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H-FER-Catalyzed Conversion of Methanol to Ethanol and Dimethyl Ether: a First-Principles DFT Study

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ABSTRACT

Methanol adsorption and dehydrogenation reactions within zeolites represent important steps in the catalytic conversion process to form long-chain hydrocarbons. Herein, first-principles density functional theory (DFT) is employed in the determination of methanol adsorption and conversion in ferrierite (FER), where we predict the fundamental adsorption geometries and energetics of methanol adsorption. The methanol molecule is shown to physisorb at all explored binding sites, stabilized through hydrogen-bonded interactions with the acid site at O$_{meth}$–H$_{bas}$ bond distances ranging from 1.33–1.51 Å. We demonstrate that the zeolites’ adsorption capability is affected by the silicon/aluminium ratio, with stronger adsorptions predicted in the material with silicon to aluminium fractions of 5 than 8. The adsorption strength is also found to vary depending on the tetrahedral binding site, with the T1O2 site yielding the most stable methanol adsorption structure in the Si/Al ratio = 5 ($E_{ads} = -22.5$ kcal mol$^{-1}$), whereas the T1O1 site yields the most stable adsorption geometry ($E_{ads} = -19.2$ kcal mol$^{-1}$) in the Si/Al ratio = 8. Upon translational and rotational motion, methanol is protonated resulting in the breaking of its C-O bond to form a methoxy species bound to the framework oxygen (O–CH, distance of 1.37 Å), whereas the water molecule is stabilized at the acid site through H-bonding (O$_{water}$–H = 2.0 Å). Further reaction between the methoxy species and a second methanol molecule results in the formation of ethanol and protonated dimethyl ether, with adsorption energies of ~42 and ~25 kcal mol$^{-1}$, respectively. The results in this study provide atomistic insight into the effect of acidity of the FER zeolite on the adsorption and conversion of methanol.

KEYWORDS

Zeolites, ferrierite, methanol adsorption, acid sites, density functional theory (DFT).

1. Introduction

Methanol is an attractive energy carrier and an abundant resource for the synthesis of important liquid fuels and hydrocarbon products. The extensively studied methanol to hydrocarbons process (MTH) is an important step in the promising route to obtaining products that are relevant to the petrochemical industry, which is crucial for the ‘Methanol Economy’ concept. The olefin- and aromatic-cycles are proposed as the central mechanism of methanol conversion, which consists of two catalytic cycles interconverting a range of surface species (hydrocarbon pool). The hydrocarbon pool mechanism can be categorized into two main parts: the olefin cycle which involves the methylation and subsequent cracking of alkenes (both small and large) and the aromatic cycle which is governed by methylation of aromatic compounds with cracking of side chains. The local concentrations of hydrocarbon species within the zeolite dictate the contribution of each cycle.

Earlier reports have shown that the platinum-based catalyst Pt-Re/Al$_2$O$_3$ shows great selectivity in the alcohol conversion process with products within the range C$_2$–C$_4$.$^1$ Even with a varying yield of 20–50 wt.%, the general implementation in severe systems is severely limited by the high cost of precious metal catalysts.$^2$ This has caused interest in the development of more earth-abundant materials as substitutes for precious metal catalysts. Zeolites, also called molecular sieves, are attractive candidates for catalytic applications.$^2,^6$ The three-dimensional (3D) frameworks of zeolites with distinctive molecular-scale features, such as pores, channels and cavities, make them very attractive candidates for methanol conversion catalysis. The channels and cages within zeolites aid distinguishing of molecules of different geometries and sizes.$^7$ Because of their excellent catalytic activity and high hydrothermal stability under a broad scope of environmental conditions, these aluminosilicate crystals have been utilized in the refining of petrochemical products through ion exchange and adsorption/separation processes.$^{10–12}$ The reaction mechanism and product selectivity in zeolites are significantly influenced by the zeolite structure.$^{13,14}$ Intermediate formation and hydrocarbon production are shown to be greatly influenced by the acidity of the zeolite.$^{4,15}$ For instance, reduced selectivity for light olefin products through cracking is promoted by higher Bronsted acid concentrations.$^{16–18}$ Cleavage of the C-O bond is considered to be the rate-determining step of the overall reaction with some theoretical studies determining its activation barrier to be 72 kcal mol$^{-1}$$^{10,19}$.

Methanol conversion to hydrocarbons requires the cleavage of the C-O bond and subsequent formation of C-C bonds, hence the determination of the thermodynamic stabilities of methanol and its dissociated products is of great relevance.$^6,^{20}$ The activation energy barrier (54 kcal mol$^{-1}$) for the surface methoxy species formation in FER can be reduced by 10 kcal mol$^{-1}$ when the C-O cleavage occurs near an additional methanol molecule. However, the data are limited to frameworks with a Si/Al ratio of 35 and there is barely any mention of the effect of increased...
acidity. Herein, we investigate the effects of silicon/aluminium ratios (5 and 8) on the methanol adsorption, using first-principles density functional theory (DFT) to elucidate the possible reaction pathways for the methanol C-O bond breaking and C-C bond formation proposed in previous studies. The results obtained give insights, on a molecular level, into the stable adsorption configuration with thermochemical data associated with the dehydrated process when methanol is converted in zeolite H-FER to possible precursors of short-chain hydrocarbons.

2. Computational Details

The optimized structures and energetics were determined from DFT calculations as implemented in the Quantum Espresso package. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was used for geometry optimizations. The kinetic-energy cut-off of the plane-wave was set to 40 Ry and the charge density cut-off to 480 Ry. This ensures that the convergence of the total energy is within 10^-6 eV and the residual Hellmann–Feynman forces on all relaxed atoms reach 0.01 eV Å^-1. Due to the very large unit cell of FER (a = 19.0 Å, b = 14.3 Å, c = 7.5 Å), a 1 x 1 x 1 Monkhost-Pack k-point mesh was used for the integration over the Brillouin zone, which was found to be statistically adequate in describing the structural parameters of the zeolite. The lowest-energy adsorption structures and energetics of methanol were determined by adsorbing it at different sites and in different adsorption configurations. The adsorption energy (E_ads), which characterized the strength and stability of the adsorbate species in the zeolite framework, was calculated using the relation:

\[ E_{\text{ads}} = E_{\text{zero-ads}} - (E_{\text{zero}} + E_{\text{ads}}) \]

where \( E_{\text{zero-ads}} \) and \( E_{\text{ads}} \) are the total adsorption energy of the zeolite with the adsorbate, isolated zeolite framework, and the free adsorbate molecule, respectively. Based on this definition, a negative or positive adsorption energy denotes an exothermic (favourable) or endothermic (unfavourable) process. The visualizations and graphical representation of all structures in this work were obtained using XCRYSDEN and VESTA software.

3. Results and Discussion

3.1. Characterization of Ferrierite

All-silica FER was modelled with space group Immm, No. 71 with an orthorhombic structure. The initial coordinates (lattice parameters and atomic positions) obtained from the International Zeolite Association (IZA) database were subjected to full geometry optimization to attain the most stable configuration for the structure and lattice parameters such as bond length and angles based on the level of theory. Silicon atoms within the fully optimized FER framework were then substituted for aluminium atoms at the various tetrahedral sites to suit the desired Si/Al ratios of 5 and 8. The distribution of the substituted Al atoms obeyed the Löwenstein’s rule, prohibiting Al-O-Al connections and also the Dempsey’s rule permitting the maximum allocation of negative charges within the framework. Figure 1 shows the fully optimized all-silica and Al-substituted H-FER. Summarized in Table 1 are the optimized structural parameters including the lattice parameters, interatomic bond distances and angles, which are all in good agreement with known experimental data and previous DFT calculations.

3.2. Methanol Adsorption in Ferrierite

The adsorption and dehydration of a methanol molecule in the zeolite framework is an important starting step in its conversion to safer and more useful renewables. We therefore first determined the lowest-energy adsorption configuration of methanol in the FER framework with Si/Al ratios of 8 and 5, and characterized the extent of C-O bond activation. The preferred methanol adsorption sites within the framework were determined by exploring the T1, T2, and T3 sites in the 10 MR channel of the H-FER zeolite. The lowest-energy adsorption structures of methanol in the FER framework with ratios of 8 and 5 are shown in Figs. 2 and 3, respectively. The methanol molecule is physisorbed at all explored binding sites where it is stabilized through H-bonding with the acid site at O_{bulk}—H_{framework} bond distances ranging from 1.33–1.51 Å. As shown in Table 2, the adsorption energies are found to be generally more stable in the Si/Al ratio of 5 than 8, which can be linked to the high concentra-
tion of acid sites within the zeolite ratio of 5 that permits the formation of more hydrogen-bonded interactions compared to a ratio of 8. The adsorption strength is found to vary depending on the tetrahedral binding site, with the T1O2 and T1O1 sites yielding the most stable methanol adsorption structure in ratio 5 \( (E_{\text{ads}} = -22.5 \text{ kcal mol}^{-1}) \) and 8 \( (E_{\text{ads}} = -19.2 \text{ kcal mol}^{-1}) \), respectively. The most stable adsorption structures are characterized by shorter O\text{meth}–H\text{fram} bond distances as shown in Table 2. The relative energies obtained are in good agreement with previously reported values of 15–27 kcal mol\(^{-1}\) in the literature.\(^{28,20}\)

| Tetrahedral sites | Si/Al = 5 | Si/Al = 8 |
|-------------------|------------|------------|
|                   | \( E_{\text{ads}} \) (kcal mol\(^{-1}\)) | \( d(\text{O\text{meth}–H\text{fram}}) \) Å | \( E_{\text{ads}} \) (kcal mol\(^{-1}\)) | \( d(\text{O\text{meth}–H\text{fram}}) \) Å |
| T1O1              | -17.1      | 1.40       | -19.2       | 1.37       |
| T1O2              | -22.5      | 1.33       | -10.1       | 1.47       |
| T1O3              | -17.8      | 1.41       | -11.8       | 1.40       |
| T2O2              | -8.8       | 1.51       | -10.3       | 1.47       |
| T2O6              | -16.2      | 1.41       | -12.1       | 1.35       |
| T3O1              | -19.8      | 1.44       | -12.5       | 1.39       |
| T3O8              | -4.7       | 1.57       | 3.4         | 1.55       |

Figure 2: Optimized adsorption structures of methanol in FER with Si/Al of 5. Atomic colour code: Al (purple), C (black), H (white), O (red), Si (orange).

Figure 3: Optimized adsorption structures of methanol in FER with Si/Al of 8. Atomic colour code: Al (purple), C (black), H (white), O (red), Si (orange).
From the differential charge density isosurface analysis (Fig. 4), we observed electron density accumulation in the \( \text{O}_{\text{meth}}-\text{H}_{\text{fram}} \) regions, which is consistent with H-bonded interactions.

Figure 4 Differential charge density iso-surface contours of the most stable methanol adsorption geometries in FER with Si/Al ratios (a) 5 and (b) 8. The green and yellow isosurfaces denote accumulation and depletion of electron density by ±0.02 e/Å\(^3\), respectively. Atomic colour code: Al (purple), C (black), H (white), O (red), Si (orange).

3.3. Methanol Dehydration to form Methoxy Species in FER

Protonation of short-chain alcohols in zeolites occurs through geometrical changes owing to a high concentration of charge. The protonation step has been described as a concerted reaction between the O-H bond of the framework and the O-H of methanol, which results in the C-O bond breaking. The protonation process is generally characterized by various translational and rotational motions\(^{39}\) that leads to the cleavage of the C-O in dehydration. Shown in Fig. 5 is the schematic of the dehydration process of methanol within the FER framework with Si/Al = 5, where the physisorbed methanol attracts a proton at the acid site, reorients such that the –CH\(_3\) end binds at an O-site, followed by the final spontaneous dehydration step. It is worth noting that stable protonated methanol (as observed in Fig. 5b), which was not observed in earlier studies, was obtained after geometry optimization.\(^{40,21}\) This structure, leading to an adsorption energy of \(-15\) kcal mol\(^{-1}\), is stabilized because of the orientation of the methanol molecule between two close and electro-negatively equivalent framework O\(_2\) oxygens (O\(_2\) are 2.63 Å apart). The methoxy species is bound at an O–CH\(_3\) distance of 1.37 Å, whereas the water molecule is stabilized at the acid site through H-bonding (O\(_{\text{out}}\)-H = 2.0 Å). The co-adsorption of the methoxy species and water molecule releases an energy of 11 kcal mol\(^{-1}\), which compared to the physisorbed methanol molecule, indicates an endothermic reaction. The understanding behind the endothermicity of the methoxy species formation is that breaking a very strong methanol HO-CH\(_3\) bond requires a greater amount of energy compared to forming the weaker framework O-CH\(_3\) and H-bonded H\(_2\)O to the framework.

Figure 5 Schematic diagram showing an encounter of the methanol molecule at a Brønsted acid site (conformation before geometry optimization), where (a) the methanol molecule attaches to the proton at the acid site, forming (b) a methoxonium ion, which appears to be stabilized by two equivalent bridging oxygens. The carbon of the methoxonium ion then forms a C-O bond when brought close to a vacant acid site in (c). The H\(_2\)O attached to the carbon in the methoxonium system in (e) then cleaves off, forming the framework methoxy and ‘free’ H\(_2\)O in (d). Atomic colour code: Al (purple), C (black), H (white), O (red), Si (orange).

3.4. Post Dehydration Reactions (Ethanol Formation)

The thermodynamic stability of the products formed when a second methanol molecule reacts with the framework methoxy species was also investigated. The incoming methanol molecule can attach to the methoxy species via two possible modes: either through its carbon end (forming a C–C bond) or the hydroxyl oxygen (forming an O–C bond). The C–C mode of attachment resulted in the formation of ethanol, which released an energy of 42 kcal mol\(^{-1}\), as clearly illustrated in Fig. 6a. The O–C mode of attachment, on the other hand, resulted in the formation of a stable protonated dimethyl ether species (Fig. 6b), which released an energy of 25 kcal mol\(^{-1}\). The increased stability of the ethanol molecule is a direct result of strong H-bond interaction between the O-H end of the ethanol and the proton of the Brønsted acid sites (O–H = 1.36 Å), which is consistent with the observed electron density accumulation in the interaction regions, as revealed by the differential charge density isosurface contour plot shown in Fig. 7a. A similar observation was made in a previous study, where the product was referred to as an ethoxonium ion.\(^{41}\) The formation of the ethanol molecule is made possible by hydrogen transfer from the carbon end of the...
incoming methanol molecule to the hydroxyl oxygen end, which finally detaches from the framework O site. Although the protonated dimethyl ether species is lower in thermodynamic stability compared to the formed ethanol, it is known to be the predominant species that is formed in the methanol to gasoline (MTG) process. The protonated dimethyl ether is observed in some experiments to form at lower temperatures, but at higher temperatures, it degenerates back to the methoxy species. H-bonding between the proton attached to the dimethyl ether and the water molecule in the channel at 1.2 Å enhances the stabilization of the ion formed (Fig. 7b). An O-H bond distance of 1.18 Å and C-O-C bond angle of 112° for dimethyl ether was observed, as can be seen in the optimized structure (Fig. 6b). This result can be attributed to the highly acidic nature of the zeolite and the existence of a water molecule as a product of dehydration in the zeolite. Water molecules are not only speculated to pose as delocalizing agents of protons in the framework, but also facilitate the thermodynamic stability of the products that are formed through H-bonding. It was also observed that the FER pore undergoes a distortion where the T-O-Si bond angle changes by 28° with a corresponding reduction in the pore diameter from 8.9 to 8.3 Å. Since the pore is charge-saturated, the framework oxygens are more likely to cause an elliptical distortion of the channel to better accommodate the ethoxonium, which has been reported previously. The adsorbed methanol molecule could undergo deprotonation and dehydration reactions to produce ethylene, based on the proposed scheme shown in Fig. 8.

Figure 7  Differential charge density iso-surface contours due to the adsorption of (a) ethanol and (b) protonated dimethyl ether species in FER with Si/Al ratio of 5. The green and yellow isosurfaces denote accumulation and depletion of electron density by ±0.02 e/Å, respectively. Atomic colour code: Al (purple), C (black), H (white), O (red), Si (orange).

Figure 8  Proposed reaction schematic for the deprotonation and dehydration of ethanol to produce ethylene.

4. Conclusion

The adsorption and conversion reactions of methanol in the FER framework with different Si/Al ratios of 5 and 8, have been studied employing first-principles DFT calculations. Based on predicted adsorption geometries and energetics, it was demonstrated that the methanol molecule is physisorbed at all explored binding sites, where it is stabilized through hydrogen-bonded interactions with the acid site at O_meth—H_meth bond distances ranging from 1.33–1.51 Å. Stronger adsorption energies were predicted for the FER with Si/Al ratio of 5 than 8, with the most stable adsorption geometries releasing energies of ~22.5 and ~19.2 kcal mol⁻¹, which suggests that the adsorption strength of methanol is affected by the Si/Al ratio. Protonation of the adsorbed methanol molecule results in translational and rotational motions leading to the breaking of the C-O bond to form methoxy species bound to the framework oxygen (O—CH₃ distance of 1.37 Å), whereas a water molecule is stabilized at the acid site through hydrogen-bonded interactions (O_wat—H = 2.0 Å). The formation of stable physisorbed ethanol and protonated dimethyl ether species is demonstrated from further reaction with a second methanol molecule. These results provide atomistic insight into the adsorption geometries and energetics of methanol and its reaction products in the FER zeolite.

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Supplementary Material

The supplementary information contains the optimized atomic coordinates for acidic FER with and without adsorbing species.

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Supporting Information

H-FER-Catalysed Conversion of Methanol to Ethanol and Dimethyl Ether: A First Principles DFT Study

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| Si | Al | T1O1 | T1O2 |
|---|---|---|---|
| O  | 30 | 70 | 100 |
| 0  | 0.603847325 | 1.248393664 | 0.202031298 |
| 0  | 1.107072951 | 0.971385544 | 5.807989421 |
| 0  | 13.100551871 | 4.820790473 | 3.957338728 |
| 0  | 13.190640083 | 2.422276511 | 5.270261241 |
| 0  | 12.684915343 | 13.020600233 | 1.853579940 |
| 0  | 6.259652972 | 9.799376388 | 3.889039510 |
| 0  | 6.104047949 | 1.318979538 | 5.468385835 |
| 0  | 0.601588389 | 13.06651792 | 5.928242238 |
| 0  | 13.021785284 | 12.876362729 | 1.908437572 |
| 0  | 3.724181229 | 5.803581010 | 5.382338488 |
| 0  | 3.943080730 | 5.792242265 | 1.909129688 |
| 0  | 3.699003480 | 3.857512252 | 1.956074173 |
| 0  | 3.024181229 | 5.803581010 | 5.382338488 |
| 0  | 15.712059305 | 5.909201827 | 5.779349797 |
| 0  | 7.709598099 | 8.532842727 | 1.659568944 |
| 0  | 0.992275581 | 0.618999938 | 2.070830416 |
| 0  | 0.341818826 | 4.040992701 | 5.711199197 |
| 0  | 6.774802372 | 3.579016156 | 2.809079630 |
| 0  | 12.706117493 | 11.098360520 | -0.187376220 |
| 0  | 11.648076706 | 5.711974407 | 8.497322072 |
| 0  | 13.890499999 | 10.717110770 | 2.310938966 |
| 0  | 7.590025478 | 10.908419896 | 2.450398987 |
| 0  | 7.590025478 | 10.908419896 | 2.450398987 |
| 0  | 7.590025478 | 10.908419896 | 2.450398987 |
| 0  | 7.590025478 | 10.908419896 | 2.450398987 |
| 0  | 7.590025478 | 10.908419896 | 2.450398987 |
| 0  | 7.590025478 | 10.908419896 | 2.450398987 |
| 0  | 7.590025478 | 10.908419896 | 2.450398987 |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| Si      | 6.416157944 | 11.4611691 | 0.600490790 |
| Si      | 12.82057072 | 2.922265646 | 5.73358707 |
| Si      | 15.61255846 | 3.82942766 | 5.39410190 |
| Si      | 17.58340786 | 0.77609966 | 2.79184324 |
| Si      | 11.96426063 | 2.802854456 | 0.54560665 |}

| Coordinates for zeolite FER Si/Al =5 |
|----------------------------------------|
| symmetry  | X       | Y       | Z       |
| T2O6      | 5.51200840 | 1.45388838 | 2.19847094 |
| T2O6      | 12.92557166 | 13.21431836 | 5.76168800 |
| T2O6      | 13.4876362 | 1.74388445 | 5.20566014 |
| T2O6      | 12.56771162 | 12.99560286 | 1.99013409 |
| T2O6      | 6.35282289 | 13.21903258 | 1.85123808 |
| T2O6      | 5.99024466 | 1.33050277 | 5.61253284 |
| T2O6      | 6.25022870 | 13.09964053 | 5.90692017 |
| T2O6      | 13.38730987 | 2.27245923 | 0.50766392 |
| T2O6      | 15.35956353 | 8.46678238 | 5.76951507 |
| T2O6      | 6.11990426 | 0.82503077 | 2.03527941 |
| T2O6      | 3.59598959 | 8.64005836 | 1.96684879 |
| T2O6      | 2.87510802 | 8.54145456 | 5.96309205 |
| T2O6      | 15.79601916 | 5.87290999 | 5.98400617 |
| T2O6      | 15.52441605 | 8.57516035 | 1.76331317 |
| T2O6      | 8.73586498 | 0.80118082 | 1.98510852 |
| T2O6      | 3.29928014 | 8.44145456 | 5.96309205 |
| T2O6      | 6.90310839 | 3.68666826 | 2.71302862 |
| T2O6      | 6.11268325 | 13.11115590 | 4.87540847 |
| T2O6      | 13.8577642 | 5.60076964 | 5.14261975 |
| T2O6      | 13.36460338 | 8.45352202 | 3.60321264 |
| T2O6      | 7.45801976 | 10.01319087 | 2.69337877 |
| T2O6      | 7.45802629 | 3.76019338 | 5.31215674 |
| T2O6      | 7.61664507 | 10.87693103 | 5.44887496 |
| T2O6      | 11.57657355 | 4.77367097 | 2.29710722 |
|          | T100 | T101 |
|----------|------|------|
| O       | 1.41039026  
5.90824854 | 0.331640505  
1.64219284 |
| H       | 7.78973169  
1.46435162  
0.33505696 | 0.972889176  
1.972889176  
0.757245286  
0.574324526 |
| Si      | 12.9346354  
6.1874710  
13.09391260  
2.12828508 | 0.385680587  
6.50458685  
0.50458685  
0.99650486 |
| Al      | 1.2935479 | 0.1494479  
0.84652468  
0.50458685  |
| C       | 1.2935479 | 0.1494479  
0.84652468  
0.50458685  |
| H       | 1.2935479 | 0.1494479  
0.84652468  
0.50458685  |
| Si      | 12.9346354  
6.1874710  
13.09391260  
2.12828508 | 0.385680587  
6.50458685  
0.50458685  
0.99650486 |
| Al      | 1.2935479 | 0.1494479  
0.84652468  
0.50458685  |
| C       | 1.2935479 | 0.1494479  
0.84652468  
0.50458685  |
| H       | 1.2935479 | 0.1494479  
0.84652468  
0.50458685  |
| Si      | 12.9346354  
6.1874710  
13.09391260  
2.12828508 | 0.385680587  
6.50458685  
0.50458685  
0.99650486 |

**Note:** The table represents the coordinates for different atoms in the T100 and T101 structures with methanol adsorption at various T sites. The columns represent the atomic species (Si, Al, C, H), followed by the Cartesian coordinates in angstroms (Å). The table is structured in a tabular format with rows for different T sites and columns for x, y, and z coordinates. The coordinates are given in a 3D Cartesian coordinate system.
Acidic Sites with Methanol adsorbed at various Coordinates for FER at Si/Al=8

**Dimethyl ether formation in the framework**

**Ethanol formation in acidic FER framework**
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 0.715187454 | 7.113071633 | 1.39876688 |
| C    | 1.576490885 | 6.171044473 | 3.774806763 |
| H    | 1.988076885 | 7.451918923 | 2.576862746 |
| H    | 2.298182310 | 7.712255805 | 4.342111142 |
| H    | 0.359727616 | 8.975353530 | 3.594207025 |
| H    | -1.675070007 | 7.533262148 | 3.345862803 |
| H    | -0.669098266 | 6.062047375 | 3.57252997 |
| H    | -0.541501471 | 7.215813737 | 1.973526062 |
| C    | 0.043938422 | 6.656397779 | 3.57908586 |
| C    | 1.646451118 | 7.248598089 | 3.59742995 |
| H    | 1.961032547 | 7.438811141 | 2.992989104 |
| H    | 0.662028262 | 7.938712213 | 1.955389976 |
| H    | 0.822739164 | 8.668585940 | 3.561003185 |
| H    | -1.869891414 | 7.649113544 | 4.44937029 |
| H    | -1.745417767 | 7.458579529 | 2.778290345 |
| H    | 0.041480032 | 5.728638878 | 2.979835064 |
| H    | 0.292638274 | 6.403397465 | 4.618766114 |
| C    | -0.714552139 | 7.112263700 | 3.052096548 |
| C    | 0.043938422 | 6.656397779 | 3.57908586 |
| C    | 0.909666084 | 7.732401551 | 3.003932055 |