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# Gas Storage in MOFs: A Friendly Strategy to Predict the Ability of Molecule Insertion

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**Abstract:** Metal-Organic Frameworks (MOFs) are materials often employed in applications such as: gas storage[1], nuclear fuel reprocessing plants[2], environmental remediation[3], sensors[4], and catalysis[5]. In this sense, the prediction of chemical properties of reactions involving this class of materials can be difficult. Hence, we advance a friendly strategy to predict the ability of inserting gas molecules in the pores of a set of MOFs, which structures can be found in the Cambridge Structural Database System (CSDS). All MOFs chosen have been reported to be capable of storing gas molecules[6–10]. The methodology employed was the full optimization of geometry of all species involved in the insertion reactions of the type: gas + MOF→ gas@MOF, where the gas molecules can be $H_2$, $CO_2$, $N_2$, or $C_2H_2$, and the MOF systems can be Zn(bpb)[9], MOF-646[7], DUT-10(Zn)[6], ZIF-71[8], or Zn(dcpa)[10]. Subsequently, we calculate the enthalpy of reaction, $\Delta_rH$, for all cases considered in our study. The semiempirical method used was the PM6[11], where the calculations were performed by using the quantum chemical software MOPAC 2016[12]. Table 1 shows the $\Delta_rH$ values for all insertion reactions of gas molecule into the pore of each MOF considered, which has been reported to be able to store it.

**Table 1.** PM6 values of $\Delta_rH$ at 298K of the insertion reactions of gas molecules in MOFs: gas + MOF→ gas@MOF. The CSD code of the MOFs can be found in the Cambridge Structural Database System (CSDS).

| CSD Code | System Gas@MOF | $\Delta_rH$ (kcal/mol) | Diameter of the pore (Å) |
|---|---|---|---|
| SUTBEP | $CO_2$@Zn(bpb) | -517 | 9.9 |
| | $C_2H_2$@Zn(bpb) | -340 | |
| VAGTUU | $H_2$@MOF-646 | -200 | 5.3 |
| XAFFAN | $CO_2$@DUT-10(Zn) | -157 | 13.6 |
| | $H_2$@DUT-10(Zn) | -54 | |
| | $N_2$@DUT-10(Zn) | -71 | |
| GITVIP01 | $CO_2$@ZIF-71 | -11 | 17.0 |
| DEYVUA | $CO_2$@Zn(dcpa) | -3 | 4.7 |
| | $H_2$@Zn(dcpa) | -3 | |
| | $N_2$@Zn(dcpa) | -4 | |

From table 1 we verify that the $\Delta_r H$ values calculated by semiempirical PM6 method are consistent with the experimental ability of the MOFs to store gas molecules. For example, the $\Delta_r H$ value for the storage of $CO_2$, and $C_2H_2$ gas molecules in Zn(bpb) MOF, leading to systems $CO_2$@Zn(bpb), and $C_2H_2$@Zn(bpb), are -517 kJ.mol$^{-1}$, and -340 kJ.mol$^{-1}$, respectively. Further, we verify that the diameter of the pore, seemingly, is not the main factor for the success of a gas molecule be stored, at least for the set of systems studied. For example, the $\Delta_r H$ value for the storage of $CO_2$ in the pore of the ZIF-71 (with diameter of 17.0 Å) is -11 Kcal.mol$^{-1}$, and for storage of the same molecule in the pore of the Zn(dcpa) (with diameter of 4.7 Å) is only -3 Kcal.mol$^{-1}$. In summary, the PM6 semiempirical method, available for free at MOPAC 2016, can be considered a friendly strategy to predict the ability of gas molecules insertion in pores of MOFs.

**Key-words**: MOF, semiempirical, MOPAC, gas storage.
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