Ab-Initio Based Grand Canonical Monte-Carlo simulations of CH₄ Uptake in Covalent Organic Frameworks (COF)

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Alternatives routes towards new energies sources have become in a mainstream research worldwide. Methane has the potential to become a future fuel, however there have been longstanding problems related to transport and storage making it not an economically viable path. Attempts to overcome these issues include conversion to methanol, better compression techniques and sorption into porous materials. The latter is of special interest because of the recent discovering of new class of materials called Covalent Organic Frameworks (COF) that are: tailored materials, highly crystalline, present a high surface area (>2000 m²/g) with a high pore volume and are made of just light atoms (C, Si, B,O and H). These properties allowed COFs to have the lowest crystalline densities among solid state materials and promising properties for storage. In order to investigate CH₄ sorption phenomena in COF an ab initio study was first performed. Accurate MP2 were performed using QZVPP basis set in order to develop the correct force fields (FFs) between CH₄/COF as well as CH₄/CH₄. With the developed FFs, a grand canonical Monte Carlo was used to simulate the methane adsorption in COFs. The FFs was also tested comparing the densities of methane obtained by simulation with experimental ones at various pressures. The experimental isotherm of COF-5 has been reproduced with this methodology; also this approach allows the designer to predict sorption properties of hypothetical COF structures.

COF-5

COF-103

COF-108