DFT Study on Mechanisms of the N₂O Direct Catalytic Decomposition over Cu-ZSM-5: The Detailed Investigation on NO Formation Mechanism

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Abstract: Nitrous oxide (N₂O) is an industrial emission that causes the greenhouse effect and damages the ozone layer. Density functional theory study on the N₂O direct catalytic decomposition over Cu–ZSM-5 has been performed in this paper. Two possible reaction mechanisms for N₂O direct catalytic decomposition over Cu-ZSM-5 were proposed (O₂ formation mechanism and Nitric oxide (NO) formation mechanism). The geometrical parameters, vibration frequency and thermodynamic data of the intermediate states in each step have been examined. The results indicate that N₂O can be adsorbed on active site Cu in two ways (O-terminal or N-terminal), and N₂O decomposition reactions can occur in both cases. The NO formation mechanism exhibits higher N₂O dissociation reaction due to lower energy barrier.

Keywords: DFT; Cu-ZSM-5; N₂O Direct Catalytic Decomposition

1. Introduction

Nitrous oxide (N₂O) is an important pollutant that can cause the greenhouse effect, and it is expected that the global temperature will rise by 0.3K for every doubling of N₂O concentration in the atmosphere [1]. At the same time, N₂O will destroy ozone in the atmosphere and form acid rain, which will undoubtedly seriously damage the human living environment [2]. Human activities (combustion of coal in fluidized bed reactors, industrial production of adipic acid and nitric acid, automobile emissions, etc.) are the main causes of imbalance of N₂O in the atmosphere [3]. Controlling N₂O emissions and developing N₂O treatment technologies as soon as possible are particularly important to protect human living environment.

Through N₂O direct catalytic decomposition process, the N₂O molecule is directly decomposed to form O₂ and N₂ at a relatively low temperature (300–700°C). This process has the significant advantages of high conversion rate (>99%), low cost, no secondary pollution, and simple operation [4,5].

Exploring catalysts, with high activity and high thermal stability, has become one of the research hotspots nowadays. As the high specific surface area, the unique pore structure, and the excellent NO decomposition activity, zeolites have been extensively studied [5–10]. It is reported that the metal cation exchanged ZSM-5 showed high catalytic activity [9,11–13]. The Cu-ZSM-5 has aroused widespread concern because of its high selectivity and activity, many researchers have devoted themselves to this field, and they have obtained many research reports on the preparation and performance of Cu-ZSM-5 for the N₂O direct catalytic decomposition process [3,5,14–16].

Many methods have been used to investigate the N₂O decomposition mechanism over Cu-ZSM-5 catalyst. Marijke’s group [17] presented a first practice of operando UV–vis diffuse reflectance
spectroscopic technique to study the decomposition of NO and N₂O over Cu-ZSM-5. They observed the role of the bis(μ-oxo) dicopper core in the catalytic decomposition process and found that the O₂ release step limits the N₂O decomposition speed. Kapteijn’s group [18] developed a detailed micro kinetic model to predict the N₂O catalytic decomposition over Co-, Fe-, and Cu-ZSM-5 catalysts. Through this model, they found that the O atom of N₂O combines with the active center and transfers to form O₂ in the next step. At the same time, they proved that this reaction is inhibited by O₂ from the view of kinetics.

Quantum chemical calculation is an effective theoretical method to deeply study the structure and energy changes of substances during the reaction [19–25]. Some computer Simulation studies were undertaken on M-ZSM-5 (where M = Fe, Cu, Co, etc.) catalysts and N₂O decomposition, to clarify the reaction mechanism and thermodynamics [26–29]. Lund’s group [30] studied the catalytic decomposition process of N₂O on different Fe-ZSM-5 density functional theory(DFT) models (24T double-layer annular model and 5T model), and found that the 24T model has a decomposition reaction energy barrier similar to the 5T model. Therefore, the authors propose that a 5T model, without considering that the pore effect can obtain sufficiently accurate results for calculating the energy barrier of N₂O catalytic decomposition. Fellah and Onal [31] investigated the cluster surfaces and channel cluster of Fe-ZSM-5 and Co-ZSM-5. They found that the calculated Co-ZSM-5 activation energy barrier was lower than that of Fe-ZSM-5, and both catalysts are limited by the process of O₂ desorption. Liu et al. [26] made a lot of efforts in their simulation study on the N₂O catalytic decomposition, they have drawn a Cu-ZSM-5 catalytic route map extended from Fe-ZSM-5 and Co-ZSM-5. They pointed out that the N₂O adaptation mechanism is similar to Fe-ZSM-5 and Co-ZSM-5. However, the N₂O decomposition mechanism is different. Chen’s group [27] investigated the N₂O decomposition over Fe-Beta, which provides us with another possible type of reaction mechanism (nitric oxides (NO) formation mechanism) with N₂O adsorption by N atom.

Nevertheless, there are still some deficiencies in the results of previous studies. In the first place, when the by-products as nitrogen oxides appear during the catalytic reaction, the decomposition mechanism of N₂O is much more complicated than estimated [28]. In the second place, there is a lack of energy data of transition states, and a lack of comparison between different reaction pathways and mechanisms.

For this study, our purpose is to discuss two possible mechanisms for the N₂O dissociation, and focus on the structure of the intermediate products, the vibration frequency of the transition states, and the thermodynamic data. By calculating the energy barrier of each reaction process, the rate-limiting step of the process is determined.

2. Results

Two possible types of reaction mechanisms for nitrous oxide direct catalytic decomposition are proposed based on the 5T Cu-ZSM-5 model, including O₂ formation mechanism (Scheme1a) and NO formation mechanism (Scheme 1b). The Cu-ZSM-5 is labeled as Cu-Z, each transition state in the reaction is marked as TS, and the IM is the short for intermediate. The symbol Cu-Z-N₂O or symbol Cu-O-Z-N₂O represents N₂O molecule adsorbs on the active site using the O-terminal respectively, and the symbol Cu-O-Z-N₂O’ means N₂O molecule is adsorbed to αO through the N-terminal. Figure 1 shows the optimization models used to study the direct decomposition mechanism of N₂O in DFT calculation and the schematic diagram of the reaction steps of the two mechanisms.

- Part A1
  
  \[
  \text{Cu-Z + N}_2\text{O} \rightarrow \text{Cu-Z-N}_2\text{O} \quad \text{Step A1}
  
  \text{Cu-Z-N}_2\text{O} \rightarrow \text{Cu-Z-N}_2\text{O-TS} \quad \text{Step A2}
  
  \text{Cu-Z-N}_2\text{O-TS} \rightarrow \text{Cu-O-Z-N}_2 \quad \text{Step A3}
  
  \text{Cu-O-Z-N}_2 \rightarrow \text{Cu-O-Z+N}_2 \quad \text{Step A4}
  
- Part A2
• Part A3

\[
\text{Cu}-\text{O}_2\text{-}\text{Z} \rightarrow \text{Cu}-\text{Z} + \text{O}_2
\]
Step A9

(a)

• Part B1

\[
\text{Cu}-\text{O} + \text{N}_2 \rightarrow \text{Cu}-\text{O}_2\text{-}\text{Z} + \text{O}_2
\]
Step B1

\[
\text{Cu}-\text{O}_2\text{-}\text{Z} \rightarrow \text{Cu}-\text{Z} + \text{O}_2
\]
Step B2

TS1 \rightarrow \text{Cu}-\text{Z}-(\text{NO})_2
Step B3

• Part B2

\[
\text{Cu}-\text{Z}-(\text{NO})_2 \rightarrow \text{TS}2
\]
Step B4

TS2 \rightarrow \text{Cu}-\text{Z}-\text{NO}-\text{NO}
Step B5

• Part B3

\[
\text{Cu}-\text{Z}-\text{NO}-\text{NO} \rightarrow \text{Cu}-\text{Z}-\text{NO}+\text{NO}
\]
Step B6

(b)

**Scheme 1.** Reaction steps of the O\textsubscript{2} formation mechanism (a); Reaction steps of the NO formation mechanism (b).

![Diagram](image)

**Figure 1.** Optimized models and the schematic diagrams of the reaction steps of the two mechanisms.
The energy profile of each mechanism and the partially optimized geometric parameters of the model in each reaction step are marked in Figure 2a,b. Table S1 shows the detailed geometric parameters of each optimized model, in which N and O atoms have been noted (O1–N1–N2 for the first N₂O, O2–N2–N3 for the second N₂O, and N1–O1 for NO). Table S2 shows the DFT energy calculation results for each reaction step.

Figure 2. Energy profile for O₂ formation mechanism (a); Energy profile for NO formation mechanism (b).
2.1. Formation mechanism of O₂ based on DFT calculations

As shown in Scheme 1a, the O₂ formation mechanism includes three parts (Part A1–Part A3) and nine steps (Step A1–Step A9). Part A1 describes the first N₂O molecule catalytic decomposition process, Part A2 explains the second N₂O molecule decomposition, and Part A3 shows the process of O₂ desorption.

2.1.1. Part A1

Reaction step A1 shows a process in which the first N₂O molecule adsorbs on the active site using the O-terminal. The adsorption energy reaches -10.12 kcal/mol, which means that the N₂O molecule can easily adsorb on the Cu and releases a small amount of heat. Since the adsorption energy is low, reverse reaction (N₂O desorption) may also occur under the reaction conditions, so step A1 can be considered as a reversible adsorption step of N₂O.

Reaction step A2 describes the process from N₂O adsorption state to the first TS, which is the key-step in Part A1. The reaction energy barrier (ΔE) is 33.08 kcal mol⁻¹, which indicates that the reaction needs to absorb lots of heat to reach the TS. The structural parameters of the TS are as follows; the bond length of Cu–ON₁ is 1.75Å, the bond length of O–N₁ is 1.80Å, the bond length of N–N is 1.11Å, and the N₂O bond angle is changed from adsorption state’s 177.9° to 143.7°. The imaginary frequency of the TS is 294.61cm⁻¹, which is confirmed by intrinsic reaction coordinate (IRC) path analysis.

Reaction step A3 has a small negative reaction energy change (−2.81kcal mol⁻¹), the reaction can proceed automatically, and the O–N₁ is broken to form highly active αO and adsorbed N₂. Then in step A4, N₂ is desorbed, and a small amount of heat energy (ΔE = 0.45 kcal mol⁻¹) is absorbed.

2.1.2. Part A2

Part A2 exhibits the second N₂O molecule catalytic decomposition process. During reaction step A5, N₂O adsorbs on the Cu center through the O-terminal. This step’s reaction energy barrier is −3.17 kcal mol⁻¹, which is as reversible as in step A1.

Reaction step A6 demonstrates the second key-step. It has a larger reaction energy barrier (28.61kcal mol⁻¹). The structural parameters of the TS are as follows: the bond length of Cu–ON₂ is 1.90Å, the bond length of O–N₂ is 1.47Å, the bond length of N–N is 1.12Å, and the bond angle of O₂–N₃–N₄ is 149.6°. The imaginary frequency of the TS is 799.38 icm⁻¹, which is determined by IRC path analysis.

Reaction step A7 explains the process of O–N₂ bond cleavage and adsorbed N₂ formation. This step releases a large amount of heat, when ΔE reaches −80.45 kcal mol⁻¹. In a while, N₂ desorbs (step A8) despite the low energy (1.31kcal mol⁻¹).

2.1.3. Part A3

The last step of Part A shows the O₂ desorption process, this step’s energy barrier is 33.59 kcal mol⁻¹. This result means that the step A9 comes to be the speed-determining step of the whole reaction process.

2.2. Formation mechanism of NO based on DFT calculations

As described above, the difference between the formation mechanism of NO and that of O₂ is the second N₂O molecule adsorption method. Therefore, this section focuses on the second N₂O molecule catalytic decomposition process which is named NO formation mechanism. As shown in scheme1b, it consists of three parts (Part B1–Part B3).

2.2.1. Part B1

Part B1 describes the process from the second N₂O adsorption state (through the N-terminal) to the transition state. Eventually, an intermediate product (IM) is created. Reaction step B1 explains
that the second N₂O adsorbs on the αO through the N-terminal process, and this step has a small adsorption energy (2.81 kcal mol⁻¹). The bond length of αO–N₂O is 2.32Å, and the bond angle of O2–N3–N4 is 179.9°.

Reaction step B2 shows the process of the first TS (Cu–O–Z–N₂O'–TS) formation, which absorbs a small amount of energy (0.79 kcal mol⁻¹). The bond angle of O2–N3–N4 changes a little, but the bond length of O1–N4 decreases rapidly. The imaginary frequency of the TS is 241.10 icm⁻¹, which is also confirmed by IRC path analysis. When the reaction (Reaction step B3) proceed from TS to IM, it carries on automatically and releases energy (14.39 kcal mol⁻¹).

2.2.2. Part B2

Part B2 demonstrates the process from IM to Cu–Z–NO–NO. The reaction step B4 shows the path from IM to the second TS. This step, which is identified by the experimental results as a reaction rate-determining step, shows a tiny energy barrier (2.43 kcal mol⁻¹). The TS’s imaginary frequency value is 280.03 icm⁻¹. During the process, the bond angle of O2–N3–N4 has been changed to 125.8°. The energy change of reaction step B5 (Cu–O–Z–N₂O'–TS2 to Cu–Z–NO–NO) is 9.12 kcal mol⁻¹, and it will perform automatically.

2.2.3. Part B3

Part B3 is the reaction process of the desorption of adsorbed NO, the release of NO and the formation of Cu-Z-NO. This automatic reaction step releases a small amount of energy.

3. Discussion

Summarizing the models constructed above, two different types of reaction mechanisms are discussed. When N₂O directly decomposes following the O₂ formation mechanism, both N₂O molecules adsorb on the active site using the O-terminal. In this work, the whole reaction process is divided into three parts: The first N₂O adsorbs on the active center Cu and produces N₂ with reaction, the second N₂O molecule adsorbs on active center Cu and reacts to release N₂, and the two O atoms combine to form O₂ and desorb from the catalyst. The three parts of the reaction process have shown three energy barriers (33.08 kcal·mol⁻¹, 28.61 kcal·mol⁻¹, and 33.59 kcal·mol⁻¹, respectively). Considering the entire reaction process, the speed-limiting step of the mechanism is O₂ desorption, which has been widely recognized in the literature [26,29]. When Kapteijn’s group [18] conducted an experiment on the N₂O decomposition process over M-ZSM-5 (Where M = Co, Fe, and Cu), they found that the process of N₂O decomposition, based on the Cu-ZSM-5, has an apparent activation energy of 32.5 ± 9.1 kcal/mol(136 ± 8K)·mol⁻¹), which is highly consistent with this study. Liu et al. [26] analyzed the decomposition reactions of three N₂O molecules in a sequence based on a similar simulation calculation Cu-ZSM-5 model and verified that the reaction energy barrier value reached 39.48 kcal/mol. Table 1 shows the comparison of energy barrier from part A1 to part A3. They also listed optimized geometric parameters and energy data of the transition state, consistent with present study, but those are not comprehensive and specific enough. Through the study of the O₂ formation mechanism by DFT, an effective calculation model is established, a reliable calculation method is verified, and more complete optimized geometric parameters and transition state energy data are given in Tables S1, S2.

| Part | Energy barrier/ kcal·mol⁻¹ | Energy barrier [30]/ kcal·mol⁻¹ |
|------|--------------------------|-------------------------------|
| A1   | 33.08                    | 35.18                         |
| A2   | 28.61                    | 28.07                         |
| A3   | 33.59                    | 39.48                         |

As the other important part of this study, we discussed the NO formation process of N₂O catalytic decomposition reaction using 5T Cu-ZSM-5 model. Mechanism design referred to the
We found that NO was generated due to the N–NO bond broken during the second N2O adsorption process, and the NO formation mechanism reaction has higher activity than the O2 formation mechanism reaction. Zhang’s group [35] pointed out that the structure of the O-terminal N2O molecule over Cu-ZSM-5, but the conclusion over other zeolites is opposite. Chen’s group [27] conducted a DFT study on the two types of formation mechanisms over Fe-beta. The energy barriers of the two types of formation mechanisms are contrary to those over Cu-ZSM-5. Table 2 shows the comparison results of energy barrier during the second N2O molecule decomposition process. This result may explain why O2 does not counteract the N2O direct catalytic decomposition reaction using Cu-ZSM-5 zeolite, and more by-products are formed during the catalytic process.

Table 2. Energy barrier comparison of the second N2O molecule decomposition process.

| Mechanism               | Energy barrier/kcal·mol⁻¹ | Energy barrier [31]/ kcal·mol⁻¹ |
|-------------------------|---------------------------|---------------------------------|
| O2 formation mechanism  | 28.61                     | 35.78                           |
| NO formation mechanism  | 0.79                      | 26.92                           |

4. Experimental and Computational Methods

In the present work, the DFT-based quantum chemistry was used to investigate the N2O direct catalytic decomposition mechanisms over Cu-ZSM-5. ZSM-5 zeolite structure model is cut out from the molecular structure database in Material Studio 4.0 software, and the cluster concerned is the 5T model [(SiH3)4AlO4Cu] shown in Figure 3b. The Al atom in the 5T model falls at the T12 site (Figure 3a), because the Si atom at T12 site is the most easily replaced by Al atom based on published literature [36,37]. A Cu+ ion compensate the Al atom and form the active site. H atoms are used to balance the boundary charge. All atoms in the calculation are relaxed.

Gaussian-09 software package (Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, USA, 2016) was used for all the simulate calculations in this paper [38–42]. B3LYP method (Becke’s three-parameter hybrid, Lee-Yang-Parr’s correlation function) was used [43,44]. In the simulation study of geometry optimization and transition state search, the LANL2DZ basis set was used to describe the atomic Cu, and the 6-31G(d) basis set was used for the other atoms (Al, Si, N, O and H). However, the 6-311++G (d, p) set was applied for energy change calculations on top of the structural optimization results to calculate the energy barrier values [45–47]. In the frequency calculation, zero-point energy (ZPE) was used for energy correction [48–53].

![Figure 3](image_url)

**Figure 3.** Structure diagram of the computational model. (a) Location of the Al atom within the crystal structure of ZSM-5; (b) optimized 5T model of Cu-ZSM-5.
5. Conclusions

During the present work, we have simulated two mechanisms of the N₂O direct catalytic decomposition, and proposed the structure parameters, vibration frequency and thermodynamic data of the intermediate states in each step using DFT calculations. The most important discovery of this work is to provide us with a theoretical calculation evidence showing that N₂O molecular can adsorb on Cu–O–Z through both O terminal and N terminal and form O₂ or NO, respectively. The O₂ desorption step is the speed-limit step for O₂ formation mechanisms, and the path from IM to the second TS (Cu–O–Z–N₂O→TS2) turns out to be the speed-limit step of NO formation mechanisms. The latter showed high N₂O dissociation activity due to a much lower energy barrier.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/10/6/646/s1, Table S1. Structural parameters (diameter in Å, angle in °) of optimized models, Table S2. Energy results of each step for O₂ formation mechanism and NO formation mechanism.

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