Benchmark Data for Interactions in Zeolite Model Complexes and Their Use for Assessment and Validation of Electronic Structure Methods

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Benchmark Data for Interactions in Zeolite Model Complexes and Their Use for Assessment and Validation of Electronic Structure Methods

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We present benchmark binding energies for five zeolite model complexes, with four of the adsorbates bound noncovalently and one covalently. The binding energies were determined as the sum of the infinite-basis-set limit of Møller–Plesset second-order perturbation theory (MP2) energies and a CCSD(T) correction term evaluated with the aug-cc-pVDZ basis set. The basis set limit of MP2 energies was determined by two-point extrapolation using the aug-cc-pVXZ basis sets for X = D and T and separate extrapolation of the Hartree–Fock and correlation energies. We found that correlation contributions beyond MP2 to the final binding energies are small; their magnitude is in the range of 0.02–1.0 kcal/mol. For the MP2 method to describe the interactions in these zeolite model systems accurately, one needs to use a basis set at least the size of aug-cc-pVTZ in conjunction with counterpoise corrections. Final binding energies (kcal/mol) of the model complexes are in the range of 3.5–19.5 kcal/mol, and they were used as reference data to test 6 wave function methods and 41 density functionals. Among the tested density functional methods, M06-L/6-31+G(d,p) gives a mean unsigned error (MUE) without counterpoise correction of 0.87 kcal/mol. With counterpoise corrections, the M06-2X and M05-2X functionals give the best performance. The MUE with counterpoise corrections for the M06-2X/6-311+G(2df,2p)//MP2/6-311+G(2df,2p) level of theory is 0.39 kcal/mol. With the DFT/6-31+G-(d,p) geometries and the 6-311+G(2df,2p) basis set, M05-2X and M06-2X give MUEs with counterpoise corrections of 0.40 and 0.52 kcal/mol, respectively. Tests against the binding energies of four complexes (two noncovalent and two covalent) of the adsoption of isobutene on a large 16T zeolite model cluster confirmed that M06-L, M06, M05-2X, and M06-2X are very promising quantum mechanical methods for hybrid quantum mechanical/molecular mechanical (QM/MM) simulations of zeolites. In fact the performance of these four Minnesota functionals, as compared to other high-quality functionals, is relatively even better for the larger 16T clusters than for the smaller 3T ones.

1. Introduction

Zeolites are microporous/nanoporous crystalline solids, and generally they contain silicon, aluminum, and oxygen in their framework, with cations, water, and/or other small molecules within their pores. The zeolitic pores are nanocavities, and they have molecular size dimensions; they are often called "molecular sieves". Zeolites have the capability of catalyzing chemical reactions that take place in their internal cages, and they provide a size-selective environment for chemical reactions. In addition, the use of heterogeneous inorganic catalysts like zeolites allows the convenient design of clean and safe technologies, and many applications of zeolites have been driven by environmental concerns, including the reduction of toxic waste and energy consumption. Indeed "every drop of gasoline we burn in our car has seen at least one zeolite catalyst on its way through the refinery."[1] Thus, computational elucidation of the catalytic mechanisms in zeolites is of considerable practical importance.

Together with experimental studies,[2–8] computational methods have been used in the past decade to model the structures of active sites,[1,9–29] the diffusion processes to and from the active sites,[30–33] adsorption,[34–46] and the mechanisms[1,47–69] of the catalytic reactions in zeolites. Despite increasing computational resources and improved algorithms, molecular modeling and simulation of zeolites at the atomic level remain a challenge. One solution is to use multilevel methods, such as methods[11,19,35,41,42,46,62,70,71] that combine quantum mechanics (QM) and molecular mechanics (MM), because their efficiency potentially allows one to perform accurate calculations for large reactive systems over long time scales.

One of the key classes of processes involved in zeolite catalysis is the adsorption and desorption of reactants and products at the active site of the catalyst. An important challenge is understanding the differing adsorption properties of alkanes and alkenes with various zeolites.[72–75] In a typical molecular mechanics force field, the interaction parameters for alkanes and alkenes are quite similar, and therefore simulations using these force fields may be inadequate for reproducing key differences in adsorption properties.[9,56] To model the complicated phenomena involved in adsorption and desorption more accurately, a quantum mechanical approach should be taken. Interaction energies of small zeolite model complexes can be used to calibrate the accuracy of quantum mechanical methods for zeolite catalysis.

In a previous paper,[76] we have studied the structures of disiloxane and silanol and the energetics of their protonation, deprotonation, and proton exchange reactions. In the present article, we use the infinite-basis (IB) method[77,78] and a multilevel scheme to obtain benchmark electronic structure results for the

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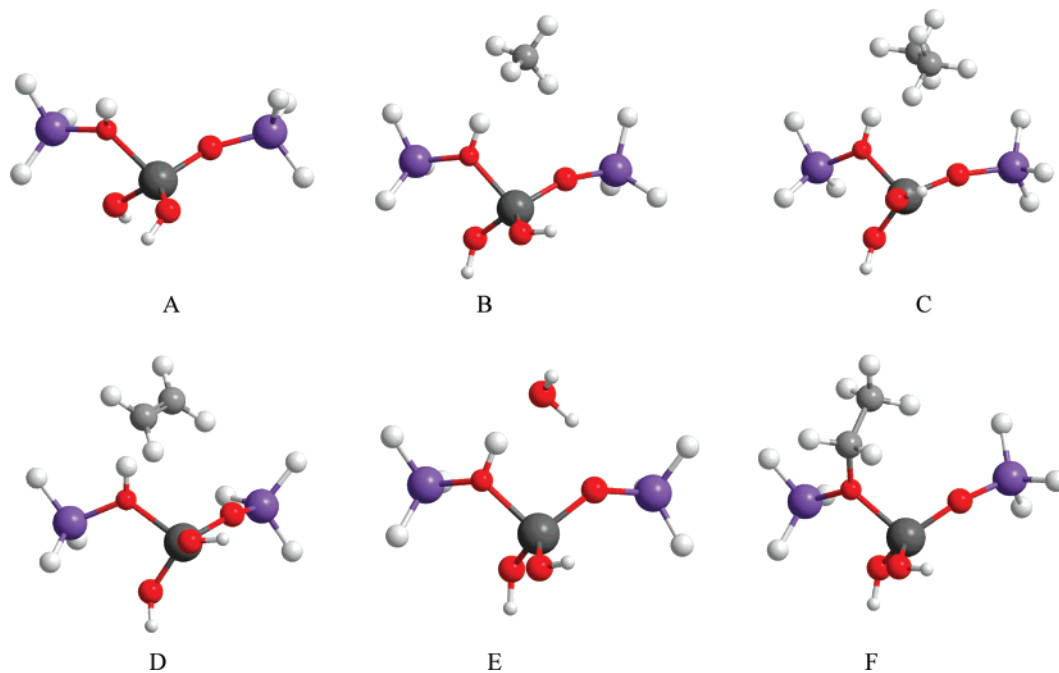
Figure 1. Geometries of the 3T zeolite model complexes. (A) HZ, (B) HZ···CH$_4$, (C) HZ···C$_2$H$_6$, (D) HZ···C$_2$H$_4$ π complex, (E) HZ···H$_2$O, (F) HZ-C$_2$H$_4$ alkoxide.

interaction energies of the complexes of water, methane, ethane, and ethylene with a zeolite model cluster. The first step is to use the IB method, which consists of separate extrapolation of Hartree−Fock and correlation energies, to obtain the infinite-basis MP2 limits, where MP2 denotes second-order Møller−Plesset perturbation theory,[79] and the second step is to add a correction for CCSD(T) effects, where CCSD(T) denotes coupled cluster theory with single and double excitations and quasiperturbative treatment of connected triple excitations.[80,81] In particular, we employ the aug-cc-pVXZ basis sets[82,83] with X = D and T for the MP2 part, and we employ the aug-cc-pVDZ basis set to estimate the CCSD(T) correction term.

For the QM/MM modeling of catalysis dynamics in zeolite systems, it is too computationally demanding to use MP2 or any other reliable wave function theory (WFT) as the QM part. Thus one goal of the present study is to validate a number of low-cost density functional theory (DFT) methods and to determine if there are DFT methods that can describe the interactions of adsorbates with zeolites sufficiently well for practical simulations of zeolites.

The computational details and DFT methods are described in Section 2, and results and discussion are in Section 3. Section 4 presents the concluding remarks.

2. Computational Methods

Cluster models of zeolites are typically named for the number of tetrahedral (Si or Al) sites; a cluster with three tetrahedral sites is called 3T (or sometimes it is called T3[84]). In the first part of the present study a 3T cluster, H$_3$Si(OH)Al(OH)$_2$OSiH$_3$ (Figure 1, A), is used to simulate the active Brønsted acidic sites in zeolites; this cluster is denoted HZ. We consider four noncovalent complexes, namely, HZ···CH$_4$, HZ···C$_2$H$_6$, HZ···C$_2$H$_4$ π complex, and HZ···H$_2$O, and one covalent complex, HZ-C$_2$H$_4$ alkoxide (Figure 1, B−F). In this article, we use "covalent" to describe the complexation in which a new chemical bond is formed.

We optimized the geometries of these complexes at the MP2/6-311+G(2df,2p) level of theory without any geometrical constraints, and the adsorbing species were also optimized in every case.

We estimated the CCSD(T) complete basis limit binding energies

$$D_e(\text{CCSD(T)/CBS}) = D_e(\text{MP2/IB}) + D_e(\text{CCSD(T)/SB}) - D_e(\text{MP2/SB}) \quad (1)$$

where CBS denotes the complete-basis limit, SB denotes a small basis (aug-cc-pVDZ), and IB denotes the separate extrapolation[77,85] of Hartree−Fock and correlation energies to the infinite-basis (IB) limit. The Hartree−Fock energies are extrapolated by

$$E^{\text{HF}}(n) = E^{\text{HF}}_\infty + A^{\text{HF}} n^{-\alpha} \quad (2)$$

and the MP2 correlation energies are extrapolated by

$$E^{\text{cor}}(n) = E^{\text{cor}}_\infty + A^{\text{cor}} n^{-\beta} \quad (3)$$

where n represents the highest angular momentum in an augmented correlation-consistent basis set, $n = 2$ for the aug-cc-pVDZ basis, and $n = 3$ for the aug-cc-pVTZ basis. The parameters α and β were determined in a previous paper;[85] the value used for α is 4.93, and that for β is 2.13. This composite approach defined in eq 1 has been shown[85] to give very good agreement with experiments for the predictions of binding energies in the H$_2$O···benzene and NH$_3$···benzene systems, and recently Jurecka et al.[86] also employed this approach for the development of a benchmark database of interaction energies with biological importance. Furthermore it is widely accepted that complete-basis CCSD(T) calculations are the most accurate currently available method for calculating noncovalent interactions.[87−92]

All MP2 and DFT calculations were carried out using a locally modified *Gaussian03*[93,94] program, and the CCSD(T)

TABLE 1: Tested Density Functionals

			exchange				correlation			
method	year	ref(s)	$\nabla\rho_\sigma, \rho_\sigma$	X	τ_σ ?	UEG ?	$\nabla\rho_\sigma, \rho_\sigma$	τ_σ ?	SCorF ?	UEG ?
BP86	1988	110, 96	B88	0	no	yes	P86	no	no	yes
BLYP	1988	96, 97	B88	0	no	yes	LYP	no	yes	no
BHandH [a]	1993	96, 97	Slater	50	no	yes	LYP	no	yes	no
BHandHLYP [a]	1993	96, 97	B88	50	no	yes	LYP	no	yes	no
B3LYP	1994	96, 97, 98	B88	20	no	yes	LYP	no	yes	no
BB95	1996	96, 111	B88	0	no	yes	B95	yes	yes	yes
B1B95	1996	96, 111	B88	28	no	yes	B95	yes	yes	yes
G96LYP	1996	97, 112	G96	0	no	yes	LYP	no	yes	no
PBE	1996	113	PBE	0	no	yes	PBE	no	no	yes
mPWPW [b]	1998	114, 115	mPW	0	no	yes	PW91	no	no	yes
mPWLYP	1998	97, 115	mPW	0	no	yes	LYP	no	yes	no
mPWB95	1998	111, 115	mPW	0	no	yes	B95	yes	yes	yes
mPW1PW [c]	1998	114, 115	mPW	25	no	yes	PW91	no	no	yes
B98	1998	116	B98	21.98	no	no	B98	no	no	no
VSXC	1998	117	VSXC	0	yes	no	VSXC	yes	yes	no
HCTH	1998	118	HCTH	0	no	no	HCTH	no	no	no
B97-1	1998	118	B97−1	21	no	no	B97−1	no	no	no
PBEh [d]	1999	99	PBE	25	no	yes	PBE	no	no	yes
MPW1K	2000	119	mPW	42.8	no	yes	PW91	no	no	yes
B97-2	2001	118	B97−2	21	no	no	B97−2	no	no	no
OLYP	2001	120	OPTX	0	no	no	LYP	no	yes	no
O3LYP	2001	120	OPTX	11.61	no	no	LYP	no	yes	no
τ-HCTH	2002	121	τ-HCTH	0	yes	no	τ-HCTH	no	no	no
τ-HCTHh	2002	121	τ-HCTHh	15	yes	no	τ-HCTHh	no	no	no
TPSS	2003	122	TPSS	0	yes	yes	TPSS	yes	yes	yes
TPSSh	2003	123	TPSS	10	yes	yes	TPSS	yes	yes	yes
X3LYP	2004	97, 124	X	21.8	no	yes	LYP	no	yes	no
BB1K	2004	96, 111, 125	B88	42	no	yes	B95	yes	yes	yes
BMK	2004	126	BMK	42	yes	no	BMK	no	no	no
MPW3LYP	2004	111, 127	mPW	20	no	yes	B95	yes	yes	yes
MPW1B95	2004	111, 115, 127	mPW	31	no	yes	B95	yes	yes	yes
MPWB1K	2004	111, 115, 127	mPW	44	no	yes	B95	yes	yes	yes
TPSS1KCIS	2005	128,122,	TPSS	13	yes	yes	KCIS	yes	yes	yes
PW6B95	2005	129	PW6B95	28	no	yes	PW6B95	yes	yes	yes
PWB6K	2005	129	PWB6K	46	no	yes	PWB6K	yes	yes	yes
M05	2005	130	M05	28	yes	yes	M05	yes	yes	yes
M05-2X	2006	107	M05-2X	56	yes	yes	M05-2X	yes	yes	yes
M06-L	2006	131	M06-L	0	yes	yes	M06-L	yes	yes	yes
M06-HF	2006	132	M06-HF	100	yes	yes	M6-HF	yes	yes	yes
M06	2008	108	M06	27	yes	yes	M06	yes	yes	yes
M06-2X	2008	108	M06-2X	54	yes	yes	M06-2X	yes	yes	yes

[a] Although inspired by Becke's paper,[133] the BHandH and BHandHLYP functionals defined in *Gaussian03* are different from the original ones in Becke's paper (see http://www.Gaussian.com/g_ur/k_dft.htm). [b] Also called mPWPW91. [c] Also called mPW1PW91, mPW0, or MPW25. [d] Also called PBE0 or PBE1PBE.

TABLE 2: Basis Set Sizes for the HZ···C_2H_4 Complexes

		number of	
basis [a]	ref	primitive Gaussians	contracted functions
aug-cc-pVQZ ≡ acQZ	82, 83	2064	1330
aug-cc-pVTZ ≡ acTZ	82, 83	1146	725
6-311+G(2df,2p)	100, 101	653	447
aug-cc-pVDZ ≡ acDZ	82, 83	650	336
6-31+G(d,p) ≡ DIDZ	102, 103	451	248

[a] Where two names are given, the first is the proper long name, and the second is the short name adopted for convenience in the text, tables, and equations.

calculations were performed with the *Molpro*[95] program. The tested density functionals are detailed in Table 1. In each case, we specify the year that the functional was first published, the functional forms used for dependence on spin densities (ρ_σ, where σ is the quantum number for the component of spin angular momentum along an axis) and gradients ($\nabla\rho_\sigma$), whether or not the functional includes spin kinetic energy densities (τ_σ) in the exchange and correlation functionals, and whether the correlation functional is self-correlation-free (SCorF). Table 1 also contains two columns (one for the exchange functional and one for the correlation functional) that tell whether or not the functional reduces to the correct uniform electron gas (UEG) limit when $\nabla\rho_\sigma \rightarrow 0$ and $\tau_\sigma \rightarrow \tau_\sigma^{\text{LSDA}}$ (where $\tau_\sigma^{\text{LSDA}}$ is the value assumed by τ_σ in the UEG limit); and another column that tells the percentage X of Hartree−Fock exchange in the functional.

We test 6 WFT methods and 41 density functionals with MP2/6-311+G(2df,2p) geometries calculated in the present work for the complexation of 5 adsorbates on the 3T cluster. We also performed geometry optimization for 3T and for these complexes with the two best performing functionals, M05-2X and M06-2X, and with two popular functionals, B3LYP[96−98] and PBEh,[99] and we retested the binding energies for these four functionals with the consistently optimized geometries. Finally, we tested 10 density functionals for four binding energies on a 16T cluster model of the H-Ferrierite zeolite using geometries and high-level reference data from Tuma and Sauer.[27]

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TABLE 3: Benchmark Results (in kcal/mol) for the Binding Energies^a of the Zeolite Model Complexes

complex	HF/IB	ΔMP2/IB^b	MP2/IB^c	Δ(CCSD(T) − MP2)^d	best estimate^e
HZ⋯CH$_4$	0.13	3.20	3.33	0.12	3.45
HZ⋯C2H$_6$	−0.88	5.14	4.27	0.24	4.50
HZ⋯C$_2$H$_4$ π	2.45	5.61	8.06	−0.27	7.79
HZ⋯H$_2$O	8.52	6.46	14.98	−0.02	14.97
HZ-C$_2$H$_4$ alkoxide	12.78	7.72	20.51	−1.00	19.51

^{a} The dissociation energy D_e is defined in the present study as the equilibrium dissociation energy of the complexes dissociated into two monomers. ^{b} The extrapolated ($\Delta E_{MP2} - \Delta E_{HF}$) results. ^{c} The sum of HF/IB and ΔMP2/IB. ^{d} This term is evaluated with the aug-cc-pVDZ basis set. ^{e} This column gives D_e estimated using eq 1.

TABLE 4: Binding Energies and Mean Errors (in kcal/mol) for WFT Methods^a

method^b	HZ⋯CH$_4$		HZ⋯C$_2$H$_6$		HZ⋯C$_2$H$_4$ p		HZ⋯H$_2$O		HZ-C$_2$H$_4$ alkoxide		mean error^c	
	D_e	D_e-Cp	D_e	D_e-Cp	D_e	D_e-Cp	D_e	D_e-Cp	D_e	D_e-Cp	MUE	MUE-Cp
best estimate^d	3.45		4.50		7.79		14.97		19.51			
MP2/acTZ	3.91	3.03	5.36	3.85	9.07	7.57	15.99	14.41	21.92	18.41	1.21	0.59
MP2/acDZ	4.07	2.11	6.06	2.67	9.77	6.69	17.14	14.20	21.97	14.60	1.76	1.99
MP2/DIDZ	3.08	1.46	4.37	1.59	8.89	5.36	17.43	13.14	22.09	13.27	1.33	3.08
CCSD(T)/DIDZ	3.28	1.46	4.71	1.61	8.60	4.84	17.40	12.75	20.85	11.14	0.99	3.68
HF/acTZ	0.26	0.03	−0.57	−1.00	2.81	2.41	8.98	8.63	13.26	12.60	5.09	5.51
HF/acDZ	0.15	−0.62	−0.34	−1.79	3.26	2.14	10.37	9.35	13.87	11.42	4.58	5.94

^{a} MP2/6-311+G(2df,2p) geometries are used for all calculations. "Cp" denotes that the calculations are counterpoise-corrected. ^{b} acDZ: aug-cc-pVDZ; acTZ: aug-cc-pVTZ; DIDZ: 6-31+G(d,p). ^{c} MUE denotes mean unsigned error (same as mean absolute deviation, MAD). ^{d} The best estimates are from Table 3.

We carried out calculations with several different basis sets in various parts of this study. The 6-311+G(2df,2p) basis sets for H and C are from Krishnan et al.[100] and those for Al and O are from McLean and Chandler.[101] The set of 41 density functionals were tested with an augmented polarized valence double-ζ basis set[102,103] labeled DIDZ for short (the full name is 6-31+G(d,p)). There are other basis sets used for new calculations reported in this work are summarized in Table 2.

For all DFT calculations, we performed calculations with and without counterpoise (Cp) corrections[104−106] for basis set superposition error (BSSE). Note that the BSSE calculations for the alkoxide structures treat the fragments as the corresponding carbenium ion and the negatively charged zeolite cluster.

3. Results and Discussion

3.1. Benchmark Calculations. Table 3 gives the benchmark results for the noncovalent interaction energies of the HZ⋯ CH$_4$, HZ⋯C$_2$H$_6$, HZ⋯C$_2$H$_4$ π complex, and HZ⋯H$_2$O complexes and the covalent interaction energy of the HZ-C$_2$H$_4$ alkoxide complex. Table 3 shows that Hartree−Fock (the HF/ IB column) theory contributes about 31%, 57%, and 66% to the total binding energies in the HZ⋯C$_2$H$_4$ π, HZ⋯H$_2$O and HZ-C$_2$H$_4$ alkoxide complexes, but it completely fails to describe the noncovalent interactions in the HZ⋯CH$_4$, HZ⋯C$_2$H$_6$ complexes. This is due to the different origin of attraction in these complexes. The attractive interaction in the HZ-C$_2$H$_4$ alkoxide complex is due to covalent interactions, and the noncovalent interaction in HZ⋯H$_2$O is dominated by hydrogen bonds; Hartree−Fock theory is known to be able to give reasonable (although not quantitative) results for covalent interactions and the electrostatic interactions in hydrogen bonds. In the HZ⋯C$_2$H$_4$ π complex, the interaction of the Brønsted acidic sites of HZ with the π cloud of C$_2$H$_4$ is called π hydrogen bond in which both hydrogen bonding and medium-range correlation energy (sometimes called a dispersion-like interaction) are responsible for the attraction. In the HZ⋯CH$_4$ and HZ⋯C$_2$H$_6$ complexes, the attractive interaction is mostly due to medium-range correlation energy, so Hartree−Fock theory

(which has no correlation energy) performs poorly for these two complexes. Table 3 shows that the MP2/IB calculations slightly underestimate the binding energies of the HZ⋯CH$_4$ and HZ⋯C$_2$H$_6$ complexes, and the small-basis CCSD(T) corrections contribute 0.12 and 0.24 kcal/mol to the final dissociation energies, respectively. Table 3 also shows that the MP2/IB calculations overestimate the binding energies of the two HZ⋯C$_2$H$_4$ complexes, and the small-basis CCSD(T) correction decreases the final dissociation energy by 0.27 and 1.0 kcal/ mol for the π complex and alkoxide complex, respectively. For the interaction in the HZ⋯H$_2$O complex, MP2 and CCSD(T) give almost identical results, and the small-basis CCSD(T) correction contributes only −0.02 kcal/mol to the best estimate of the dissociation energy.

Although the goal of this work is not to compare models to experiment or to examine convergence with respect to cluster size (this has been done by others[35,56]), a brief comparison to some experimental and previous theoretical studies on extended systems is provided for perspective. The trends in the benchmark results in Table 3 for the HZ⋯CH$_4$, HZ⋯C$_2$H$_6$, and HZ⋯C$_2$H$_4$ complexes are in agreement with the adsorption isotherm experiment of Berlier et al.[3] Table 3 shows that the interaction strengths increase as the order HZ⋯CH$_4$ < HZ⋯C$_2$H$_6$ < HZ⋯C$_2$H$_4$, whereas Berlier et al. found that the amount of gas adsorbed on a G5 zeolite increases in the same order. In another experiment, Yang et al.[7] found a heat of adsorption of methane in sodium-exchanged faujasites of 3.3 kcal/mol. For the same system, Calero et al.[38] calculated (by molecular mechanics) 2.9 kcal/mol for CH$_4$ and 4.0 kcal/mol for C$_2$H$_6$, an increase of 36%, which compares reasonably well to our increase of 30% (in ethane as compare to methane) for adsorption on the 3T cluster. The experimental results for high-silica zeolites[5] are 2.7−6.6 kcal/mol for CH$_4$, depending on zeolite structure, and 4.7−10.0 kcal/mol for C$_2$H$_6$ for the same structure (averaging 53% larger over seven structures)

3.2. Performance of WFT Methods. Table 4 presents the results for five WFT methods. Among the tested levels of theory, Hartree−Fock theory gives the worst performance. This is not surprising because Hartree−Fock theory does not include correlation energy. The counterpoise-corrected MP2/aug-cc-

TABLE 5: Binding Energies and Mean Errors (in kcal/mol) for DFT Methods[a]

method	HZ···CH4		HZ···C2H6		HZ···C2H4 π		HZ···H2O		HZ-C2H4 alkoxide		mean error[b]	
	D_e	D_e-Cp	D_e	D_e-Cp	D_e	D_e-Cp	D_e	D_e-Cp	D_e	D_e-Cp	MUE	MUE-Cp
best estimate[c]	3.45		4.50		7.79		14.97		19.51			
M05-2X	3.29	2.96	4.54	3.89	8.36	7.67	17.43	15.78	23.59	20.83	1.46	0.67
M06-2X	3.20	2.86	4.85	4.20	8.33	7.64	17.78	16.07	23.97	21.27	1.68	0.78
M06	2.88	2.56	4.60	4.00	7.63	6.97	15.86	14.38	23.27	20.83	1.09	0.82
M06-L	2.75	2.40	4.61	3.95	6.80	6.15	15.23	13.87	21.78	19.22	0.87	0.93
M05	2.79	2.42	3.22	2.54	6.81	6.09	15.41	13.76	21.82	19.35	1.13	1.21
M06-HF	3.13	2.68	4.55	3.76	9.26	8.40	19.37	17.25	25.05	21.85	2.36	1.35
PWB6K	2.58	2.24	3.60	2.95	6.66	5.97	15.55	13.90	23.27	20.67	1.45	1.36
PBEh	2.14	1.79	2.14	1.48	6.40	5.69	16.53	14.81	22.55	19.89	1.93	1.46
PBE	2.33	1.99	2.30	1.62	6.64	5.90	17.16	15.40	20.40	17.84	1.51	1.67
B97-1	2.34	2.00	2.45	1.79	6.59	5.87	16.10	14.42	20.12	17.55	1.22	1.72
MPWB1K	1.90	1.56	2.67	2.03	5.87	5.20	14.92	13.28	22.74	20.15	1.72	1.85
PW6B95	2.10	1.77	2.90	2.26	6.09	5.39	15.03	13.38	20.22	17.73	1.08	1.94
MPW1B95	1.81	1.48	2.50	1.87	5.78	5.10	14.94	13.29	21.22	18.71	1.48	1.95
τ-HCTHh	1.68	1.35	1.48	0.85	5.93	5.23	16.28	14.59	20.04	17.48	1.70	2.14
MPW3LYP	2.23	1.88	2.12	1.41	6.30	5.53	16.67	14.97	18.06	15.53	1.65	2.18
BMK	1.23	0.93	1.59	1.00	5.42	4.77	14.73	13.30	22.22	19.75	2.09	2.19
MPW1K	1.48	1.10	1.24	0.55	5.55	4.83	15.51	13.80	22.93	20.13	2.29	2.21
B98	1.96	1.63	1.86	1.20	6.11	5.39	15.80	14.11	19.30	16.72	1.37	2.23
BH and HLYP	1.70	1.35	1.56	0.88	5.62	4.88	15.60	13.95	19.70	17.07	1.54	2.42
MPW1PW91	1.36	1.01	0.97	0.31	5.40	4.68	15.58	13.87	20.90	18.24	2.00	2.42
TPSSh	1.19	0.84	0.79	0.13	5.10	4.38	15.44	13.72	20.75	18.11	2.07	2.61
X3LYP	1.82	1.48	1.57	0.88	5.82	5.06	16.22	14.54	17.68	15.16	1.92	2.62
MPWB95	1.69	1.35	2.21	1.55	5.66	4.95	15.27	13.56	17.88	15.46	1.62	2.67
BB1K	1.08	0.76	1.51	0.90	4.85	4.20	13.92	12.31	21.18	18.61	2.20	2.69
TPSS	1.15	0.80	0.69	0.04	5.06	4.34	15.59	13.86	19.93	17.35	1.98	2.77
TPSS1KCIS	1.37	1.02	0.95	0.29	5.17	4.44	15.29	13.55	19.34	16.75	1.75	2.83
mPWPW	1.25	0.91	0.70	0.02	5.27	4.53	15.88	14.13	18.27	15.73	2.14	2.98
MPWLYP	2.03	1.64	1.68	0.91	5.99	5.16	16.59	14.82	15.03	12.48	2.43	3.04
TPSSKCIS	1.30	0.96	0.81	0.14	5.10	4.36	15.46	13.71	18.26	15.72	2.06	3.07
BP86	0.83	0.51	0.25	-0.38	4.96	4.26	15.92	14.25	17.84	15.34	2.46	3.25
B1B95	0.81	0.50	1.07	0.47	4.53	3.88	13.74	12.12	19.26	16.77	2.16	3.30
B3LYP	1.26	0.92	0.76	0.08	5.10[d]	4.35[e]	15.47	13.81	16.49	13.98	2.43	3.41
τ-HCTH	1.13	0.77	0.13	-0.56	4.80	4.06	15.30	13.50	16.59	13.99	2.59	3.69
B97-2	0.88	0.53	0.23	-0.44	4.56	3.84	14.13	12.41	17.92	15.26	2.50	3.72
BH and H	5.11	4.77	6.71	6.05	10.68	9.97	22.50	20.80	32.59	29.90	5.47	4.25
HCTH	1.74	1.33	0.94	0.15	4.79	3.95	13.62	11.74	14.17	11.43	2.99	4.33
BB95	0.34	0.03	0.33	-0.30	4.00	3.31	13.61	11.96	15.68	13.30	3.25	4.38
BLYP	0.71	0.35	-0.15	-0.89	4.36	3.56	14.96	13.25	12.90	10.40	3.49	4.71
VSXC	7.27	6.93	17.21	16.55	14.57	13.85	16.44	14.64	25.57	22.82	6.17	5.05
O3LYP	-0.33	-0.75	-2.00	-2.80	2.37	1.53	11.82	9.91	13.39	10.63	4.99	6.34
G96LYP	-1.76	-2.09	-3.61	-4.29	1.41	0.66	12.39	10.76	10.37	7.94	6.28	7.45
OLYP	-1.00	-1.45	-3.12	-3.96	1.35	0.45	10.71	8.71	10.86	8.06	6.29	7.68

[a] The 6-31+G(d,p) basis set and MP2/6-311+G(2df,2p) geometries are used for all calculations. "Cp" denotes that the calculations are counterpoise-corrected. [b] MUE denotes mean unsigned error (same as mean absolute deviation, MAD). [c] The best estimates are from Table 3. [d] Kasuriya et al.[35] obtained 5.39 kcal/mol for this case with B3LYP/6-311++G(d,p)//B3LYP6-31G(d,p). [e] Kasuriya et al.[35] obtained 7.61 kcal/mol for this case with B3LYP/6-31G(d,p).

pVTZ method gives the best performance, with an mean unsigned error (MUE) of 0.59 kcal/mol, and MP2 with smaller basis sets (such as aug-cc-pVDZ and 6-31+G(d,p)) gives much larger errors. The counterpoise-corrected CCSD(T)/6-31+G-(d,p) level of theory gives an error about 6 times greater than that of the counterpoise-corrected MP2/aug-cc-pVTZ calculations; this is mainly due to the size of the basis set being small. Table 4 tells us that, in order to describe the noncovalent interaction in the zeolite systems accurately, one needs to use a basis set at least the size of aug-cc-pVTZ, and one also needs to do the counterpoise correction to eliminate the basis set superposition error. Note that the counterpoise-corrected MP2/aug-cc-pVTZ calculations are very expensive and they are practical only for small clusters. For the simulation of large clusters, one needs to use the more affordable methods like DFT, and their performance is discussed in the next section.

3.3. Performance of DFT Methods. Table 5 gives the DFT results using the 6-31+G(d,p) basis set, which is smaller than acDZ and much smaller than acTZ (see Table 2). For the HZ···H2O and HZ-C2H4 alkoxide complexes, most of the tested

functionals give reasonable predictions with the major exceptions being BHandH, O3LYP, G96LYP, and OLYP functionals. For the interaction in the HZ···CH4, HZ···C2H6, and HZ···C2H4 complexes, most of the tested functionals fail except the M05-2X and the M06-class functionals. Interestingly, M06-L/6-31+G(d,p) without counterpoise correction give the lowest MUE, which is 0.87 kcal/mol. With the counterpoise corrections, M05-2X and M06-2X give the lowest MUEs.

The results in Table 5 are based on the MP2/6-311+G(2df,-2p) geometries, and some functionals give negative binding energies, which means that these functionals predict repulsive interactions at the optimum MP2 geometries. In the next section, we discuss the effects of geometry and the size of the basis sets on the performance of DFT functionals

3.4. Effect of Geometries and Basis Sets. Table 6 presents results for four functionals, two of which are the best performing functionals in Table 5, M05-2X[107] and M06-2X,[108] and two of which are popular functionals, B3LYP[96-98] and PBEh.[99] Table 6 shows that increasing the basis set from 6-31+G(d,p) to 6-311+G(2df,2p) the MUEs of the M05-2X and M06-2X

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TABLE 6: Effects of Geometries and Basis Sets[a]

method[b]	HZ···CH_4 D_e	HZ···CH_4 D_e-Cp	HZ···C_2H_6 D_e	HZ···C_2H_6 D_e-Cp	HZ···C_2H_4 D_e	HZ···C_2H_4 D_e-Cp	HZ···H_2O D_e	HZ···H_2O D_e-Cp	HZ-C_2H_4 alkoxide D_e	HZ-C_2H_4 alkoxide D_e-Cp	mean error[c] MUE	mean error[c] MUE-Cp
best estimate[d]	3.45		4.50		7.79		14.97		19.51			
M05-2X/DIDZ//MP2/TZ	3.29	2.96	4.54	3.89	8.36	7.67	17.43	15.78	23.59	20.83	1.46	0.67
M05-2X/DIDZ//M05-2X/DIDZ	3.19	2.84	4.52	3.83	8.57	7.79	17.26	15.50	23.63	20.83	1.49	0.63
M05-2X/TZ//MP2/TZ	3.42	3.13	4.59	4.05	7.73	7.23	15.85	15.03	21.66	20.15	0.64	0.41
M05-2X/TZ//M05-2X/DIDZ	3.38	3.12	4.62	4.09	8.21	7.73	15.64	14.78	22.04	20.53	0.76	0.40
M06-2X/DIDZ//MP2/TZ	3.20	2.86	4.85	4.20	8.33	7.64	17.78	16.07	23.97	21.27	1.68	0.78
M06-2X/DIDZ//M06-2X/DIDZ	3.90	3.33	5.32	4.53	8.82	8.00	17.91	16.04	24.13	21.37	1.98	0.66
M06-2X/TZ//MP2/TZ	3.49	3.20	5.10	4.58	8.25	7.77	16.11	15.24	22.27	20.85	1.00	0.39
M06-2X/TZ//M06-2X/DIDZ	4.01	3.62	5.70	5.09	8.49	7.98	16.06	15.15	22.46	21.00	1.30	0.52
PBEh/DIDZ//MP2/TZ	2.14	1.79	2.14	1.48	6.40	5.69	16.53	14.81	22.55	19.89	1.93	1.46
PBEh/DIDZ//PBEh/DIDZ	2.34	2.09	2.64	2.19	6.37	5.70	16.09	14.26	22.67	20.21	1.73	1.43
PBEh/TZ//MP2/TZ	2.33	2.06	2.31	1.80	6.22	5.74	14.95	14.04	20.92	19.58	1.26	1.43
PBEh/TZ//PBEh/DIDZ	2.39	2.22	2.76	2.41	6.16	5.77	14.80	13.86	21.09	19.78	1.24	1.34
B3LYP/DIDZ//MP2/TZ	1.26	0.92	0.76	0.08	5.10	4.35	15.47	13.81	16.49	13.98	2.43	3.41
B3LYP/DIDZ//B3LYP/DIDZ	1.56	1.33	1.66	1.24	5.54	4.89	15.23	13.52	16.63	14.19	2.02	3.01
B3LYP/TZ//MP2/TZ	1.32	1.07	0.72	0.25	4.68	4.24	13.81	12.98	14.32	13.00	3.07	3.74
B3LYP/TZ//B3LYP/DIDZ	1.49	1.34	1.62	1.32	4.98	4.63	13.68	12.83	14.42	13.15	2.81	3.39

[a] Cp denotes calculations with counterpoise correction. [b] DIDZ: 6-31+G(d,p); TZ: 6-311+G(2df,2p). [c] MUE denotes mean unsigned error (same as mean absolute deviation, MAD). [d] The best estimates are from Table 1.

TABLE 7: Test against a Benchmark Data of Binding Energies (kcal/mol) in Four Complexes Involving the Adsorption of Isobutene on a 16T Zeolite Cluster Model[a]

method[b]	π complex D_e	π complex D_e-Cp	tert-butoxide D_e	tert-butoxide D_e-Cp	tert-butyl carbenium ion D_e	tert-butyl carbenium ion D_e-Cp	isotutoxide D_e	isotutoxide D_e-Cp	mean error[c] MUE	mean error[c] MUE-Cp
best estimate[d]	15.1		13.9		−9.8		13.9			
M05-2X	15.5	11.7	19.7	14.9	−3.9	−8.1	18.6	14.0	4.2	1.6
M06-2X	16.3	12.7	21.1	16.6	−5.2	−9.1	20.0	15.6	4.8	1.9
M06-L	17.2	14.4	19.3	15.6	0.7	−2.3	16.9	13.5	5.3	2.6
M06	16.2	13.3	19.7	16.0	−0.8	−3.9	18.0	14.4	5.0	2.6
M06-HF	18.7	12.4	25.9	18.6	−6.1	−12.5	25.8	18.8	7.8	3.7
MP2/TZVP(P)[d]	18.6	10.8	23.4	10.0	−5.5	−13.4	21.7	9.1	6.3	4.1
PBEh	6.9	2.9	9.3	4.7	−11.5	−15.6	9.2	4.7	4.8	9.1
PBE	7.0	3.2	6.7	2.3	−8.9	−12.8	6.3	2.0	5.9	9.6
B97-1	7.6	3.9	6.6	2.2	−10.5	−14.3	7.2	2.9	5.5	9.6
TPSSh	3.4	−0.9	6.7	1.8	−13.3	−17.7	6.3	1.6	7.5	12.1
B3LYP	1.0	−2.5	−1.3	−5.5	−17.1	−20.7	−0.6	−4.8	12.7	16.6

[a] See Figure 2 for the 16T model cluster and four complexes. [b] The 6-311+G(2df,2p) basis set is employed for all density functionals in this table. [c] MUE denotes mean unsigned error (same as mean absolute deviation, MAD). [d] Best estimates were calculated from the two last rows in Table 3 of Tuma and Sauer.[27] The geometries and MP2/TZVP(P) results are also from Tuma and Sauer.[27] Other results in this table are from the present work.

methods get smaller, whereas the MUE of B3LYP gets larger. If we let MUE-Cp denote the mean unsigned error when counterpoise corrections are included, then it is encouraging that M05-2X and M06-2X give a small MUE-Cp of 0.4−0.5 kcal/mol with the 6-311+G(2df,2p) basis set, which is smaller than the MUE-Cp of MP2/aug-cc-pVTZ (see Table 3). The PBEh functional has much better performance than B3LYP, but it gives much larger errors than M05-2X and M06-2X.

3.5. Tests for a Large Zeolite Cluster. The previous sections give results for small 3T clusters. In Table 7, we present tests against the benchmark data of Tuma and Sauer[27] on a 16T H-Ferrierite zeolite model cluster. This benchmark data consists of four MP2/CBS binding energies of the complex products of the adsorption of isobutene on the cluster. The structures of the unloaded 16T cluster and the four 16T-isobutene complexes are presented in Figure 2. Table 7 shows that, without the counterpoise corrections, M05-2X gives the best performance, followed by M06-2X and PBEh. When counterpoise corrections are included, M05-2X and M06-2X are the best performers, followed by M06-L and M06, and these four functionals give a smaller MUE-Cp than the MP2/TZVP(P) method. It is interesting that the best functional in Table 7 has an MUE-Cp that is a factor of 5.7 times smaller than the best non-Minnesota

functional in the table (PBEh), whereas the factor is 2.2 for the smaller complex in Table 5.

For the two local density functionals, PBE and M06-L, we also performed calculations using Dunning's aug-cc-pVXZ (X = D, T, Q) basis sets[82,83] with the resolution of identity (RI, also called density fitting) algorithm. The calculations are extrapolated to a complete basis set (CBS) by the aug-Schwartz4(TQ) extrapolation scheme of Martin,[109] which yields

$$E(CBS) = \frac{2.7326E(aVQZ) - E(aVTZ)}{1.7326} \quad (4)$$

Table 8 present the results of these large basis set RI-DFT calculations. Table 8 shows, at the CBS limit, that M06-L gives an MUE of 4.5 kcal/mol and MUE-Cp of 2.5 kcal/mol, whereas PBE gives an MUE of 9.3 kcal/mol and an MUE-Cp of 9.9 kcal/mol. These large basis calculations give results consistent with those in Table 7.

As shown by Tuma and Sauer,[27] the 16T cluster results still deviate substantially from the full periodic limit (Table 5 of Tuma and Sauer[27]), and this deviation is nonuniform for different complexes. For example, *tert*-butylcarbenium, which is non-bonding to 16T in the gas phase, becomes bonding in the full
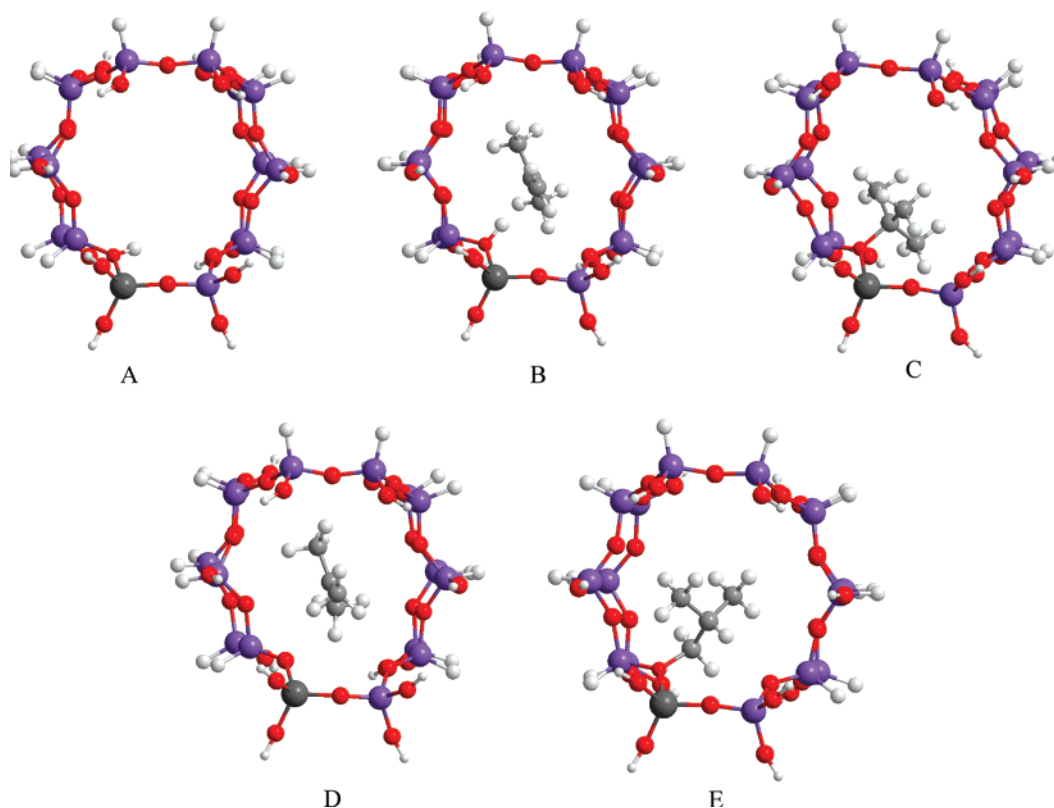
Figure 2. Geometries of the 16T zeolite model complexes. (A) 16T, (B) 16T···isobutene π complex, (C) 16T *tert*-butoxide, (D) 16T *tert*-butyl carbenium ion, (E) 16T isobutoxide.

TABLE 8: DFT/CBS Calculation for the Binding Energies (kcal/mol) in Four Complexes Involving the Adsorption of Isobutene on a 16T Zeolite Cluster Model[a]

	π complex		tert-butoxide		tert-butyl carbenium ion		isotutoxide		mean error[c]	
method[b]	D_e	D_e-Cp	D_e	D_e-Cp	D_e	D_e-Cp	D_e	D_e-Cp	MUE	MUE-Cp
best estimate	15.1		13.9		−9.8		13.9			
M06-L/aVDZ	22.6	15.3	27.1	18.5	10.2	3.0	24.1	15.8	12.7	4.9
M06-L/aVTZ	18.5	16.1	20.7	17.6	3.4	1.1	18.6	15.9	7.0	4.4
M06-L/aVQZ	17.0	15.1	19.3	16.7	1.3	−0.7	17.2	14.8	5.4	3.2
M06-L/CBS[d]	16.1	14.5	18.4	16.1	0.1	−1.8	16.5	14.1	4.5	2.5
PBE/aVDZ	12.0	4.5	14.0	4.7	−0.1	−7.8	13.1	4.1	3.4	7.9
PBE/aVTZ	5.6	3.4	5.2	2.5	−10.8	−13.0	4.9	2.4	7.1	9.4
PBE/aVQZ	4.4	3.3	3.7	2.4	−12.5	−13.5	3.6	2.3	8.5	9.7
PBE/CBS[d]	3.7	3.2	2.8	2.3	−13.4	−13.8	2.9	2.3	9.3	9.8

[a] See Figure 2 for the 16T model cluster and four complexes. The best estimates were calculated from the two last rows in Table 3 of Tuma and Sauer.[27] The geometries and MP2/TZVP(P) results are also from Tuma and Sauer.[27] *[b]* All DFT calculations in this table employ the resolution of identity (or density fitting) algorithm. *[c]* MUE denotes mean unsigned error (same as mean absolute deviation, MAD). *[d]* The aug-Schwartz4(TQ) extrapolation scheme of Martin[109] is used for complete basis limit (CBS) extrapolation.

periodic limit, and the two butoxides are no longer energetically degenerate, but the isobutoxide becomes more stable than *tert*-butoxide.

4. Concluding Remarks

In the present study, the benchmark binding energies for four noncovalent zeolite model complexes were determined as the sum of the infinite-basis-set limit of MP2 energies and a CCSD-(T) correction term evaluated with the aug-cc-pVDZ basis set. The basis set limit of MP2 energies was determined by two-point extrapolation using the aug-cc-pVXZ basis sets for X = D and T and separate extrapolation of the Hartree−Fock and correlation energy. Final binding energies (kcal/mol) are in the range of 3.5−19.5 kcal/mol, and they were used as reference data to test 6 WFT methods and 41 density functionals. We found the following:

(1) The small-basis CCSD(T) contributions to the final best estimates of the binding energies are small, with magnitudes in the range of 0.01−1.0 kcal/mol.

(2) In order for the MP2 method to describe the noncovalent interaction in these zeolite model systems accurately, one needs to use a basis set at least the size of aug-cc-pVTZ in conjunction with the counterpoise correction to eliminate the BSSE.

(3) Among the tested density functionals, M06-L/6-31+G-(d,p) gives an MUE of only 0.87 kcal/mol, and it is a much more affordable method than MP2/aug-cc-pVTZ.

(4) When counterpoise corrections are included, M06-2X and M05-2X give the best performance for the five 3T clusters. The MUE-Cp (mean unsigned error after counterpoise correction) for the M06-2X/6-311+G(2df,2p)//MP2/6-311+G(2df,2p) level of theory is 0.39 kcal/mol. With DFT/6-31+G(d,p) geometries

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and the 6-311+G(2df,2p) basis set, M05-2X and M06-2X give MUE-Cps of 0.40 and 0.52 kcal/mol, respectively.

(5) Tests against the binding energies of the four complexes of the adsoption of isobutene on a large 16T zeolite model cluster showed that M06-L, M06, M05-2X, and M06-2X are promising QM methods for the QM/MM simulation of zeolite catalysis. It would be interesting, for example, to apply these functionals to the larger clusters, up to 46T[41] and 84T,[35] that have been used in QM/MM calculations of ethylene adsorption on zeolite.

Although computer times and memory requirements depend strongly on the computer program and the computer, the DFT methods tested here are much more affordable than reliable wave function theory and this becomes more and more so as system size is increased. Therefore, it is very encouraging that new density functionals are capable of useful accounting for zeolite adsorption. The local M06-L method is especially efficient for calculations on large systems.

Supporting Information Available: The MP2/6-311+G-(2df,2p) geometries for all 3T complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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