

## Theoretical Study of Gas Adsorption in Zirconium Clusters

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**Abstract :** The progress of new porous materials has increased rapidly over the past decade for use in applications such as catalysis, gas storage and removal of environmentally unfriendly species due to their high surface area and high thermal stability. In this work, a theoretical study of the zirconium-based metal organic framework (MOFs) were examined in order to determine their potential for gas adsorption of various guest molecules: CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>. The zirconium cluster consists of an inner Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> core in which the triangular faces of the Zr<sub>6</sub>- octahedron are alternatively capped by O and OH groups which bound to nine formate groups and three benzoate groups linkers. General formula is [Zr(μ-O)<sub>4</sub>(μ-OH)<sub>4</sub>(HCOO)<sub>9</sub>((phyO<sub>2</sub>C)<sub>3</sub>X)] where X= CH<sub>2</sub>OH, CH<sub>2</sub>NH<sub>2</sub>, CH<sub>2</sub>CONH<sub>2</sub>, n(NH<sub>2</sub>); (n = 1-3). Three types of adsorption sites on the Zr metal center have been studied, named according to capped chemical groups as the '-O site'; the H of (μ-OH) site removed and added to (μ-O) site, '-OH site'; (μ-OH) site removed, the 'void site' where H<sub>2</sub>O molecule removed; (μ-OH) from one site and H from other (μ-OH) site, in addition to no defect versions. A series of investigations have been performed aiming to address this important issue. First, density functional theory DFT-B3LYP method with 6-311G(d,p) basis set was employed using Gaussian 09 package in order to evaluate the gas adsorption performance of missing-linker defects in zirconium cluster. Next, study the gas adsorption behaviour on different functionalised zirconium clusters. Those functional groups as mentioned above include: amines, alcohol, amide, in comparison with non-substitution clusters. Then, dispersion-corrected density functional theory (DFT-D) calculations were performed to further understand the enhanced gas binding on zirconium clusters. Finally, study the water effect on CO<sub>2</sub> and N<sub>2</sub> adsorption. The small functionalized Zr clusters were found to result in good CO<sub>2</sub> adsorption over N<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub> due to the quadrupole moment of CO<sub>2</sub> while N<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> weakly polar or non-polar. The adsorption efficiency was determined using the dispersion method where the adsorption binding improved as most of the interactions, for example, van der Waals interactions are missing with the conventional DFT method. The calculated gas binding strengths on the no defect site are higher than those on the -O site, -OH site and the void site, this difference is especially notable for CO<sub>2</sub>. It has been stated that the enhanced affinity of CO<sub>2</sub> of no defect versions is most likely due to the electrostatic interactions between the negatively charged O of CO<sub>2</sub> and the positively charged H of (μ-OH) metal site. The uptake of the gas molecule does not enhance in presence of water as the latter binds to Zr clusters more strongly than gas species which attributed to the competition on adsorption sites.

**Keywords :** density functional theory, gas adsorption, metal- organic frameworks, molecular simulation, porous materials, theoretical chemistry

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