

Hydrogen adsorption of Be-, Zn-, and Cd-zeolitic imidazolate framework-23: A comparative study

Suphagrid Wongprakarn¹, Jariyanee Prasongkit², and Pornjuk Srepusharawoot^{3,4,5*}

¹Materials Science and Nanotechnology Program, Faculty of Science, Khon Kaen University, 40002 Khon Kaen, Thailand

²Division of Science, Faculty of Liberal Arts and Science, Nakhon Phanom University, 48000 Nakhon Phanom, Thailand

³Department of Physics, Faculty of Science, Khon Kaen University, 40002 Khon Kaen, Thailand

⁴Integrated Nanotechnology Research Center, Khon Kaen University, 40002 Khon Kaen, Thailand

⁵Nanotec-KKU Center of Excellence on Advanced Nanomaterials for Energy Production and Storage, 40002 Khon Kaen, Thailand

E-mail: spornj@kku.ac.th

Received January 2, 2014; accepted May 30, 2014; published online July 17, 2014

Hydrogen adsorption energies of Be-, Zn-, and Cd-zeolitic imidazolate framework-23 were investigated using the Van der Waals density functional theory implemented in the Quantum ESPRESSO program. From the structural parameters of these systems, we found that the imidazole ligand is unchanged and only the tetrahedral metal nitride cluster is varied. Moreover, our results revealed that the Cd-zeolitic imidazolate framework-23 has the highest electric dipole moment followed by Zn- and Be-zeolitic imidazolate framework-23. On the basis of hydrogen adsorption energy calculations, we found that hydrogen molecules cannot bind with either Be- or Zn-zeolitic imidazolate framework-23 at any of the considered adsorption sites, whereas hydrogen molecules can be trapped on the Cd-zeolitic imidazolate framework-23 with the hydrogen binding energy in the range from 60 to 130 meV. This result suggested that replacing Zn in the metal nitride cluster with a larger metal can enhance the hydrogen adsorption energy of zeolitic imidazolate framework-23. © 2014 The Japan Society of Applied Physics

1. Introduction

It has long been known that energy crisis and global warming issues are expected to be very serious issues in the near future. Hydrogen energy is a solution to these problems because of its abundance and cleanness. However, it is very difficult to store hydrogen gas into a hydrogen storage medium because its density is very low, namely 0.088 kg/m³.¹⁾ As a result, the size of the storage medium is very large. Therefore, one challenging task for many researchers is to investigate a suitable hydrogen storage medium for practical applications. According to the 2015 DOE requirements,²⁾ the hydrogen storage medium must (i) have high hydrogen capacity (9 H₂ wt%), (ii) be cheap, (iii) operate over the temperature range of -40 to 60 °C, (iv) have long service life (about 1500 charge/discharge cycles), and (v) be environmentally friendly. Currently, storing hydrogen in high-surface-area materials, such as metal organic frameworks (MOFs),³⁻⁶⁾ covalent organic frameworks (COFs),⁷⁻¹⁰⁾ carbonaceous materials,¹¹⁻¹³⁾ zeolite,^{14,15)} and zeolitic imidazolate frameworks (ZIFs),^{16,17)} has been shown to be promising because they contain numerous hydrogen adsorption sites, easily trap/release hydrogen, and have tunable pore size. Besides the surface area and pore size of the host material, another important parameter related to the hydrogen capacity is the hydrogen adsorption energy. For practical application, the ideal hydrogen adsorption energy should be about 40 kJ/mol.¹⁸⁾ For most high-surface-area materials, the hydrogen adsorption energy is very low because the interaction between adsorbed hydrogen molecules and the materials is governed by weak dispersive interaction. Currently there are several approaches¹⁹⁻²²⁾ to improving the hydrogen adsorption energy of the high-surface-area materials. One successful route, shown by Srepusharawoot et al.,²³⁾ is to open the metal oxide cluster of the MOF-5 by replacing Zn with Cd. They found the hydrogen adsorption energy to be improved for 15% for the adsorption sites near the metal oxide cluster.

Zeolitic imidazolate frameworks (ZIFs) are new classes of high-surface-area materials, successfully synthesized by Yaghi's research group.^{24,25)} As shown by Banerjee et al.,²⁵⁾ both pore size and surface area of these materials can be tuned by adjusting the metal nitride (MN₄) unit (M = Zn, Co, Cu) and imidazole ligands. Consequently, the ZIFs can be used in various applications such as catalysts,²⁶⁾ biosensors,²⁷⁾ and gas storage media, e.g., N₂,²⁸⁾ CO₂,^{28,29)} and CH₄.²⁸⁾ Both theoretical and experimental studies^{16,30)} show the great promise of ZIFs as hydrogen storage materials. According to the results of neutron diffraction experiments at 30 K and ambient pressure,¹⁶⁾ ZIF-8 can trap 28 hydrogen molecules corresponding to 4.2 H₂ wt%. By increasing the temperature to 77 K, the hydrogen capacity is dramatically decreased to 1.3 wt%.³¹⁾ The grand canonical Monte Carlo simulations showed that ZIF-11 can uptake about 3.96 wt% hydrogen at 77 K and 100 bar. When the pressure is reduced to 1 bar, the hydrogen uptake is slightly reduced to 2.39 wt%.³²⁾ For zeolitic imidazolate framework-23 (ZIF-23), there is no report in the literature related to hydrogen adsorption. This motivates us to investigate the hydrogen adsorption properties of this system.

The ZIF-23 or Zn-ZIF23 system consists of tetrahedral clusters of ZnN₄ covalently bonded to the organic linker 4-azabenzimidazolate. Its unit cell contains 108 atoms consisting of 4 Zn atoms, 24 N atoms, 48 C atoms, and 32 H atoms. The crystal structure of ZIF-23 is an orthorhombic crystal system with space group P212121. The lattice constants are $a = 9.5477$ Å, $b = 10.1461$ Å, and $c = 12.4459$ Å. Its crystal density is 1.662 g/cm³.²⁴⁾ In the present work, we investigated the structural parameters and the hydrogen adsorption energies of Be-, Zn-, and Cd-based ZIF23 structures, referred to in the following as Be-, Zn-, and Cd-ZIF23, respectively. The crystal structures of M-ZIF23 (M = Be, Zn, and Cd) are shown in Fig. 1.

2. Computational details

Electronic and hydrogen adsorption properties of M-ZIF23 (M = Be, Zn, and Cd) were investigated using the