Adsorption of ethylene, benzene and ethylbenzene over faujasite zeolites investigated by the ONIOM method

Computer Simulation in Chemistry and Chemical Engineering

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Kasuriya S., et al., J Catal. 219 (2003) 320-328

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- Introduction& Objectives
- Models and Method
- Results and discussion
  - Comparison of ONIOM results and experimental results
  - Interactions of ethylene, benzene and ethylbenzene with faujasite zeolite
- Conclusions

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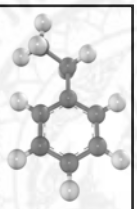
Introduction



- Ethylbenzene
  - 90% to styrene
  - Paint solvents and pharmaceuticals
- Ethylene + Benzene to ethylbenzene
- Benzene alkylation with $AlCl_3$
- Problems concerning environment friendly

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Zeolites

- Petroleum and chemical industries as solid catalysts
- Bronsted acid and Lewis acid sites, size-shape selectivity.
- Proton-zeolite, metal-zeolite

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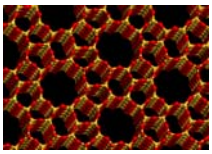
Zeolites

- *Crystalline silicates or aluminosilicates*
- *Catalysis, storage and separation*



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Advantages of zeolite catalysts

- *High surface area*
- *High adsorption capacity*
- *Shape selectivity control*
- *Activating the reactants by confinement effects*

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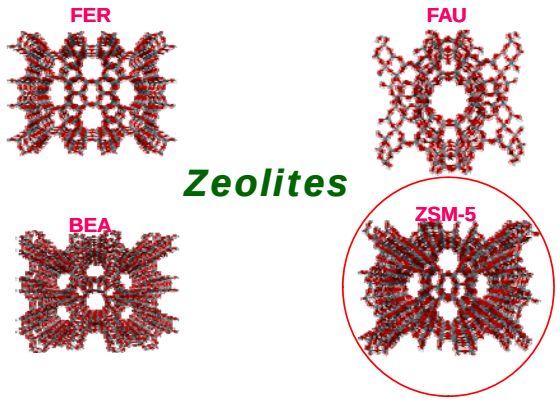

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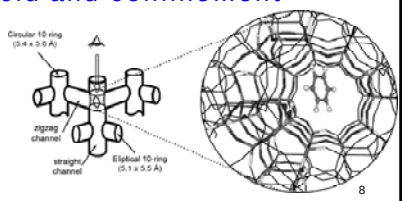
ZSM-5

- *Cracking, isomerization, alkylation and methanol to olefins (MTO)*
- *The pore system of interconnected straight and zigzag channels.*
- *Brønsted acid and confinement effect*



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Confinement Effect

- *Important in the zeolites*
- *Attractive forces*
- *Long-range electrostatic*
- *Short-range van der Waals*
- *Contribute to the remarkable sorption and catalytic properties of zeolites by stabilizing adsorbed molecules, intermediates, and reaction transition states*

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Experiment study

- The adsorptions are elementary steps of the catalytic processes.
- FTIR, NMR
- Heat of adsorption of ethylene on H-Y zeolite -9.1 kcal/mol
- Benzene < Ethylbenzene < 1,4-diethylbenzene ≅ 1,3-diethylbenezne

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- Periodic ab initio calculations, too expensive
- Combinded quantum mechanics/ molecular mechanics (QM/MM) methods.
- ONIOM

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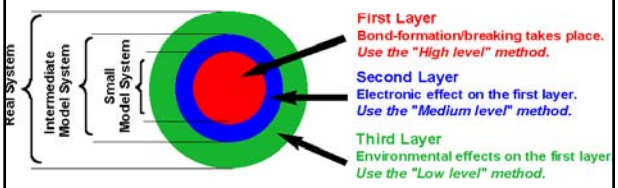
Hybrid Methods: MO/MO and QM/MM

- The active site region is treated using high-level molecular orbital theory, while the most distant parts of the enzyme are treated using low-cost molecular mechanics.



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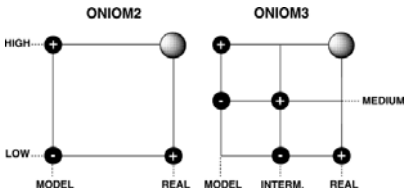
ONIOM Method

- Morokuma & co-workers JCC **1995**, *16*, 1170;Theochem **1999**, *461*, 1; TCA **2003**, *109*, 125; JCC **2003**, *24*, 760.

$$E_{real}^{ONIOM} = E_{real}^{low} - E_{model}^{low} + E_{model}^{high}$$



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Objectives

- To study the adsorption of ethylene, benzene and ethylbenzene on zeolites using the ONIOM model
- To understanding the role of H-FAU in catalyzing the process of producing ethylbenzene

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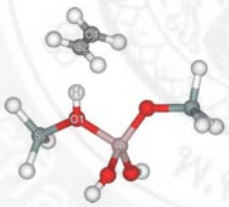
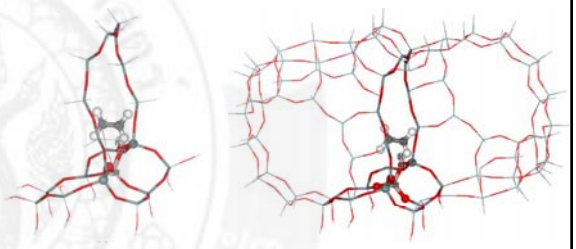
Method

- 3T (T means tetrahdedral of Si or Al atoms) cluster
- One Si is replaced by Al atom and a proton is added
- Si-H bonds are fixed





20T 84T

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- ONIOM approach
  - Inner layer: B3LYP, HF
  - Outer layer: HF, semiempirical and UFF
- Only 3T acitve region and probe are allowed to relax
- BSSE correction is taken into account
- B3LYP/6-311++G(d,p) // B3LYP/6-31G(d,p)

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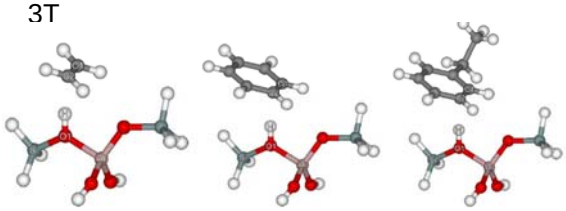
Results and Discussion

- Ethylene, benzene and ethylbenzene on 3T



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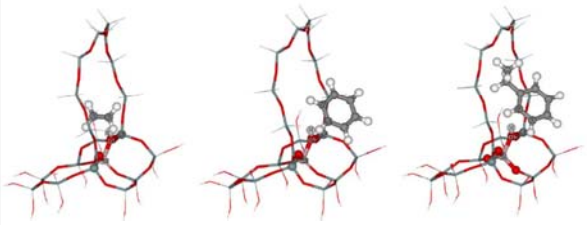
- Ethylene, benzene and ethylbenzene on 20T



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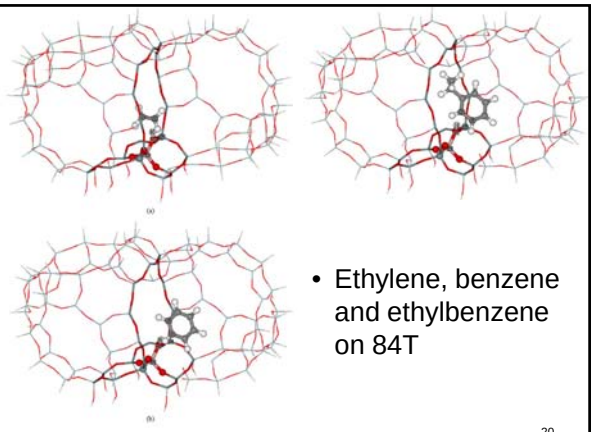

- Ethylene, benzene and ethylbenzene on 84T

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Table 1
Structural parameters of faujasite obtained at full HF/3-21G and various two-layer ONIOM2 schemes (bond distances in pm and bond angles in degrees)

Parameters	3T	20T					84T
	Full HF	Full HF	HF:MNDO	HF:AM1	HF:PM3	HF:UFF	HF:UFF
O1–H	96.8	97.2	96.9	97.0	96.8	96.8	96.8
Al–O1	184.2	185.6	183.0	183.2	185.8	180.5	180.5
Si–O1	171.9	170.1	171.3	167.5	172.1	169.4	169.4
∠Al–O1–Si	127.4	129.4	126.9	124.1	125.5	126.0	126.0
Al–H	233.5	239.6	231.5	230.3	235.6	230.2	230.3

The HF is Hatree–Fock with 3-21G basis set.

Table 2
Structural parameters of faujasite obtained at full B3LYP/6-31G(d,p) and various ONIOM2 schemes (bond distances in pm and bond angles in degrees)

Parameters	3T	20T						84T
	Full B3LYP	Full B3LYP	B3LYP:HF	B3LYP:MNDO	B3LYP:AM1	B3LYP:PM3	B3LYP:UFF	B3LYP:UFF
O1–H	96.7	96.9	97.2	96.8	96.8	96.7	96.8	96.8
Al–O1	191.6	191.4	193.7	190.1	191.1	193.8	186.0	186.0
Si–O1	170.9	170.4	168.2	170.5	166.0	170.8	168.6	168.6
∠Al–O1–Si	126.7	128.4	129.0	126.0	122.6	123.9	125.6	125.5
Al–H	246.0	250.8	254.3	243.4	244.6	249.6	240.0	240.2

The B3LYP is density functional theory with 6-31G(d,p) basis set; HF is Hartree–Fock with 3-21G basis set.

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- r(Al - - H) of Faujasite 238.0 ± 4 pm
- HF/3-21G gives too small
- ONIOM2 (B3LYP/6-31G(d,p):UFF) 240.2 pm

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Table 5
Binding energy of ethylene, benzene, and ethylbenzene on the Bronsted proton of faujasite zeolites (binding energy in kcal/mol)

Methods/models	3T			20T			84T		
	Ethylene	Benzene	Ethylbenzene	Ethylene	Benzene	Ethylbenzene	Ethylene	Benzene	Ethylbenzene
B3LYP/6-31G(d,p)	−8.14	−7.48	−7.76	−10.93[a]	−14.28[a]	−15.90[a]	–	–	–
B3LYP/6-31G(d,p):UFF	–	–	–	−10.78	−14.94	−18.35	−11.49	−17.15	−22.99
B3LYP/6-31G(d,p)+BSSE[d]	−7.61	−6.54	−6.69	−10.25	−13.93	−17.30	−10.96	−16.15	−21.94
B3LYP/6-311++G(d,p)[b]	−5.39	−5.35	−5.78	−8.03	−12.23	−16.40	−8.75	−15.17	−21.08
HF/3-21G	−8.37	−9.49	−9.88	−10.90	−13.16	−17.23	–	–	–
HF/3-21G:UFF	–	–	–	−10.48	−16.76	−19.73	−11.43	−18.33	−24.09
HF/3-21G+BSSE[d]	−7.85	−8.42	−8.29	−10.05	−15.74	−18.50	−10.91	−17.21	−22.84
HF/6-311++G(d,p)[c]	−3.28	−3.47	−3.91	−6.21	−10.31	−11.74	−6.54	−13.69	−19.63
B3LYP/6-31G(d,p):HF/3-21G	–	–	–	−10.98	−11.40	−12.00	–	–	–
B3LYP/6-31G(d,p):MNDO	–	–	–	−6.99	−3.37	−3.23	–	–	–
B3LYP/6-31G(d,p):AM1	–	–	–	−7.67	−4.49	−4.99	–	–	–
B3LYP/6-31G(d,p):PM3	–	–	–	−5.41	−1.95	−1.13	–	–	–
HF/3-21G:MNDO	–	–	–	−7.10	−5.67	−5.65	–	–	–
HF/3-21G:AM1	–	–	–	−7.34	−6.50	−7.25	–	–	–
HF/3-21G:PM3	–	–	–	−5.63	−4.31	−4.12	–	–	–

Experimental adsorption energies of ethylene on H-FAU is −9.1 kcal/mol, taken from Ref. [6]. Experimental adsorption energies of benzene and ethylbenzene on H-FAU are −15.31 and −19.6 kcal/mol, respectively, taken from Ref. [10].

[a] Mixed basis sets of 6-31G(d,p) and 3-21G.
[b] Indicates single-point energy at indicated level of theory on the optimized B3LYP/6-31G(d,p): UFF structure.
[c] Indicates single-point energy at indicated level of theory on optimized HF/3-21G: UFF structure.
[d] Basis set superposition error corrected.

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Conclusions

- Adsorption of ethylene, benzene and ethylbenzene on H-FAU
- 3T B3LYP/6-31G(d,p) predicts the binding energies of -8.14, -7.48 and -7.76 kcal/mol, respectively.
- ONIOM2(B3LYP/6-311++G(d,p):UFF) predicts the binding energies of -8.75, -15.17 and -21.08 kcal/mol, respectively compared well with experiment of -9.1, -15.3 and -19.6 kcal/mol.

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