

Methane Activation by CuO, CuO⁺ e CuO²⁺: A DFT and CCSD(T) Study

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Abstract

B3LYP and CCSD(T) calculations were used to investigate the mechanisms of methane activation by CuO, CuO⁺ and CuO²⁺.

Introduction

The growing concern for world oil demand has increased the searching for alternative energy resources. The natural gas, whose the main constituent is methane, arises as a viable choice due to the high availability of its reserves.¹ Furthermore, natural gas can be considered as a clean fuel due to its low contaminant levels. Nowadays, the direct oxidation of methane to methanol by transition metal (TM) oxides shows to be of great interest for both experimental and theoretical studies.² The experimental findings have pointed out CuO⁺ ion as the most efficient metal oxide to react with methane in the gas-phase.³ In literature, there is missing information about mechanisms and energetics of copper oxides and methane, varying the metal oxidation state of metal. In present work, gas-phase reactions of methane with CuO, CuO⁺, CuO²⁺ were theoretically evaluated in order to provide insights into mechanisms, reactivities and energetics involved in the investigated reactions. DFT and CCSD(T) calculations were performed to evaluate three different mechanisms for each reaction under investigation. The structural and energy properties were obtained to describe the kinetics and thermodynamics of these gas-phase reactions.

Results and Discussions

While the DFT(B3LYP and BP86)/CBSB7 results for optimized structures are shown in **Figure 1**, and CCSD(T)/Aug-cc-pVTZ energies are displayed **Figure 2**. These results were obtained for the CuO⁺ and CH₄ reactions. The main analyses of these results in comparison to those found for the remaining copper oxides show that the hydrogen abstraction mechanism via direct and four-center pathways show to be kinetically and thermodynamically feasible than oxidative addition pathway for all investigated copper(II) monoxides. Moreover, it was observed that the increase of charge on the metal center favors pronouncedly the kinetics and thermodynamics of reactions under investigation.

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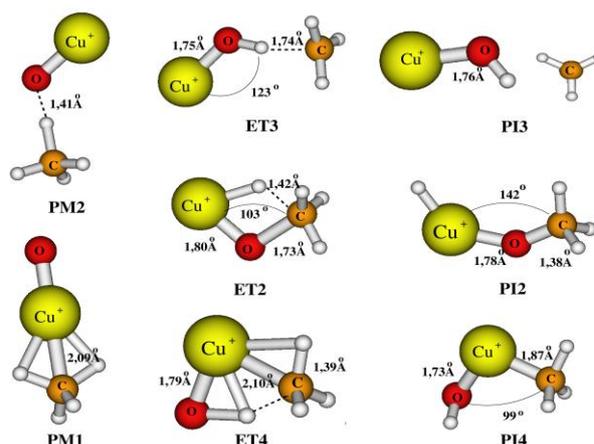


Figure 1. Optimized structures involved in CuO⁺ and CH₄ reaction mechanisms.

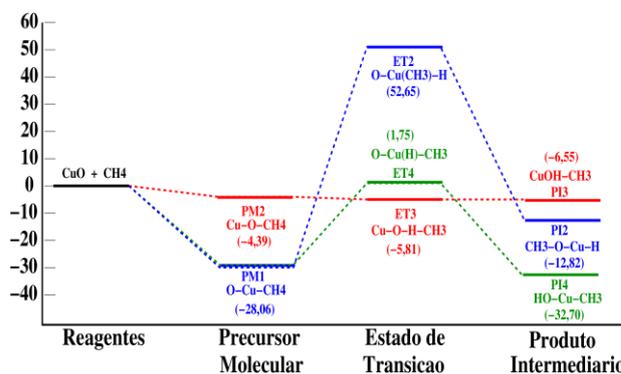


Figure 2. Energy profile for CuO⁺ and CH₄ reaction mechanisms.

Conclusion

Based on the obtained structures and energies of three reactions investigated, we can concluded that different features can be highlighted for explaining the differences of reactivity of copper oxides investigated.

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