

EXAMINING THE ADSORPTION OF ALCOHOLS ON VARIOUS ZEOLITIC SURFACES WITH THE ONIOM METHODOLOGY. A COMPARISON OF POPULAR HYBRID FUNCTIONALS

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ΠΕΡΙΛΗΨΗ

The adsorption of alcohols on modified Y zeolites was studied computationally using ab initio, DFT and MM methods. The investigation has been carried out by employing the successful model 84T [$\equiv\text{SiO}(\text{H}\mu)\text{X}(\text{O})_2\text{OY}\equiv$], ($\text{X}=\text{Al}$, Ti και $\text{Y}=\text{Si}$, P) including one hydroxyl Brønsted acidic site (BAS). This model, has been studied with the help of the three-layered ONIOM3: (B3LYP/6-31+G(d,p):HF/6-31G:UFF), (M06-2X/6-31+G(d,p): HF/6-31G:UFF) and (B3LYP-D3/6-31+G(d,p):HF/6-31G:UFF) approach, to test its ability to reproduce the experimental heats of adsorption available in the literature. Stabilization of the adsorption complexes results from hydrogen bonding between the guest molecule and the framework, as well as from embedding, i.e., van der Waals interactions with the pore walls. The 84T cluster model^[1] is shown to offer an attractive alternative to periodic simulations on the entire H-FAU unit cell, resulting in virtually identical final adsorption enthalpies with the latter method.

The QM/MM zeolite models were developed using the ONIOM method, as implemented in the Gaussian 09 suite of programs^[2]. We have employed the three-layer ONIOM model, whereby the total energy of the system is given by

$$E_{\text{ONIOM3}} = E_{\text{Low}}^{\text{Real}} + E_{\text{Medium}}^{\text{Intermediate}} - E_{\text{Medium}}^{\text{Model}} + E_{\text{High}}^{\text{Model}} - E_{\text{Low}}^{\text{Intermediate}}$$

The DFT calculations using the B3LYP^[3] functional describe the interaction of the alcohols with the acidic site rather well, but fail to account for the van der Waals interactions between the molecule and the inert inner wall of the zeolite. The results show that, in the extended 84T zeolite model, the calculated complexation energy of alcohol molecules is 3-5 kcal mol⁻¹ lower than the/that experimentally predicted.

Finally, we attempted to change the methodology to include the contribution of remote interactions in our calculation in a different way. For this purpose, the B3LYP functional was initially replaced by the M06-2X which led as to improved results. The energy values we calculated in relation to B3LYP are increased by about 3 kcal / mol for the unmodified zeolite without changing the specified stresses. However, it was not reasonable to increase the adsorption energy of 5-7 kcal mol⁻¹ in the case of the modified zeolite where aluminum is replaced with the titanium atom. Based on the experimental value of the adsorption enthalpy of methanol in ZSM-5 structure zeolite, the values of the B3LYP-D3^[4] methodology appear to be more reasonable. In particular, the enthalpy of ethanol adsorption -28.95 kcal mol⁻¹ is close to the experimental value, -31.3 ± 1.2 kcal mol⁻¹ calculated for the ethanol molecule in the ZSM-5 zeolite and furthermore the B3LYP-D3 methodology gives an increase in adsorption energy by increasing the alcohol chain by 2 kcal mol⁻¹ when the experimentally observed increase in ZSM-5 zeolite is found to be about 3 kcal mol⁻¹. The difference in the value of 1 kcal mol⁻¹, can be attributed to the larger pore diameter available for the model FAU zeolite.

The Ti-modified cluster shows a considerable reduction of the order of 6 to 8 kcal mol⁻¹ in adsorption capacity in contrast to that of P atom. Thus, the modification of the zeolite surface by incorporating the Ti atom within it, (by replacing Al with Ti) shows a great effect on zeolite acidity. Namely, it makes the zeolite less acidic with its increased basic character as opposed to the phosphorus atom when replacing the tetrahedral silicon atom, the reduction in acidity it causes to the zeolite is insignificant.

ΒΙΒΛΙΟΓΡΑΦΙΑ

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