efeitos dos substituintes nessa classe de ligantes, acoplados ao centro metálico de rutênio nas reações de hidrogenação do dióxido de carbono. 9 substituintes diferentes foram empregados (entre doadores e retiradores de elétrons) para investigar os efeitos eletrônicos na atividade catalítica. Os substituintes doadores de elétrons apresentaram os melhores resultados, minimizando a energia do estado de transição para a etapa limitante.

Palavras-chave: DFT, CO₂, hidrogenação, catálise homogênea, ligantes-pinça.

ABSTRACT – The conversion of CO₂ into higher value-added compounds such as oxygenated molecules (alcohols, carboxylic acids and esters) is of significant financial, environmental and industrial interest while representing a challenge for catalysis. The greatest difficulty is the optimal integration of the catalytic functionalities for the molecular hydrogenation activation and CO₂ hydrogenation, linked to the stability of the catalyst. PNP-type pincer ligands have been worthy of attention for their ability to support highly active catalysts through a wide variety of transformations. Thus, this research aims to propose a computational study, using DFT, to elucidate the effects of pincer ligands (PNP) substituents on homogenous ruthenium catalyst in the hydrogenation reactions of carbon dioxide. 9 different substituents were employed to investigate their electronic effects on the catalyst activity. The electron donor substituents presented the best results, minimizing the transition state energy for the limiting step.

Keywords: DFT, CO₂, hydrogenation, homogenous catalysis, pincer ligands.

Introduction

Longer chain compounds (C₂₊) have a thermodynamically more favorable synthesis when compared to obtaining methanol from the catalytic hydrogenation of carbon dioxide. (1) Due to its high stability and high oxidation level, CO₂ reduction has a high energy input ($\Delta_f G_{298K} = -396 \text{ kJ} \cdot \text{mol}^{-1}$) to convert it into more complex and chemically active molecules (C₂₊), therefore the use of catalysts in such reactions is essential. (2) In addition, the production of hydrocarbons and longer-chain oxygenated compounds is challenging due to their low selectivity. The greatest difficulty is the optimal integration of the catalytic functionalities for the molecular hydrogen activation and CO₂ hydrogenation, linked to the stability of the catalyst.

PNP-type pincer ligands have attracted significant attention for their ability to support highly active catalysts through a wide variety of transformations. (3) Therefore this study aims to investigate the use of a PNP pincer ligand to support a ruthenium catalyst for CO₂ hydrogenation.

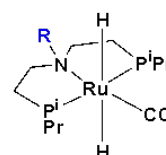


Figure 1. Ru-MACHO catalyst applied in this study.

Methods

Computational Methods.

During this study, a total of 9 substituents (SiH₃, OH, OMe, Me, H, Ph, CF₃, CN, NO₂) were applied to the pincer ligand

focusing on investigating their electronic effects on the catalyst's activity. The calculations were performed using Gaussian-16 software with the M06 functional and Ahlrich's basis set (Def2-SVP for optimization and Def2-TZVP for single-point energy corrections). The solvation effects were modeled implicitly using SMD and THF as solvent. Transition states were determined by presenting a single imaginary frequency and Intrinsic Reaction Coordinate (IRC) calculations ensured that such TS's were connected to two minima, reactants and products.

Results and Discussion

The reaction mechanisms, as well as their energy profiles are shown.

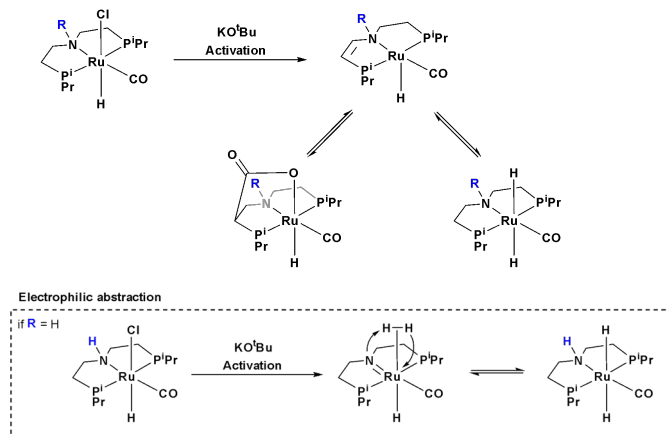


Figure 2. Elucidated mechanisms for catalyst activation.

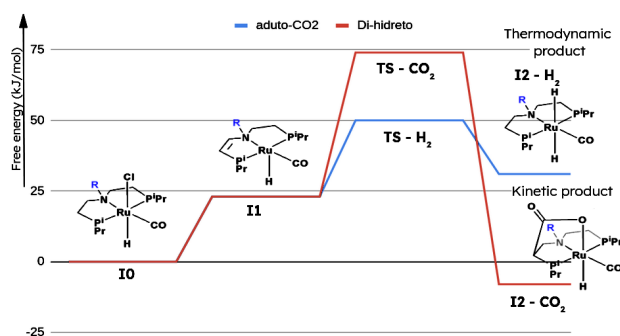


Figure 3. Energy profile for catalyst activation.

Conclusions

Some of this work's findings are: two types of catalysts (Noyori and Milstein) for molecular hydrogen activation, depending on the substituents; electron donor groups enhance the catalytic activity; in the presence of an aprotic solvent the CO₂ insertion is the limiting step.

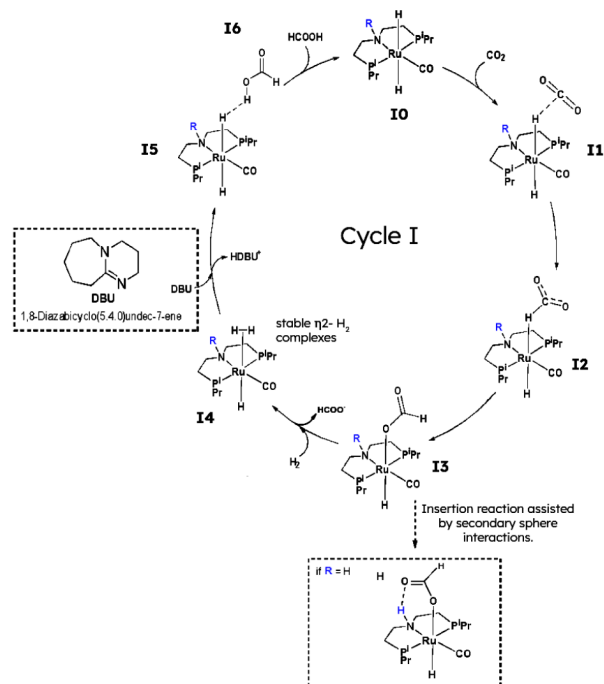


Figure 4. The proposed mechanism to obtain formic acid and formate.

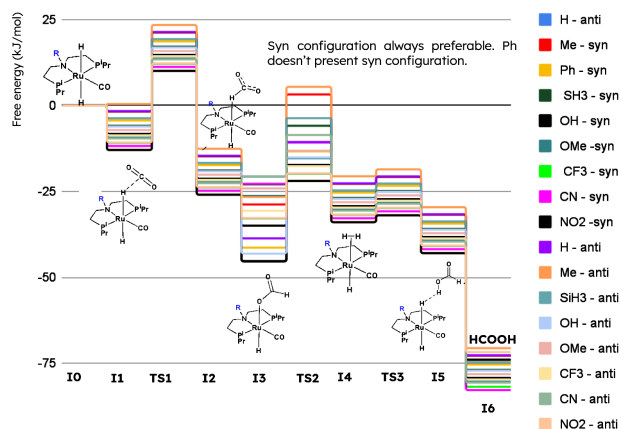


Figure 5. Energy profile for the cycle I.

Acknowledgments

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