



Computational study of ethanethiol conversion reactions catalyzed by acidic zeolites

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ABSTRACT

The reaction mechanism, of the ethanethiol transformation over acidic zeolite surface: ethanethiol-H_p-zeolite → H_p-zeolite + ethene + H₂S, has been investigated computationally with the use of ab initio, density functional theory (DFT) and MM methods. The investigation has been carried out by employing two model zeolite clusters, each including one hydroxyl Brønsted acidic site (BAS). The first model, denoted 20T, has been studied with the help of the two-layered ONIOM2 (M06-2X/6-31 + G(d,p):UFF) methodology and the second one denoted 38T, has been investigated using the three-layered ONIOM3 (M06-2X/6-31 + G(d,p):HF:UFF) approach. The calculations using both models show that the reaction mechanism involves two competing channels, a direct t2 type dehydrosulfidation (DHS) channel, and a stepwise Sw2 type pathway through the intermediate formation of an alkoxy species. The detailed examination of the two pathways, i.e., the direct mechanism and the stepwise mechanism, indicate that the latter is strongly favored over the direct t2 type mechanism. Finally, the consistency of the results from both methodologies suggests that the ONIOM approach yields an accurate and practical method to study the degradation mechanism of sulfur containing compounds on acidic zeolite surface.

1. Introduction

The environmental pollution, resulting climate change and the worsening quality of life can be partly attributed to the usage of fossil fuels over the last century. Some of the major pollutants produced by burning fossil fuels are the sulfur dioxide and sulfur monoxide. They are both very toxic for living organisms and considered as greenhouse effect gases. Along with nitrogen oxides they are responsible for the phenomenon called acid rain.

The formation of the sulfur oxides is the result of the burning of the Organo-Sulfur Compounds (OSCs) contained in the fossil fuels, like diesel and gasoline, which are the common transport fuels. The main OSCs found in fuels are the thiols, also called mercaptanes (R-SH), sulfides and disulfides (R-S-R', R-S-S-R') and thiophenes, benzothiophenes and dibenzothiophenes [1]. Except for the forming of harmful sulfur oxides, another effect of the OSCs is the poisoning and degradation of the catalysts used in transport vehicles exhaust systems, which leads to higher pollutants emissions.

All of the above have led various multinational organizations, like EU, enforcing stricter environmental regulations concerning the amount of OSCs contained in fossil fuels. The techniques used for the removal of the OSCs from the fuels are called Deep Desulfurization

Processes [1–4]. The most used and studied of these processes is the hydrodesulfurization. During this process the fuel is treated with H₂, at elevated temperatures, in the presence of alumina supported NiMo, NiW and CoMo catalysts. The resulting products are hydrocarbons and H₂S. Because of the easy poisoning of the catalysts and the usage of H₂, this is considered to be an expensive process. This is the reason why researchers are looking for cost effective and more efficient processes. One of these processes is the selective adsorption during which the OSCs are adsorbed on the active sites of the adsorbent and removed by various techniques [1,4–6]. The most common adsorbents used are the zeolites, in their acidic or ion exchanged form [6–9].

Zeolites are aluminosilicate microporous materials, extensively used in the oil refinement industry. Their enormous ion exchange capability and tailorable physicochemical properties (e.g. acidity, hydrophilicity, etc.) along with their abundance, either from natural deposits or industrial production, have led zeolites to be considered as the top catalytic materials. Among these zeolites, faujasite (FAU) is a prominent member, displaying a wide range of commercial uses in such processes. FAU is characterized by its stable crystal structure and large pore volumes. Depending on their aluminum content, it possesses two synthetic forms of identical cages namely X and Y types, respectively. Type X and Y refer to Si/Al ratios per cell ranging between 1 and 1.5 and higher

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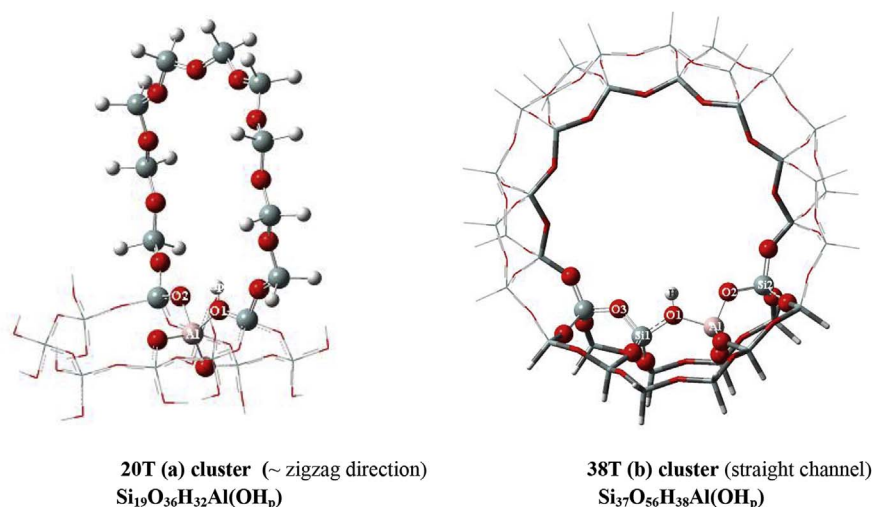


Fig. 1. Schematic representation of the two model zeolite clusters (20T, 38T) employed in the present study. a) Side view of the 20T model cluster and b) front view of the second model, straight channel. In both models a 12-membered-ring window connects two super cages of faujasite.

than 1.5, respectively [10].

Novel physical chemistry research protocols involve both experimental work and theoretical molecular modeling in the elucidation of the reaction mechanism in the degradation of adsorbed species. Experimental studies, for example, of Ziolk and Decyk [11] reporting on the adsorption and transformation of $\text{C}_2\text{H}_5\text{SH}$ and diethyl sulfide on faujasite-type zeolites, have demonstrated that protonated forms of zeolites are highly active in the transformation of sulfur compounds, due to the formation of hydrogen bonding complexes. The existence of this hydrogen bonding between the S atom of the OSC and the acid proton of zeolites can be studied very effectively by theoretical methods, where the zeolites may be represented by cluster models of finite dimension. Thus, various researches have taken place dealing with the theoretical study of the interaction of OSCs with zeolites, using *ab initio* and DFT methods. Three forms of adsorption structure have been proposed by Garcia and Lercher [12] for these complexes: (a) a linear hydrogen-bonding complex between the thiol and the SiOHAl framework of the zeolite, (b) a cyclic hydrogen bonding zeolite–thiol complex, and (c) a cyclic protonated zeolite–thiol complex, where the sulfur compound is hydrogen bonded to oxygens on the zeolite surface. Sosun et al. [13,14] have studied the adsorption of methanethiol and ethanethiol on acidic zeolites, while other groups have studied the interaction of other OSCs with zeolites [15]. However, the theoretical studies on the degradation mechanism of organosulfur compounds have been focused so far to the best of our knowledge, on the investigation of the adsorption process and have not been extended to the elucidation of the detailed reaction pathways and the intermediates involved.

In this research project we have investigated computationally the degradation reactions of ethanethiol, catalyzed by an acidic zeolite of the FAU form. Specifically two reaction pathways are considered, the dehydrosulfidation (DHS), i.e., the t2 direct elimination channel and a Sw2 (stepwise) type channel, leading to final products through the intermediate formation of a stable ethoxide complex. The results are discussed and compared with whatever findings exist in the literature on similar systems [16].

2. Theoretical methods and computational details

To study reactions inside zeolites, their pore structure must be taken into account, since the confinement effect of the zeolite micropores plays important roles in reactions taking place on its surface. Several theoretical models, including periodic boundary conditions calculations, have been proposed to study crystalline zeolite systems [17–21]. Nevertheless, zeolites that have high impacts in industrial processes usually possess hundreds of atoms per unit cell. This renders the use of these sophisticated methods computationally too expensive and even

impractical when very large zeolites are concerned. Therefore, their electronic properties are usually modeled with quantum chemical methods for relatively small clusters, where focus lies only on the most important part of the zeolite structure [22–24]. Regardless of the small size of these models, such studies have given interesting details of the adsorption process and the catalytic mechanism. However, due to the small size of the clusters employed, the effect of the framework that plays an important role in the structure and energetics of the system is not taken properly into account. As a result, the contribution of the van der Waals interactions between adsorbed species and the zeolite walls in the energetics of adsorption/desorption process, is frequently underestimated. The recent development of hybrid approaches, such as the combined quantum mechanics/molecular mechanics (QM/MM) methods, allows the use of much larger model systems with a moderate increase of computational cost. The hybrid methods lead to quite reliable results that may be compared with periodic calculations. One such method is the original ‘Our-own-N-layer Integrated molecular Orbital + molecular Mechanics (ONIOM)’ approach, which has been developed by Morokuma and co-workers [25,26] and extended to the regime of large chemical and biological systems. The ONIOM scheme that uses a high level computational methodology for the active site, i.e., a limited number of tetrahedra and molecular mechanics techniques for the remaining of the cluster, has found a wide applicability in the investigation of many catalytic processes on zeolite surfaces [27–39].

In this paper the reaction mechanism of the ethanethiol transformation was investigated over acidic zeolite surface using 20T and 38T model clusters, simulating the FAU zeolite Y with a framework Si/Al ratio of about 16 [40,41]. Two different ONIOM schemes, ONIOM2 and ONIOM3, using *ab-initio*, density functional theory (DFT) and MM methods have been employed. The models subdivide the cluster into two and three layers respectively, the active region and the remaining framework (further subdivided into two regions in ONIOM3) and they are well adapted for computational efficiency.

The 20T cluster including one hydroxyl Brønsted acid site (BAS) and corresponding to the molecular formula $\text{Si}_{19}\text{O}_{36}\text{H}_{32}\text{Al}(\text{OH}_p)$, is represented by a 12-membered-ring (MR) window consisted of 11 tetrahedral Si atoms and one Al tetrahedral atom and connecting two supercages of faujasite (Fig. 1a). Eight more tetrahedral Si atoms are included at the base next to the Al atom. This model has been studied with the help of the two-layered ONIOM2 methodology. The high method employed is the recent highly accurate empirical M06-2X functional developed by Zhao and Truhlar [42], combined with the 6-31 + G(d,p) basis set, that has been used to treat the 12T ring atoms along with the ethanethiol molecule. The remainder of the cluster is treated by molecular mechanics force fields (UFF) [43]. The total

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