

# Examining the adsorption of alcohols on various zeolitic surfaces with the ONIOM methodology. A comparison of popular hybrid functionals.

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## ABSTRACT

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 [ $\equiv\text{SiO}(\text{H}_p)\text{X}(\text{O})_2\text{OY}\equiv$ ], ( $\text{X}=\text{Al}$ ,  $\text{Ti}$  και  $\text{Y}=\text{Si}$ ,  $\text{P}$ ) 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 and van der Waals interactions with the pore walls. The 84T cluster model 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 Ti-modified cluster shows a considerable reduction of the order of 6 to 8 kcal mol<sup>-1</sup> in adsorption energy in contrast to that of P-modification which presents no significant effect. Comparing calculated stretch frequencies of the zeolite acid sites and the adsorbate functional groups with experimental IR data additionally confirms that the cluster approach provides an appropriate representation of the adsorption complexes.

*Keywords* : Adsorption enthalpies; ONIOM3 methodology; B3LYP-D3, M06-2X functionals; acidity; modified zeolites.

## 1. INTRODUCTION

Many industrially important processes start with the adsorption of guest molecules inside the pores of an acidic zeolite catalyst. Great efforts have been devoted in past decades to elucidating the reaction mechanism and kinetics of methanol to olefins conversion (MTO) [1]. Also many reported experimental studies focus on designing and applying Ti-containing molecular sieves in fuel production [2]. Ti atom is actually responsible for its catalytic activity in oxidative desulfurization (ODS) proved by theoretical [3] and experimental studies [4]. In addition to the numerous experimental studies, theoretical modeling in recent years has been proven a highly useful tool to complement experimental investigation in gaining a deeper understanding of the complex reaction mechanisms taking place inside the zeolite pores. One of the most effective and most widely applied methods, is the so-called DFT-D scheme proposed by Grimme [5]. In this method, an empirical damped-potential term is added to energies obtained with standard functionals, at a negligible computational cost.

In this work, the adsorption of a series of alcohols, ROH (R = Me, Et, 1-Pr, i-Pr) on various zeolitic surfaces (zeolite, titanosilicate, silicoaluminophosphate) is studied computationally with the ONIOM methodology by employing the successful model 84T [ $\equiv\text{SiO}(\text{H}_p)\text{X}(\text{O})_2\text{OY}\equiv$ ] (X=Al, Ti and Y=Si, P), with the aims of: a) comparing the changes in structures and bonding of the different framework structures of catalysts and their complexes, b) determining the effect of the structure on the adsorption capacity in alcohol molecules of zeolites, titanosilicates and SAPO, and c) combining the cluster approach with different contemporary DFT methods to test their ability to account properly for the dispersion contributions.

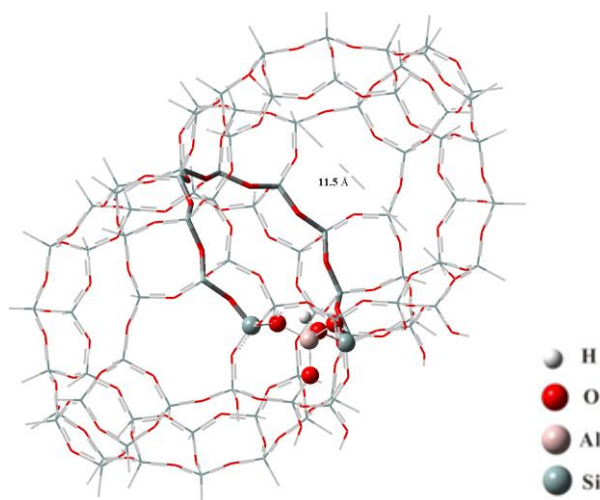
## 2. METHODS AND COMPUTATIONAL DETAILS

The QM/MM zeolite models were developed using the ONIOM method, as implemented in the Gaussian 09 suite of programs [6]. We have employed both two- and three-layer ONIOM models, whereby the total energy of the system is given by

$$E_{\text{ONIOM}2} = E_{\text{Low}}^{\text{Real}} + E_{\text{High}}^{\text{Model}} - E_{\text{Low}}^{\text{Model}} \quad (1)$$

$$E_{\text{ONIOM}3} = E_{\text{Low}}^{\text{Real}} + E_{\text{Medium}}^{\text{Intermediate}} - E_{\text{Medium}}^{\text{Model}} + E_{\text{High}}^{\text{Model}} - E_{\text{Low}}^{\text{Intermediate}} \quad (2)$$

The main calculations presented in this work, employ a larger cluster model to represent the various zeolitic surfaces. A fragment containing 84 tetrahedral atoms was cut from the crystallographic structure, such that the model includes a sufficiently large portion of the framework surrounding the active site to account for relevant confinement effects (Fig. 1). This model denoted 84T, is known to comprise 297 atoms from two interconnecting supercages. The aforementioned model (84T) is subdivided into three layers (3T:9T:72T) and it is investigated according to the ONIOM3 (QM:QM:MM) scheme and more specifically, using the three-layered ONIOM3 methodology. The inner layer representing the active region consists of the adsorbed molecules and the 3T cluster [ $\equiv\text{-SiO}(\text{H}_p)\text{Al}(\text{O})_2\text{OSi}\equiv$ ] (represented by balls) is treated at the high-level, (DFT) method, the intermediate region (represented by sticks) is treated at the medium level, (Hartree-Fock level) and the framework (the remaining atoms represented by lines) is treated using a low-level (UFF) methods.



**Fig.1:** A larger cluster model, the fragment containing 84 tetrahedral atoms cut from the crystallographic structure, which was used in this work to represent the various zeolitic surfaces

Three series of calculations have been performed using the 84T model and three DFT methodologies namely B3LYP, M06-2X and B3LYP-D3. More specifically, the calculation of the inner layer is performed at the B3LYP/6-31+G(d,p), M06-2X/6-31+G(d,p) and B3LYP-D3/6-31+G(d,p) theory levels.

The findings of this theoretical study indicate a partial inadequacy of the B3LYP functional for the description of the interactions between the alcohols molecules and the framework surrounding the active site of the zeolite (84T/Al model cluster), on account of being unable to include dispersion forces. The theoretical values predicted from the B3LYP energies significantly underestimate the experimental reference data [7] with about 5 to 6 kcal mol<sup>-1</sup> lower, for all adsorbates considered, regardless of their size. The improvement of the complexation energy  $\Delta E$  of methanol molecule (from 22.6 to 25.1 kcal mol<sup>-1</sup>) by the extension of the simulation model is considered to be significant but still with a significant substantial deviation from the experimental one, (-27.7±1.2 kcal mol<sup>-1</sup>). Nevertheless, the adsorption energy increases by about 1.5 kcal mol<sup>-1</sup> with each additional C-atom in the carbon chain of alcohol molecules, a result that is in partial agreement with the experimental observation that, across a series of similar compounds of increasing size (in this case alcohols) the adsorption enthalpy on ZSM-5 zeolite surface increases steadily by about 3 kcal mol<sup>-1</sup>. Also, the results of this simulation show that the extension of the 20T model to the 84T, improves the results as described below. Particularly, the deprotonation energy has been improved (from 302.7 to 314.3 kcal mol<sup>-1</sup>), compared with the accepted range of the faujasite deprotonation energy (321–330 kcal mol<sup>-1</sup>) as shown in reference. Second, our computed r(Al-H<sub>p</sub>) distance of the 84T cluster is improved (from 2.371 to 20T cluster to 2.387 Å) in comparison to the experimentally calculated by Freude et al [8] of 2.38 ± 0.04 Å, and third the calculated vibrational frequency of the acidic O1–H<sub>p</sub> bond, is reduced from 3777 to 3757 cm<sup>-1</sup> in better agreement with the reported experimental estimates between 3600 cm<sup>-1</sup> and 3623 cm<sup>-1</sup> [8].

### 3. RESULTS AND DISCUSSION

The adsorption of alcohols on various zeolitic surfaces with the ONIOM methodology has been investigated at different levels of theory. The DFT calculations using the B3LYP 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<sup>-1</sup> 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<sup>-1</sup> for the unmodified zeolite without changing the specified stresses. However, it was not reasonable to increase the adsorption energy of 5-7 kcal mol<sup>-1</sup> in the case of the modified zeolite where aluminum is replaced with the titanium atom.

Based on the experimental values of the adsorption enthalpy of methanol and ethanol in ZSM-5 structure zeolite, the values of the B3LYP-D3 methodology appear to be more reasonable. In particular, the enthalpy of ethanol adsorption -28.95 kcal mol<sup>-1</sup> is close to the experimental value, -31.3 ± 1.2 kcal mol<sup>-1</sup> 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<sup>-1</sup> when the experimentally observed increase in ZSM-5 zeolite is found to be about 3

kcal mol<sup>-1</sup>. The difference in the value of 1 kcal mol<sup>-1</sup>, 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<sup>-1</sup> in adsorption energy in contrast to that of P atom (Table 1). 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.

**Table 1.** Complexation energies,  $\Delta E$  (kcal mol<sup>-1</sup>) of alcohol ROH, R= (CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, nC<sub>3</sub>H<sub>7</sub>, iC<sub>3</sub>H<sub>7</sub>) of the three 84T/X (X=Al, P, Ti) model clusters using ONIOM3-B3LYP-D3/6-31+G(d,p):HF/6-31G:UFF, and M06-2X/6-31+G(d,p):HF/6-31G:UFF methods.

Adsorption complexes	MeOH			EtOH	
	B3LYP-D3	M06-2X		B3LYP-D3	M06-2X
84T/Al	-28.89 <sup>b</sup> -28.41 <sup>c</sup> -28.14 <sup>d</sup>	-28.88 -27.7±1.2 <sup>a</sup>	-28.68	-31.08	-29.82
84T/P		-27.39	-27.85	-28.65	-28.05
84T/Ti		-22.43	-25.16	-23.45	-25.83
Adsorption complexes	nPrOH			iPrOH	
84T/Al		-33.02	-31.61	-32.03	-30.13
84T/P		-29.98	-28.36	-30.44	-29.07
84T/Ti		-25.54	-27.58	-25.61	-27.20

<sup>a</sup> From Ref.[8] (exp).

<sup>b</sup> Indicates 84T/Al (3T:9T:72T) ONIOM3:B3LYP-D3/6-31+G(d,p):HF/6-31G:UFF results.

<sup>c</sup> Indicates 84T/Al (12T:72T) ONIOM2: B3LYP-D3/6-31+G(d,p) :UFF results.

<sup>d</sup> Indicates 84T/Al (12T:8T:64T) ONIOM3: B3LYP-D3/6-31+G(d,p) :HF/6-31G:UFF results.

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