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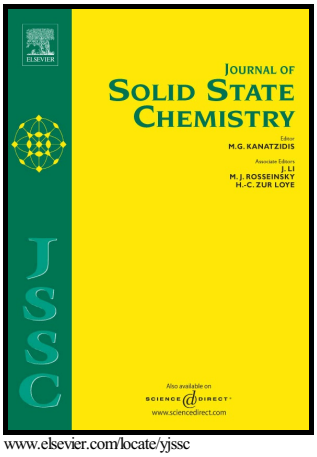

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Tuning the hydrogen adsorption properties of Zn–based metal–organic frameworks: Combined DFT and GCMC simulations

Suye Yu[a], Shina Li[b], Xianhe Meng[a], Chubin Wan[a], Xin Ju[a,*]

[a]Department of Physics, University of Science and Technology Beijing, Beijing 100083, China

[b]Institute of Theoretical Physics Shanxi University, Taiyuan Shanxi 030006, China

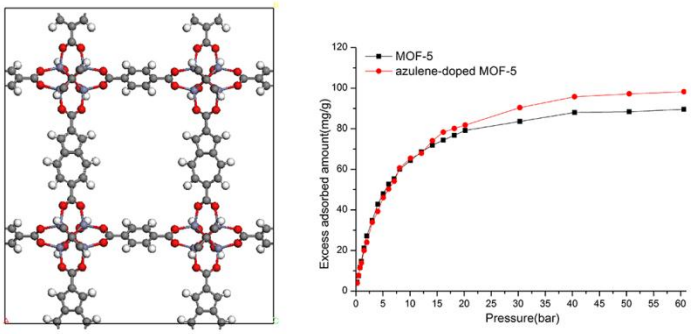
*Corresponding author. Tel.: +86 10 62333921; Fax: +86 10 62333921; E-mail: jux1962@163.com

Abstract

This study aims to guide the future design of metal-organic frameworks (MOFs) for hydrogen storage. At 77 K, azulenedicarboxylate (ADC)-substituted MOF-5 increases the hydrogen adsorption rate and hydrogen uptake capacity when the pressure exceeds 12 bar. At 297 K, ADC substitution significantly increases hydrogen adsorption when the pressure exceeds 5 bar. The grand-canonical Monte Carlo (GCMC) detailed analyses indicate that with increased pressure, hydrogen molecules in MOFs tend to be located at the corner region, organic linkers, and the center of cores. Meanwhile, high pressure adsorption shows that the large space due to ADC substitution leads to reduced steric effect around metal sites. Analysis of density of states illustrates that the introduced organic linkers may contribute sufficient electrons and enhance electron flow. These electrons can induce an electric field-effect, which increases the polarisation of hydrogen atoms and molecules surrounding linkers. Amongst the studied MOFs, substitution with Ni exerts no obvious effect on hydrogen storage.

Graphical abstract

At 77 K, ADC-substituted MOF-5 increases the hydrogen adsorption rate and hydrogen uptake capacity when the pressure exceeds 12 bar.



Keyword: MOF-5; azulenedicarboxylate; GCMC; Hydrogen adsorption

1. Introduction

Currently, metal–organic frameworks (MOFs) are always stable and porous, and these characteristics make them potential candidates as functional materials in separation, catalysis, gas storage and photoelectric processes [1-6]. They can also be controlled by varying the structural components, metals or their clusters and ligands [7-9]. Many