

H-ZSM-5 分子筛上环己烯芳构化反应历程的理论研究

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摘要 基于 76T 簇模型, 采用量子力学和分子力学联合的 ONIOM2 (B3LYP/6-31G(d, p):UFF) 方法研究了 H-ZSM-5 分子筛上环己烯芳构化反应历程。结果表明, 环己烯首先吸附在分子筛酸性位上, 与酸性质子共同脱除一个 H₂ 分子后, 在分子筛骨架氧上生成烷氧配合物中间体; 然后再脱质子得到环己二烯, 同时酸性位复原; 再经历脱氢和脱质子历程, 最后得到产物苯, 并吸附在复原的分子筛酸性位上。计算得到脱氢的活化能依次为 279.64 和 260.21 kJ/mol, 脱质子的活化能依次为 74.64 和 59.14 kJ/mol。所有脱氢反应都是吸热过程, 生成表面烷氧活性中间体, 随后的脱质子反应能垒较低, 而且是放热过程。此外, 比较了环己烯在分子筛酸性位上的三个竞争反应, 即脱氢、质子化和氢交换反应的活化能垒, 证明环己烯优先发生脱氢反应。

关键词: H-ZSM-5 分子筛 环己烯 芳构化 脱氢 量子力学 / 分子力学

Abstract: By using the QM/MM hybrid ONIOM2 (B3LYP/6-31G(d,p):UFF) method, the dehydro-aromatization reaction of cyclohexene over H-ZSM-5 zeolite was studied. The calculation was based on the 76T cluster model with Al substituted at the T12 site. The results indicated that cyclohexene was adsorbed on the Brønsted acid (B-acid) site of H-ZSM-5 zeolite. The dehydrogenation reaction consisted of cleavage of a C-H bond by acidic proton. After release of dihydrogen, the carbonium moiety was bonded with the basic framework oxygen, resulting in surface cyclohexene alkoxide intermediate. Then the alkoxide released the proton to the framework oxygen which led to generation of B-acid site, and the produced cyclohexene was adsorbed on the B-acid site. After subsequent dehydrogenation and deprotonation steps, a benzene molecule was produced as final product. The activation energy for dehydrogenation steps was 279.64 and 260.21 kJ/mol, respectively, and the activation energy for deprotonation process was 74.64 and 59.14 kJ/mol, respectively. All dehydrogenation steps are endothermic to lead to surface alkoxide intermediates, and the subsequent deprotonation have lower energy barriers and are exothermic. In addition, the three competitive reactions of cyclohexene, i.e. protonation, hydrogen exchange, and dehydrogenation, were also compared. It was found that cyclohexene preferred to dehydrogenate with zeolite proton.

Keywords: H-ZSM-5 zeolite, cyclohexene, aromatization, dehydrogenation, QM/MM

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