Methane Removal Using Zeolites: A Computational Analysis

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ABSTRACT

Global warming is a pressing problem in the world today and it is exacerbated by the release of greenhouse gases, such as methane, into the atmosphere. Zeolites are being examined as a potential solution to the methane problem because they can act as catalysts for chemical reactions due to their unique structure. In particular, zeolites containing transitional metals show promise in being catalysts for the selective oxidation of methane to methanol, which can turn the greenhouse gas into a usable fuel source. In my project, I model the synthetic zeolite ZSM-5 using the modeling software SPARTAN. I change the structure of the zeolite to contain different transition metals (Au, Co, Cu, Fe, Ni) and calculate the energy as a methane molecule passes through the molecular sieve. By looking at the energy of the zeolite as the methane passes through, and comparing the energy between the different zeolites, I can determine their effectiveness relative to each other. This allows me to determine which zeolites are more promising in their potential for atmospheric methane removal.

INTRODUCTION

Climate change, an enormous problem that we are facing today, is exacerbated by the release of greenhouse gases. These gases have different atmospheric lifetimes and warm the Earth to different degrees. Though methane stays in the atmosphere for only about 12 years, it is the number-two greenhouse cause of climate change because it reflects around 100 times as much heat as CO_2. Also, unlike CO_2, most methane emissions are human-driven. This means that it is up to us to either decrease methane production or find effective ways to remove it from the atmosphere.

Zeolites are one potential solution to the methane problem. They are solids made of aluminum, silicon, and oxygen and they have no known harmful effects on the environment. Zeolites are important because they have a unique structure that consists of tube-like pores that can trap molecules and atoms inside them. Since these pores have a fixed size, synthetic zeolites can be made to trap certain molecules while letting others pass through. The zeolite can be used as a catalyst since trapped molecules can undergo chemical reactions inside the pores.

The reaction to focus on with methane is methane oxidation. The greenhouse gas can be removed from the atmosphere while also being turned into methanol, which can be reused as a fuel source. Research has been done to show that the direct methane to methanol conversion can be done using certain transition metals with the synthetic zeolite ZSM-5. Further research on these different zeolites could be beneficial to optimizing methods of methane removal. This can have huge impacts on our strategies to combat global warming and may help minimize methane's crushing hold on our environment.

METHODOLOGY

The goal of this project was to research the effectiveness of different zeolites as catalysts for methane oxidation. To do this, the software Spartan was used to model a Si-ZSM-5 zeolite, which has the MFI framework type. In order to model the zeolite in SPARTAN, its XYZ coordinates were needed, which were obtained from software that was able to read the coordination sequence and vertex symbols of the MFI framework. Then, the focus was placed on a smaller section of the whole zeolite (to cut down on computational time) by removing all the atoms that were not a part of the channel and adding hydrogen to the oxygen atoms that needed electrons. At the beginning of the channel, a methane molecule was placed. Copies of the zeolite were made, changing the location of the methane so it was 1 Å farther in the channel, until there were 20 molecules that moved through the zeolite in steps. Afterwards, a MMFF calculation was run to find the energy of the zeolite in each of the 20 methane locations, which were also graphed.

Once the Si-ZSM-5 was established as a baseline, modeling zeolites containing different transition metals (Au, Co, Cu, Fe, Ni) was necessary. To begin, I needed to figure out which Si atoms to replace with the transition metal. The energy when each of the six Si molecules at the beginning of the channel was replaced with a transition metal was calculated. After finding the location where the molecule had the lowest energy, the corresponding Si atom and symmetrical Si atoms were changed to the transition metal. The location of atoms in real zeolites has some randomness, so to imitate this in the computer model only every other atom was changed. Then, the methane passing through the channel was modeled and the energy at each step was calculated again, using MMFF calculations. This entire process was repeated for each transition metal and the results were graphed.

TABLES, FIGURES, IMAGES fully captioned

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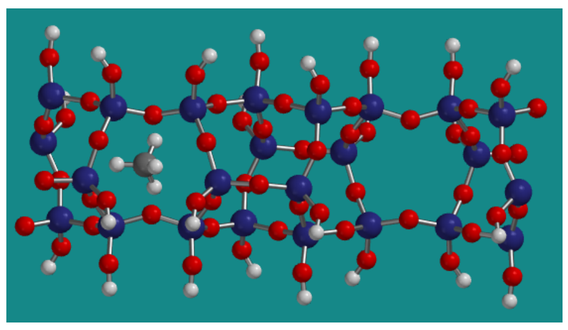
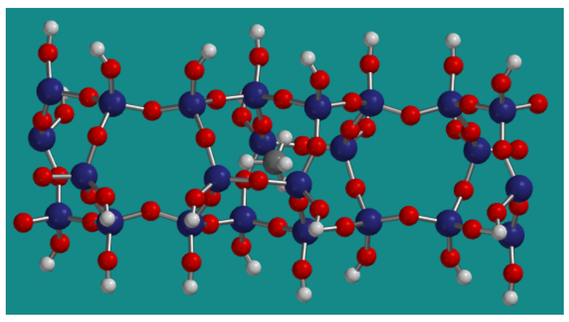


(3b)



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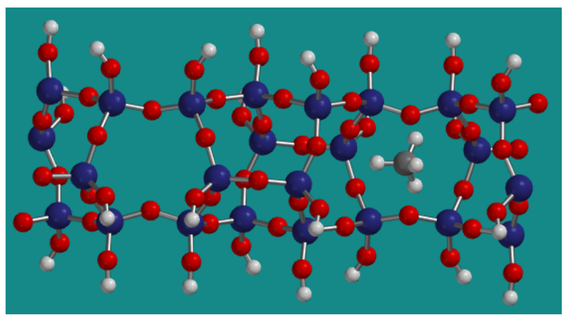


Fig. 3. A methane molecule inside Si-ZSM-5 channel at 4 Å (3a), 9 Å (3b) and 14 Å (3c).

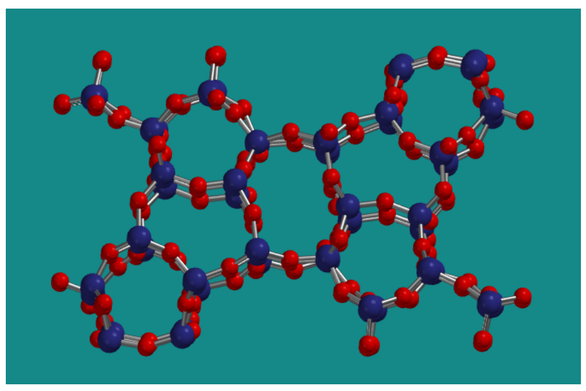


Fig. 1. Si-ZSM-5 zeolite structure using XYZ coordinates

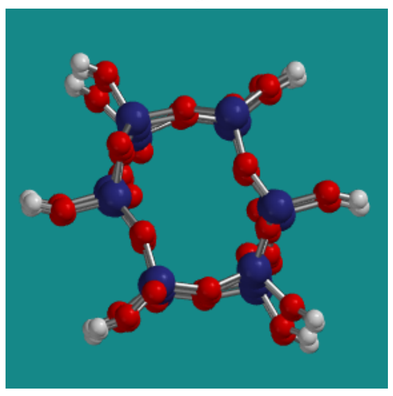
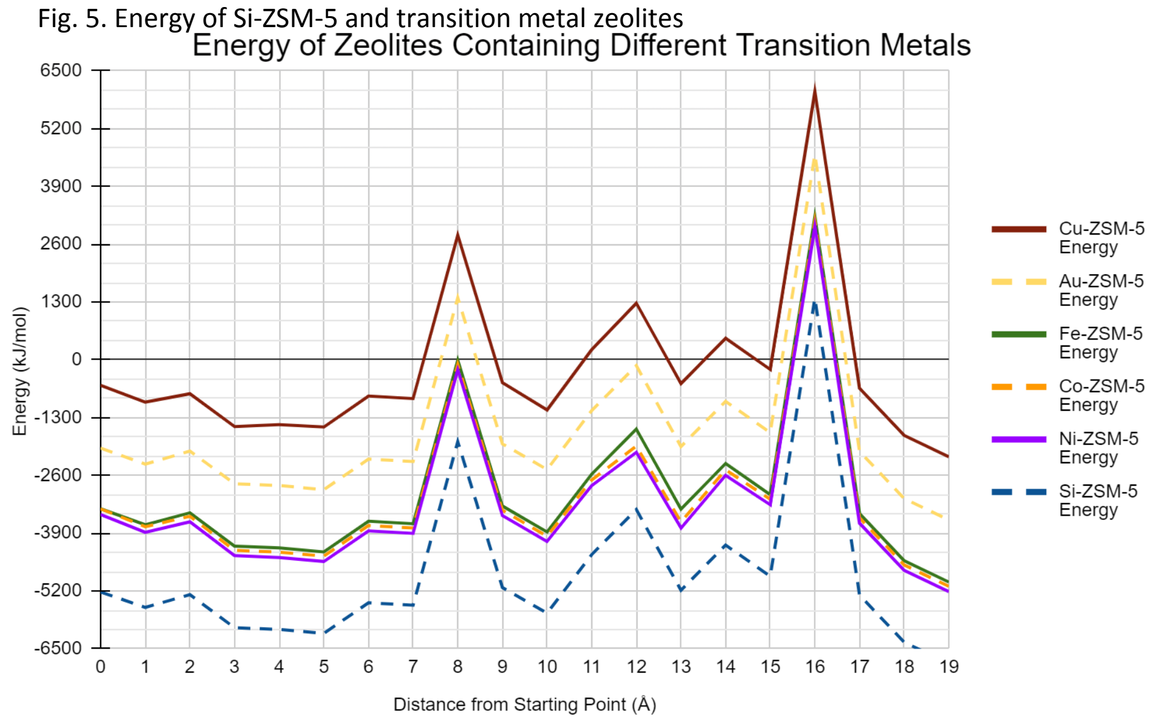
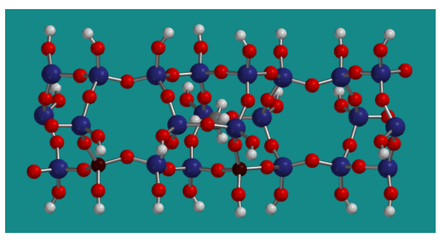


Fig. 2. One Si-ZSM-5 channel with added hydrogen atoms

Fig. 5. Energy of Si-ZSM-5 and transition metal zeolites



(4a)



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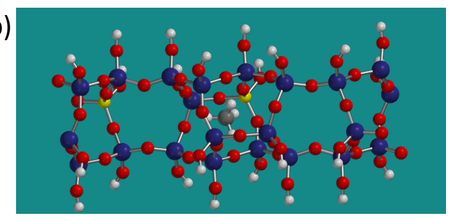

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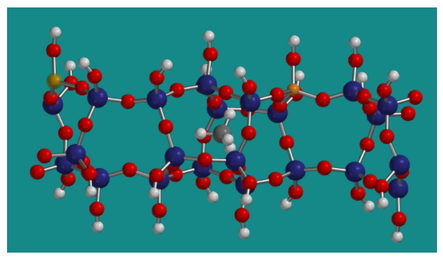
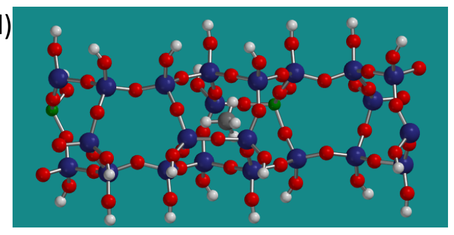


(4d)



(4e)

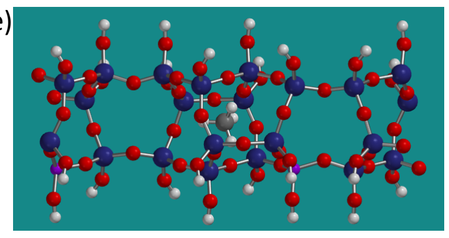


Fig. 4. A methane molecule at 9 Å in Cu (4a), Au (4b), Fe (4c), Co (4d), and Ni (4d) ZSM-5 zeolites.

CONCLUSIONS

All six zeolites had similar energy graphs (Figure 5), with two major jumps in energy at 8 Å and 16 Å inside the channel. During both those jumps, the methane molecule was less than 1 Å away from an oxygen atom in the zeolite. This could explain the increase in energy since the hydrogen in the methane would react with the oxygen. The increase in energy means that it takes a lot of energy for the molecule to get to those two locations while it can pass through the rest of the zeolite using less energy. While the changes in the energy look similar as the methane moves through the zeolite, the magnitudes of energy are different. The Si-ZSM-5, which was the baseline for the other zeolites, needed the least energy. When comparing the zeolites containing transition metals, it is visible that Cu-ZSM-5 required the most energy, followed by Au-ZSM-5. Higher energy levels mean that the selective oxidation of methane to methanol using the zeolite as a catalyst would require higher temperatures. These high temperatures can make it difficult to put the theory into practice so Cu-ZSM-5 and Au-ZSM-5 may not be the best zeolites to try to use as catalysts. Next are Fe-ZSM-5, Co-ZSM-5 and Ni-ZSM-5, with energy levels that are very close to each other. This could possibly be caused by their close proximity on the periodic table, along with their similarities in physical and chemical characteristics. They require less energy for the methane molecule to pass through a channel and would work as a catalyst at lower temperatures. Future experimental research could be done by looking at the different zeolites in this analysis and trying to catalyze the methane to methanol reaction at different temperatures. Continued computational research could also look at more transition metals in ZSM-5 and begin to examine other zeolite frameworks too.

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