

Effects of Aluminum Substitution Configurations on the Catalytic Performance of Iron-Substituted Zeolite MFI for N_2O Activation

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Abstract— This study investigates the catalytic performance of iron-substituted zeolite MFI for N_2O activation, focusing on the impact of aluminum substitution configurations on the catalytic performance of the zeolite. Our results indicate that the preferable site for the substitution of aluminum is in the T11-T2 position, with the strongest adsorption observed in the T11-T1 position. Furthermore, the most favorable activation of N_2O was found to occur in the T7-T1 position. These findings provide crucial insights into the role of aluminum substitution in the design of high-performance zeolite catalysts for N_2O activation. Overall, this study contributes to the advancement of efficient and sustainable strategies for the removal of N_2O from industrial processes.

Keywords—DFT, Zeolite, N_2O

I. INTRODUCTION

Nitrous oxide (N_2O) is a potent greenhouse gas and a significant contributor to climate change. It has a global warming potential 265 times greater than carbon dioxide (CO_2) over a 100-year timescale.[1], [2], [3] In addition to its impact on climate, N_2O is also a major air pollutant and a potent ozone-depleting substance.[4] Reduction of N_2O emissions is therefore an important global challenge. The concentration of NO_2 in the atmosphere has risen in the last years as is shown in Figure 1.

Catalytic reduction of N_2O is a promising approach to mitigate its emissions. This process involves using catalysts to convert N_2O into harmless nitrogen gas (N_2) and oxygen (O_2) by adding a reducing agent such as hydrogen (H_2) or carbon monoxide (CO). Various types of catalysts have been investigated for N_2O reduction, including noble metals, mixed metal oxides, and zeolites.[5], [6], [7], [8], [9], [10], [11]

Noble metal catalysts, such as platinum (Pt) and palladium (Pd), have been extensively studied for N_2O reduction due to their high activity and selectivity.[6], [9] However, their high cost and susceptibility to deactivation by sulfur and other impurities in the feed gas limit their practical applications. Mixed metal oxides, such as ceria-zirconia, have shown promising results for N_2O reduction at low temperatures.[5], [7]

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They also have high stability and resistance to poisoning.

However, their activity and selectivity depend on their composition and synthesis method, which makes optimization challenging.

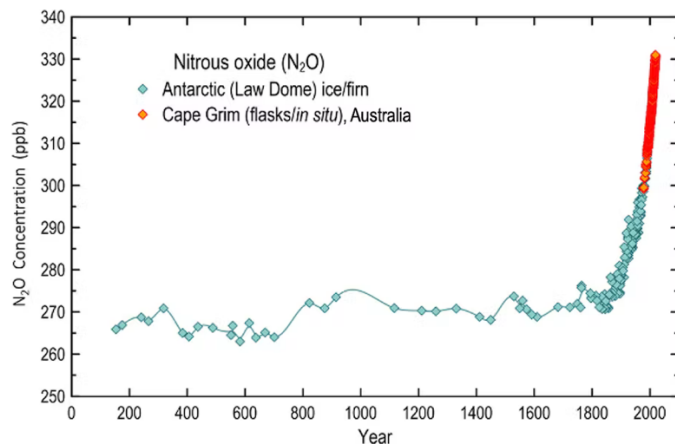


Figure 1. NO_2 concentrations, observations taken from ice cores and atmosphere.

Zeolites are microporous aluminosilicate minerals that have attracted attention as catalysts for N_2O reduction due to their unique structure and catalytic properties. Zeolites are abundant, low-cost, and have high thermal stability.[12] They also have a high surface area and uniform pore size, which allows for efficient diffusion of reactants and products.[8] Several studies have demonstrated the effectiveness of zeolites for N_2O reduction, including the use of copper-exchanged zeolites[12] and iron-exchanged zeolites.[8]

Several types of zeolites have been investigated for N_2O conversion, including ZSM-5, beta, Y, and mordenite, among others. The performance of these zeolites as N_2O catalysts is influenced by various factors such as their Si/Al ratio, crystal size, and acidity, among others. For instance, ZSM-5 zeolites with a high Si/Al ratio have been shown to have a higher activity for N_2O conversion than those with a low Si/Al ratio due to the presence of more acidic sites that can facilitate the reaction.[13]

The catalytic activity of zeolites for N_2O conversion can be enhanced through modification with various metals and metal oxides, such as copper, iron, and cobalt, which serve as active sites for the reaction. For instance, copper-modified zeolites have been shown to exhibit high catalytic activity for N_2O

conversion due to the strong interaction between copper and N_2O . [14]

The mechanisms involved in the N_2O conversion process over zeolite catalysts are complex and not yet fully understood. However, studies have suggested that the conversion of N_2O to N_2 and O_2 occurs through various pathways, including direct decomposition and reduction with hydrogen or methane, among others. [15]

The use of zeolites as catalysts for N_2O conversion has significant potential for mitigating the impacts of N_2O emissions on the environment. This has led to increased research efforts in this area, aimed at developing more efficient and effective zeolite catalysts for N_2O conversion.

In this study, we aim to analyze the catalytic performance of zeolite MFI substituted with iron for the activation of N_2O . Specifically, we will investigate how the substitution of aluminum atoms in different configurations within the zeolite affects its catalytic activity. The substitution of aluminum atoms with iron is known to introduce active sites that can facilitate the activation and reduction of N_2O , resulting in increased catalytic performance. By examining the impact of different substitution configurations on the catalytic performance of the zeolite, we can gain insights into the optimal conditions for the design of high-performance zeolite catalysts for N_2O activation.

II. METHODOLOGY

In this study, we analyzed the properties of Fe-substituted MFI zeolite for the adsorption and activation of the pollutant gas NO_2 . Density functional theory was employed to calculate the properties using the VASP program. [16] The computational calculations were carried out on the clusters of the National Energy Research Scientific Computer Center (NERSC) at Lawrence Berkeley National Laboratory.

Figure 2 illustrates the unit cell of zeolite MFI, which exhibits an orthorhombic symmetry with geometric parameters of $a = 20.09 \text{ \AA}$, $b = 19.738 \text{ \AA}$, and $c = 13.142 \text{ \AA}$. [17] The substitution of Fe in the α -ring of MFI was analyzed (as shown in Figure 3), which has been reported as the most catalytically active ring. [18] To stabilize the charge of the Fe^{+2} substitution, two aluminum atoms were replaced in the ring. All possible combinations for the replacement of two Si atoms with Al atoms were systematically analyzed, with the only imposed restriction being Loewenstein's rule, which specifies that two consecutive Al substitutions are not allowed. [19]

The activation energies for N_2O were obtained using periodic DFT calculations. These calculations were performed using the VASP 5.4 computational package, with the generalized gradient approximation Perdew-Burke-Ernzrhof (PBE). [20] Standard PAW potentials were used for all elements

(Si, O, Al, N), [21] except for the Fe atom, for which higher electronic PAW pseudopotentials were used instead of the default ones. Dispersion interactions were taken into consideration using the DFT-D3 method. [22] The Brillouin zone was restricted to the G point, and the energy cutoff was set to 500 eV. A total optimization of the atoms was performed, with the parameters of the unit cell held fixed. Convergence was assumed when the force on all atoms was less than 0.05 eV/\AA .

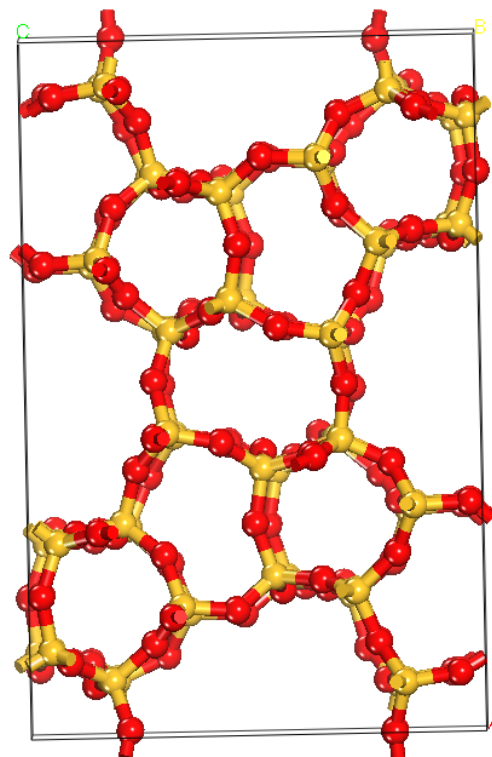


Figure 2. Zeolite MFI unit cell

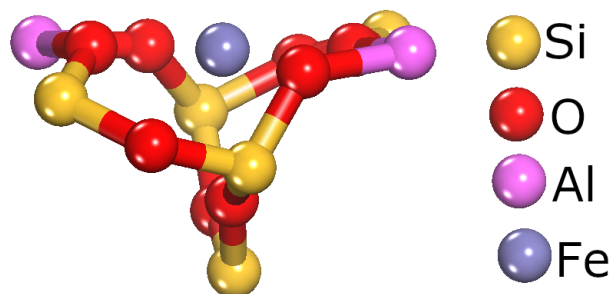


Figure 3. α -ring of MFI

III. RESULTS AND DISCUSSION

The relative energies of the α -ring of MFI with respect to the most stable aluminum substitution are displayed in Figure 4. The most stable substitution occurs at the T11-T2 site, followed by T8-T1. The most unstable substitution is at T7-T5 and has an energy that is 70 kJ/mol higher than that obtained for T11-T2. Upon comparing the optimized structures with the substitution, it is noteworthy that Fe is always located at the center of the α -ring, coordinated with four oxygen atoms.

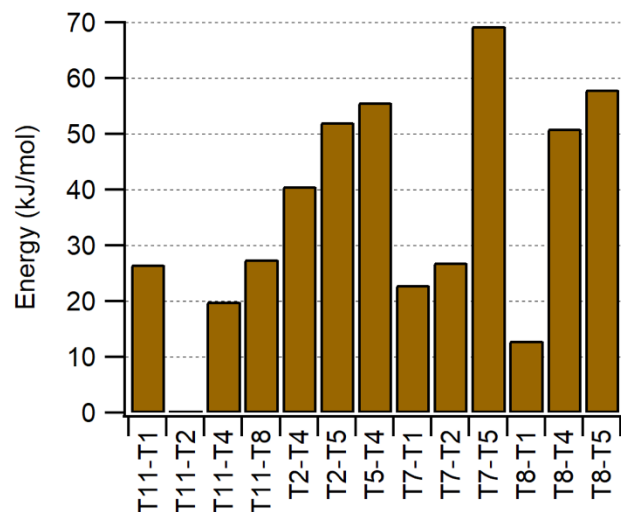


Figure 4 Relative energies for Al substitution at different sites

The distances obtained for the Fe-O bonds are comparable to those obtained by other authors for the substitution of Fe and Cu in MFI.[23] It is noteworthy that for the substitution at T11-T2, which has the most stable energetic configuration, the two Fe-Al distances are almost equal with values of 2.901 and 2.921 Å. Additionally, the O-Al-O angles formed in this configuration are similar with values of 89.5° in T11 and 91° in T2. Therefore, the addition of Al atoms at the T11-T2 sites leads to a symmetric configuration, in contrast to the asymmetric configurations obtained for less stable configurations. Figure 5 shows the optimized geometry for the substitution at T11-T2.

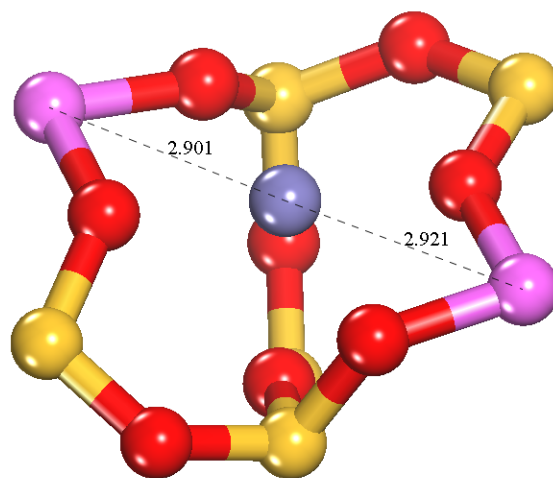


Figure 5. Optimized geometry for substitution in T11-T2

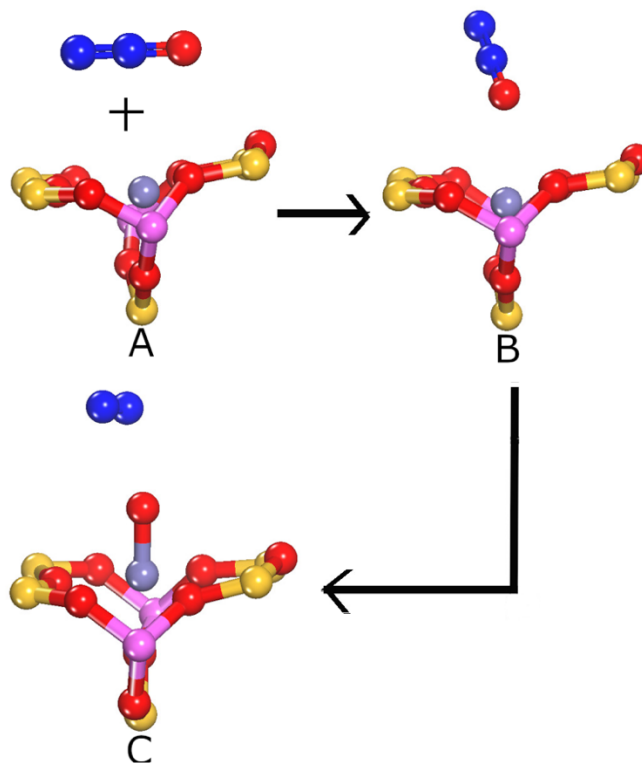


Figure 6. A mechanism for the activation of N₂O

The activation of N₂O requires two elementary steps: (1) the adsorption of N₂O and (2) the detachment of an oxygen atom to form nitrogen (N₂) as well as the site (Fe-O) in the zeolite. Figure 6 shows in detail the mechanism for the activation of N₂O. Complex B is formed by N₂O adsorbed in the zeolite, while complex C is composed of N₂O dissociated in the zeolite.

The energy of N₂O adsorption is presented in Figure 7. Positive energies were obtained for the T11-T2, T11-T8, T2-T4, T5-T4, and T8-T1 configurations, while negative energies were obtained for the other configurations. It is possible to obtain positive values for adsorption energies. Adsorption energy is defined as the energy released or gained when a

molecule or atom adsorbs onto a surface. Positive adsorption energy indicates that energy is required for the adsorption to occur, which means that the interaction between the adsorbate and the surface is unfavorable. This can happen when the adsorbate has a repulsive interaction with the surface or when the surface is not suitable for the adsorption of the specific adsorbate. However, in some cases, positive adsorption energy can also indicate weak physisorption or van der Waals interaction between the adsorbate and the surface. Hence, it can be concluded that for certain aluminum configurations, the interaction between N₂O and the zeolite is repulsive.

The strongest adsorption is achieved by substituting T11-T1, followed by T8-T5, with values of -77 kJ/mol and -62 kJ/mol, respectively. The weakest adsorption is achieved by the substitutions T8-T1 and T11-T8, both with positive values of 82 kJ/mol and 66 kJ/mol respectively. These values can be compared to those reported in the literature for N₂O adsorption on other zeolites.[24] The range of N₂O adsorption energies in Fe-MFI (-77 kJ/mol to 82 kJ/mol) is quite broad and varies significantly depending on the position of the aluminum atoms in the zeolite.

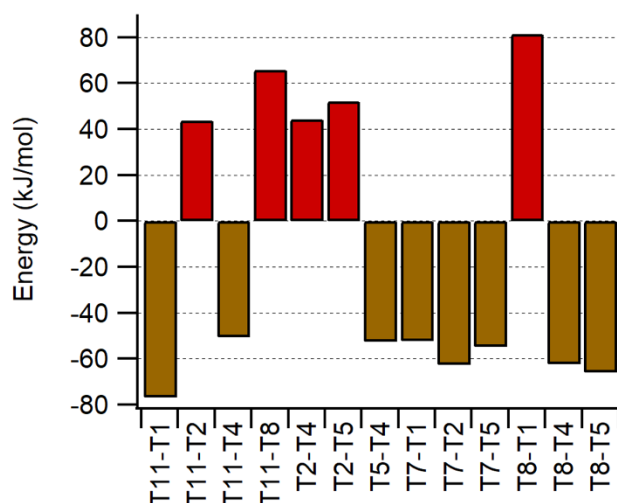


Figure 7. N₂O adsorption energies on Fe-MFI

Upon analyzing the geometries obtained for N₂O adsorption in Fe-MFI, it can be concluded that the geometric parameters of the α ring in complex B are quite similar to those obtained for the α ring in complex A. On the other hand, upon examining the distances obtained in complex B between the N₂O oxygen and Fe-MFI (O-Fe), a direct relationship between O-Fe distances and N₂O adsorption energies can be noted. For instance, the strongest adsorption energy (-77 kJ/mol) corresponds to the shortest O-Fe bond distance (2.28 Å). Thus, the N₂O adsorption energy is stronger as the O-Fe distance decreases.

After the adsorption of N₂O on Fe-MFI, the dissociation process occurs in step B \rightarrow C, as shown in Figure 6. The dissociation energies are presented in Figure 8 ranging from -21 kJ/mol to -194 kJ/mol for T5-T4 and T8-T1, respectively. All the obtained energies are negative, indicating that this step of the mechanism is an exothermic reaction that generates energy.

It is important to mention that the dissociation energy obtained for the T8-T1 configuration (-194 kJ/mol) is highly favorable because the adsorption step for this configuration is highly unfavorable, with an adsorption energy of 82 kJ/mol. Hence, despite the strong dissociation energy, the T8-T1 configuration would not be suitable for the overall process due to the low affinity between the zeolite Fe-MFI and N₂O during the adsorption process.

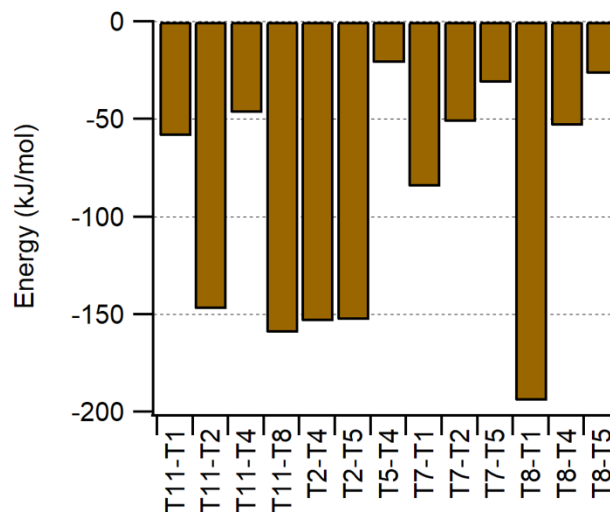


Figure 8. N₂O dissociation energies on Fe-MFI

The dissociation energies obtained are less strong than those reported by other authors. For instance, Kustov et al. obtained a dissociation energy of -266 kJ/mol for Zn-MFI.[25] Therefore, incorporating Fe into MFI zeolite would be viable for synthesizing a catalyst intended for N₂O activation.

To determine the most suitable configuration for N₂O activation, it is necessary to calculate the dissociation energies with respect to the isolated components of Fe-MFI and N₂O. The lowest energies obtained were for the T11-T1 and T7-T1 configurations. The reaction energy paths for the activation of N₂O for the T11-T1 and T7-T1 configurations are shown in Figure 9

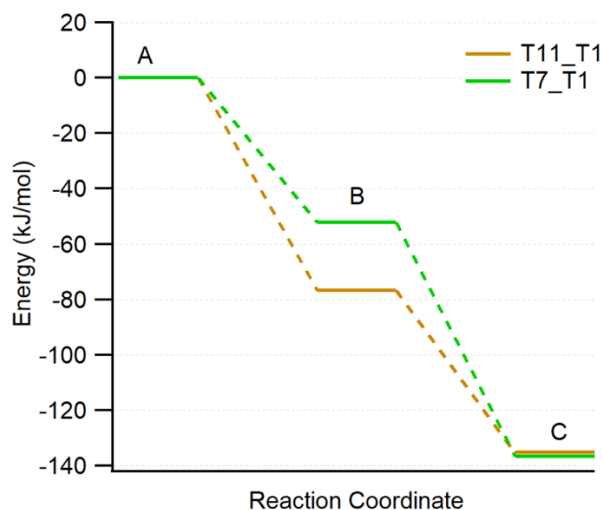


Figure 9. Reaction energy path for N_2O activation

IV. CONCLUSION

A systematic DFT study was conducted to analyze the effect of the distribution of Al in the α -ring of Fe-MFI zeolite. The results demonstrate that the most stable configuration of Fe-MFI in the α -ring is obtained when Al atoms are in the crystallographic sites T11-T2 of the zeolite. The results indicate that the adsorption energies of N_2O in Fe-MFI are in the range of -77 to 82 kJ/mol. Additionally, the results also demonstrate that the dissociation energies of N_2O obtained using Fe-MFI are strong ranging from 21 kJ/mol to -194 kJ/mol for T5-T4 and T8-T1, respectively. Therefore, this catalyst is suitable for reactions involving the activation of N_2O . This work contributes to the rational design of catalytic materials for the activation of N_2O , which can provide experimentalists with ideas for the synthesis of highly active zeolites for this type of reaction.

V. FUTURE WORK

As a future work, could be possible to determine the transition states for the dissociation of N_2O and quantify the energy barriers for this step. Additionally, a similar procedure could be performed to determine the reaction energies by substituting other divalent metals such as Cu, Mg, and Co in the 13-aluminum configuration of the MFI zeolite.

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