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

Computer Simulation in Chemistry and Chemical Engineering

Bundet Boekfa
E-mail: bundet.b@ku.ac.th


Introduction

- Ethylbenzene
  - 90% to styrene
  - Paint solvents and pharmaceuticals
- Ethylene + Benzene to ethylbenzene
- Benzene alkylation with AlCl₃
- Problems concerning environment friendly

Zeolites

- Crystalline silicates or aluminosilicates
- Catalysis, storage and separation

Advantages of zeolite catalysts

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

- FER
- FAU
- BEA
- ZSM-5

**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

**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-diethylbenzene

**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.
ONIOM Method


\[ E_{\text{ONIOM}}^{\text{real}} = E_{\text{low model}}^{\text{real}} - E_{\text{low model}}^{\text{low}} + E_{\text{high model}}^{\text{high}} \]

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

Method

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

- ONIOM approach
  - Inner layer: B3LYP, HF
  - Outer layer: HF, semiempirical and UFF

- Only 3T active region and probe are allowed to relax
- BSSE correction is taken into account
- B3LYP/6-311++G(d,p) // B3LYP/6-31G(d,p)

Results and Discussion

- Ethylene, benzene and ethylbenzene on 3T
• Ethylene, benzene and ethylbenzene on 20T

Table 1: Bonding energy of ethylene, benzene, and ethylbenzene on H-FAU

<table>
<thead>
<tr>
<th>Compound</th>
<th>3T B3LYP/6-31G(d,p)</th>
<th>ONIOM2(B3LYP/6-31++G(d,p):UFF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>-8.14</td>
<td>-8.75</td>
</tr>
<tr>
<td>Benzene</td>
<td>-7.48</td>
<td>-15.17</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>-7.76</td>
<td>-21.08</td>
</tr>
</tbody>
</table>

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/6-31++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.