Partial Methane Oxidation to Methanol on Ru-Porphyrins – on the Role of Non-Innocent Ligands and Spin Crossover

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Streszczenie

The partial oxidation reaction of CH_4 led to the formation of CH_3OH in the presence of Ru-porphyrin oxo complexes (denoted as POR, POR-O and POR-OH where in the case of the last two, oxygen atom and the OH group were attached to the active site, respectively), in which Ru was present on different oxidation states. The simulations were performed based on Density Functional Theory (DFT) with extended geometric and electronic structure analyses of each reaction step. Moreover, the reaction pathways were investigated in different spin states. The Spin Crossover (SCO) phenomenon was found to play an important role in the kinetics of the reaction in the presence of POR and POR-O. Harmonic Oscillator Model of Aromaticity (HOMA) index was applied for different spin states to estimate the aromaticity changes of the pyrrole rings in the Ru-porphyrin complexes. In order to characterize the nature of bonding, the Natural Bond Orbitals (NBO) analysis including the Wiberg Bond Index (WBI) and Natural Population Analysis (NPA) was carried out. Finally, the Non-Covalent Interactions (NCI) index was employed to gain insight into interactions between the components of the reaction. It was found that the non-covalent interactions cannot be neglected in the studied reaction paths.

Słowa kluczowe

partial oxidation of methane, Ru-porphyrin, spin crossover, non-covalent interactions, DFT

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