INFORMATION OF DOCTORAL DISSERTATION

Title: HYDROGEN STORAGE IN METAL-ORGANIC FRAMEWORK MIL-88S: A COMPUTATIONAL STUDY

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Abstract

Fossil fuel-based energy consumption causes serious environmental impacts such as air pollution, greenhouse effect, and so on. Therefore, searching clean and renewable energy sources is urgent to meet the demand for sustainable development of the global society and economy. Hydrogen gas (H_2) is a reproducible, clean, and pollution-free energy carrier for both transportation and stationary applications. Hydrogen gas has a much higher energy density than other fuels; and thus, it becomes one of the most promising candidates to replace petroleum. Therefore, in recent years, the interest in the research and development of hydrogen energy has grown constantly. A safe, efficient, and commercial solution for hydrogen storage is based on adsorption in porous materials, which have the exceptionally large surface area and ultrahigh porosity such as metal-organic framework (MOF) materials. In order to be selected as porous materials for gas storage, MOFs must be stable to avoid collapsed under humid conditions. MIL-88 series (abbreviated as MIL-88s including MIL-88A, MIL-88B, MIL-88C and MIL-88D) is highly stable and flexible sorbents. For these reasons, MIL-88s becomes a suitable candidate for the storage of hydrogen gas based on the physisorption. Moreover, coordinatively unsaturated metal centers in MIL-88s are able to enhance gas uptakes significantly at ambient temperatures and low pressures. These materials have been investigated and highly evaluated for various applications such as gas storage/capture and separation of binary gas mixtures in recent years; however, they have not yet been evaluated for hydrogen storage. These outstanding features have attracted my attention to consider the hydrogen storage capacity in MIL-88 series.

In this dissertation, the van der Waals dispersion-corrected density functional theory (vdW-DF) calculations were used to examine the stable adsorption sites of the hydrogen molecule in MIL-88s and clarify the interaction between H_2 and MIL-88s via electronic structure properties. This observation showed an implicit role of electronic structures on the H_2 adsorption capacity at the considered temperature and pressure conditions. Besides, it was found that the H_2@MIL-88s interaction is dominated by the bonding state (σ) of the hydrogen molecule and the p orbitals of the O and C atoms in MIL-88s. For MIL-88A and B, the d orbitals of the metals also play an important role in the interaction with H_2.

Moreover, grand canonical Monte Carlo (GCMC) simulations were used to compute hydrogen uptakes in MIL-88s at the temperatures of 77 K and 298 K and the pressures up to 100 bar. For Fe based-MIL-88 series, we found that MIL-88D is very promising for the gravimetric hydrogen storage (absolute/excess uptakes = 5.15/4.03 wt% at 77 K and 0.69/0.23 wt% at 298 K), but MIL-88A is the best alternative for the absolute/excess volumetric hydrogen storage with 50.69/44.32 g/L at 77 K and 6.97/2.49 g/L at 298 K. Via this research, scandium (Sc) was also found as the best transition metal element for the replacement of Fe in MIL-88A for the hydrogen storage, in which absolute/excess uptakes are 5.30/4.63 wt% at 77 K and 0.72/0.29 wt% at 298 K for gravimetric uptakes; 51.99/45.51 g/L at 77 K and 7.08/2.83 g/L at 298 K for volumetric uptakes. The hydrogen storage capacity is the decrease in the order: Sc-, Ti-, V-, Cr-, Mn-, Fe-, and Co-MIL-88A. The calculations showed that the results are comparable to the best MOFs for the hydrogen storage up to date. The results also elucidated that the gravimetric hydrogen uptakes depend on the special surface area and pore volume of the MIL-88s. These important structural features, if properly improved, lead to an increase in the capability of hydrogen storage in MIL-88s.

The main scientific contributions

This dissertation has contributions as follows:

- We provide the approach combining DFT calculations and Murnaghan EOS to optimize the unit cell of MOFs.

- The overlapping between DOS curves of the adsorbed gas molecule and MOF is suggested to evaluate the interaction between them.

- The wave-function overlapping between gas and the atoms of the MOF is used to show the gas – sorbent interaction.

- GCMC simulations show the gravimetric and volumetric uptakes of the adsorbed gas in MOFs as well as sorbents.

- The calculation results show Sc-MIL-88A in the researched MIL-88 series is the best candidate for the volumetric hydrogen storage, while MIL-88D is the best one for gravimetric hydrogen storage.

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