

Adsorption and reaction steps in nano-porous systems - accurate prediction by quantum chemistry and molecular statistics

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Introduction

Accurate quantum chemical predictions of adsorption and reaction steps for nanoporous systems such as metal-organic frameworks (MOF) and zeolites are limited by the inability of currently used density functionals to properly account for dispersion interactions. We employ a hybrid approach which combines MP2 calculations for the reaction site with DFT calculations for a large system under periodic boundary conditions [1] and apply it to adsorption of H₂ in metal-organic frameworks [2] and to catalytic hydrocarbon reactions in zeolites [3].

Materials and Methods

Density functional theory (DFT) is applied to H₂/MOF-5 and alkene/methanol/H-MFI systems. The PBE functional is used with periodic boundary conditions. A semiempirical 1/r⁶ term is added (DFT+D).

Second order Moller-Plesset perturbation theory is applied to large finite model systems. Extended basis sets are used such as aug-cc-pVTZ, function counterpoise corrections are made for the basis set superposition error and extrapolation to the complete basis set limit is applied. For H₂ adsorption on MOF-5 the MP2 results for the large finite size models can be used without any long-range contributions and vibrational frequencies are calculated by MP2. For the methylation of alkenes in H-MFI the hybrid MP2(cluster model):DFT(periodic model) method [1] is employed to evaluate periodic corrections to the cluster results. Vibrational frequencies are calculated by DFT for the periodic models.

Results and Discussion

A multi-site Langmuir model is applied to predict adsorption isotherms using free energies for the different adsorption sites in MOF-5 calculated from ab initio (MP2) results. Assuming the H₂ molecules retain their two rotational degrees of freedom, the predicted isotherms confirm some measurements [4], whereas other, also recent, experiments yielding different results [5] cannot be confirmed (Figure 1).

The hybrid MP2:DFT method presented here reproduces reaction barriers for the methylation of alkenes in the presence of zeolite catalysts with near chemical accuracy (deviations between 0 and 13 kJ/mol). This is a significant improvement compared to periodic model PBE results which show much larger deviations from experiment and fail to reproduce the decrease in the ethene, propene, *t*-2-butene series, see Figure 2. This can be partly rectified when augmenting DFT with a semi empirical dispersion term (PBE-D), but the barriers still remain systematically too low (by 14 to 19 kJ/mol) as typical for this type of functionals.

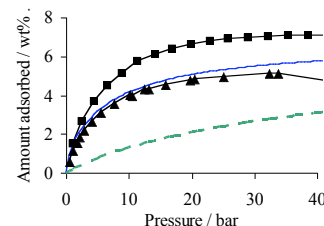


Figure 1. H₂ adsorption isotherms. Experiments; squares [4], triangles [5]. Ab initio calculations; two free rotations of adsorbed H₂ (blue) and rotations treated as vibrations (green).

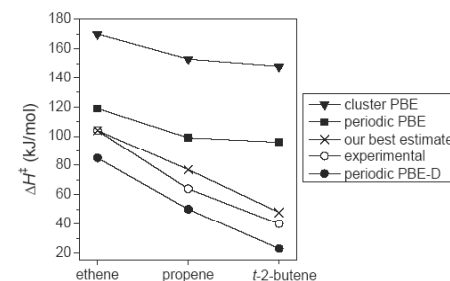


Figure 2. Apparent enthalpy barrier for the methylation of alkenes in H-MFI obtained with different methods.

Significance

The reliable ab initio prediction of isotherms for H₂ adsorption in MOFs is possible and can be used to direct the synthesis of new hydrogen storage materials.

Activation enthalpies for individual steps of hydrocarbon synthesis and conversion reactions in zeolites can be calculated by hybrid MP2:DFT calculations with near chemical accuracy. With this, substantial progress has been made towards the simulation of complex reaction networks in zeolites such as the hydrocarbon pool mechanism.

References

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