

UNIVERSITY OF OKLAHOMA
GRADUATE COLLEGE

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COMPUTATIONAL STUDY AND MANIPULATION OF LOCAL
CHEMICAL ENVIRONMENT IN HETEROGENEOUS
CATALYSIS AND SEPARATION

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ABSTRACT

Reactive separation is proposed as a less energy-intensive chemical process with functions of catalytic reaction and separation. It offers an active chemical conversion combined with selective separation to obtain the desirable products. Catalytic membranes are one of the successful examples and the design of it requires understanding the structure-activity relationship between catalyst and membranes.

To guide the process design, this thesis gives computational insight on the following aspects: catalyst design focused on selectivity and activity in aqueous environments, and a porous structure suitable for incorporating catalytic active sites and responsible for separation. For catalyst design, the aim is to understand the role of the local chemical environment on reaction activity and selectivity. It is promising to tune the reaction activity by manipulating its solvation environments and coordination environment for the catalyst. By understanding the interplay between catalytic performance and the local chemical environment, a catalytic active site with a well-defined structure is proposed for further catalytic membrane design. Additionally, a well-established membrane for gas separation is studied to characterize cavity formation with tunable membrane contents. The study encompasses fundamental aspects of catalysis, including electronic structure, kinetic principles, and temperature-dependent separation processes, while analyzing detailed polymer structures.

Firstly, the aldol condensation reaction of cyclopentanone (CPO) over metal oxide MgO is investigated. Functionalized groups grown on an oxide catalyst highlights the tunable kinetic performance and promotional role of water in association with functionalized groups. Density Functional Theory (DFT) calculations show the strong adsorbate-adsorbate interaction results in hindered C-C coupling step, which contributes to low reaction rates observed on the functionalized surface. The role of water is identified in facilitating CPO adsorption and reducing the kinetic barrier of the kinetic-relevant step. Water thereby promotes the reaction rate by alleviating serious adsorbate-adsorbate interactions on the functionalized surface. This study paves a way to understand the solvent effect on the heterogeneous catalyst.

With an emphasis on denitrification in wastewater treatment, palladium has been proposed as an active catalyst for wastewater treatment, but the detailed mechanism and the solvent effect are not well understood. To address this, DFT calculations were employed to investigate the detailed reaction mechanism and kinetics for nitrite reduction. This study revealed that the overall activity is primarily determined by the activity of NO and a comprehensive kinetic model is developed to explain the observed reaction order. Interestingly,

water played a promotional role in the nitrite hydrogenation reaction over the palladium catalyst. DFT analysis demonstrates that water facilitates a lower-energy pathway for hydrogenation by shuttling surface hydrogen to the reactants. The tuned free energy pathway aligns with the experimental findings on the reaction order.

The solvent effect is associated with the micro-solvation environments created by a polymer (n-isopropyl acrylamide) overlayer that shows temperature-dependent behavior. Growing this NIPAM overlayer on the catalyst support alters the selectivity and activity of palladium along with the tuned solvation environment. Molecular dynamics simulations propose a lower activation barrier introduced by NIPAM due to polymer-water interactions. The presence of polymer in the aqueous phase forms a structured water layer on the palladium, favoring the reaction pathway through the proton-shuttling mechanism. These findings enhance our understanding of designing and manipulating the micro-solvation environments for a tunable solvent effect.

As revealed on metal catalysts, the binding energy of NO provides crucial insights to promote reaction activity and selectivity. The binding energy determines the activation of NO bond hydrogenation is highly associated with the structure of the active sites. The investigation extends to the activity of single atoms in nitrite reduction powered by renewably generated electricity and examines the denitrification mechanisms across dispersed Co and La-based catalysts. The enhanced charge transfer is identified on NO bonded with La, and different mechanisms are investigated including entropic stabilization and the solvent effect. The study suggests that atom-dispersed metal is one of the promising catalysts toward a high activity and selectivity of NO reductions which dominates the denitrification reaction.

The catalytic membrane requires a stable polymer structure to selectively filter out the ions. We conducted a simulation on membrane synthesis using a triptycene-based membrane (TPBO) with tunable cavity distribution based on the content of triptycene. By manipulating the content of the triptycene unit, the free volume distribution corresponding to the triptycene molecule content is obtained. These structure-properties relationships reveal the flexibility of TPBO-based polymers for gas separation. Our study on polymer structure provides a foundation acknowledge for further membrane design which is critical to catalytic membranes.

Overall, this dissertation suggests a synergetic combination that takes advantage of polymer structures and single-atom catalysis to achieve enhanced activity and selectivity in reactive separation. This approach holds great promise for advancing catalytic technologies and addressing challenges in fields such as separation science and environmental sustainability. This study on catalysis research has been extensively focused on understanding the

fundamental principles governing catalyst performance, with a growing recognition of the significance of the local chemical environment. Fine-tuning and manipulating this environment presents novel avenues for catalyst design.

This dissertation is dedicated to my entire family

献给陈家和颜家以及我的所有家人们

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CHAPTER 1

INTRODUCTION

1.1 Importance of energy-efficient processes

The growing importance of energy and the need for sustainability and carbon neutrality are driving efforts to develop energy-efficient processes. From the perspective of chemical engineering, one of the key concerns of engineering processes is to reduce low energy consumption or to explore alternative energy sources which are renewably generated.

Energy is vital for driving chemical reactions and the separation process, and thermal energy is commonly used but can be expensive. However, when thermal energy alone is insufficient to overcome reaction barriers, catalysis plays a crucial role. Catalysts are substances that can reduce the energy required for a reaction and enable valuable chemical production that would be impractical using only catalyst-free thermal processes. A classic example is the hydrogenation reaction. Hydrogenation requires high temperatures to overcome the barrier of breaking the H-H bond^{1,2,3,4}. However, with catalysts like transition metals, the H-H bond is weakened, significantly reducing the required temperature and pressure^{2,5}. Catalytic hydrogenation became much more energy-efficient with a catalyst. Normally, energy-efficiency is not merely dependent on the catalyst. The growing number of studies showed the reaction environment of the catalyst could further enhance the activity and reduce the energy input further.

Thus, extensive research has been conducted to identify the most-efficient process powered by the catalyst, considering both the chemical conditions and detailed kinetics. Consequently, there is a growing appreciation for studying the fundamental aspects of catalysis. Researchers have recognized that, in addition to the catalyst material itself, the local environment surrounding the catalyst surface has a significant role in low-energy dependent process^{6,7}. The local chemical environment refers to the conditions in the vicinity of the reaction site, including temperature, pressure, coordination with support or neighboring atoms, and solvation environment^{6,7,8,9,10,11}. Numerous studies have shown that tailoring the local chemical environment, particularly the solvent and coordination structure, can optimize catalytic performance in terms of activity, selectivity, and stability⁷.

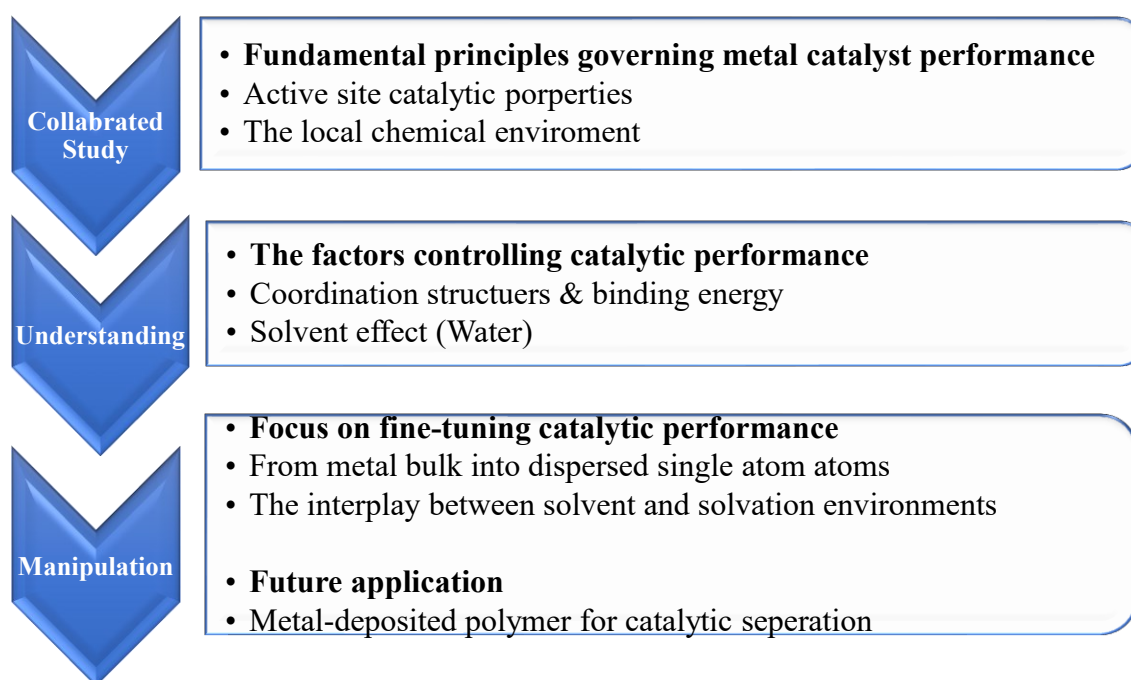


Figure 1.1 Introduction outlines.

1.2 The interplay between the local chemical environment

The interface between various factors in the local chemical environment plays a crucial role in catalysis. Among these factors, the solvent effect has been recognized as a key player, as it can significantly influence catalytic reactions. Recent studies have shown that the role of the solvent varies depending on the specific environment created by the functionalized ligand or a polymer structure^{12,13,14}. Interestingly, while solvent can have a detrimental effect by poisoning the active site, the solvent can also have a positive influence on the reactivity by stabilizing the reactant and participating in the reaction.

Considering these observations, researchers have explored the potential of introducing functionalized groups to tune the catalytic surface. The rationale behind this approach is that the interactions between the catalyst, solvent, and reactant are modulated by the solvation environment leading to enhanced catalytic performance. However, the interplay between the solvent and the functionalized group in this context requires a detailed investigation to fully comprehend its underlying mechanisms.

1.3 Tuning the solvation environment

Functionalized groups have emerged as promising methods for energy-saving catalyst design. They result in catalysts with distinct catalytic performance, and studies have shown that the use of functionalized groups or polymers to decorate catalysts can influence the reaction rate and alter the role of water. They can act as site blockers, increasing catalyst stability and

selectively controlling reaction pathways. It is assumed that they interact with water or other solvent molecules and alter the role of water in catalysis. Particularly the use of hydrophobic polymers can alter the solvated environment around the active site, enhancing the reaction rate^{11,15,16,17}. This dissertation investigates several examples of the water promotional role under different solvated environments and understands the interplays between solvent and solvation environments with the purpose of manipulating the catalyst activity.

1.4 The coordination structure: from thousands of atoms to one

The binding energy of the reactant is a key factor that determines the catalytic performance of metal catalysts. The binding energy is influenced by the electronic structure and coordination environment of the metal site which in turn affect the structure, electronic properties, and reaction pathways of single atom catalysts^{18,19,20,21}. In general, single-atom catalysts (SACs) exhibit superior catalytic activity compared to the normal metal surface for various reactions due to a low coordination number and unsaturated bonding. These factors can modulate the d-band structure and strengthen the adsorption of reaction intermediates²². Dispersed atom sites have the potential to optimize the catalytic performance through a well-defined coordination structure with the support^{23,24,25,26,27}. However, the development of SAC highly relies on the simulation tool of the difficulty in verifying the structures experimentally^{24,25}. Computational methods based on density functional theory play a crucial role in providing insights for controlling binding energy and reactions with dispersed active sites.

1.5 Scope and outlines

We aim to elucidate the relationship between the solvent and the functionalized group in catalysis. Through this comprehensive analysis, we seek to fine-tune the catalyst by understanding the interplay between the local chemical environment, specifically the solvent, and functionalized groups, to improve the reactivity and selectivity of the catalyst. The research will focus on the following aspects:

- 1) The effect of water was analyzed on the intermediates, followed by the elementary steps with collaborative studies. For example, the aldol condensation of cyclopentanone was studied over a functionalized MgO surface where water can stabilize the reactant adsorption and the kinetic relevant step, both of which were greatly altered by the functionalized groups grown on the catalyst. Moreover, the influence of water on the nitrite hydrogenation pathway was examined. As the solvent, the water flattened the free energy diagram by providing a feasible pathway for nitrite hydrogenation. The water shuttling mechanism greatly promotes the kinetic-relevant step and enhances the

overall reaction rate.

- 2) To control the micro-solvation environment, a NIPAM polymer was introduced. Experimental findings suggest that the reduction of nitrite over the Pd-NIPAM surface exhibited lower activation energy, which is associated with the alteration of the water structure by the polymer. Ab initio molecular dynamics (AIMD) simulations verified the alteration of the metal-water interface, forming a more structured water overlayer.
- 3) The binding energy of nitrite and N-containing compound is a key factor in the nitrite reduction activity. The metal atoms atomically dispersed on the graphene substrate were analyzed. By studying the electronic structure of the metal, it has been observed that NO was significantly activated by excess charge transfer from single atoms. It is predicted that the improved electrocatalytic NO reduction activity of single-atom catalysts. The promotional role of water was also explored in relation to the associated pathway on single-atom catalysts.
- 4) This research aims to establish a connection with previous research on polymer structure investigation for separation purposes. The objective is to deposit single atoms into a porous system. A specially designed polymer based on a triptycene unit was investigated. Triptycene is a three-dimensional organic molecule consisting of a polymer backbone and it provides static-free volume independent of aging and deactivation. Preliminary tests were conducted to examine the formation of free volumes to investigate the relationship between free volume and the concentration of TPBO. It is crucial to understand the subsequent reactant adsorption and separation on the membranes. The investigation paved the way for the future application of catalytic separation.

Conclusion

In conclusion, this dissertation provides a comprehensive catalysis study, aiming to fine-tune the local environment through the use of computational tools. Through fundamental studies and the analysis of complex catalytic phenomena using thermodynamic and kinetic analysis, our aim is to effectively manipulate catalysts and their local environments in order to achieve lower energy-intensive catalytic performance. By gaining a deeper understanding of the interplay between catalysts, solvents, functionalized groups, and reactants, we seek to optimize catalytic processes and contribute to the development of more sustainable and efficient chemical reactions.

CHAPTER 2

ROLE OF WATER ON FUNCTIONALIZED MGO SURFACE

2.1 Introduction

This chapter focuses on the effects of steric and solvent effects on aldol condensation on metal oxides, specifically when the surface is modified using octadecyl trichlorosilane (OTS) to make them more hydrophobic and water-resistant. We will highlight the reactivity of aldol condensation of cyclopentanone on functionalized by the OTS group.

What makes it interesting is that functionalized group has adjusted the reaction order and the role of water in the reaction^{12,13}. This chapter provides computational insight into how OTS and water alter the reactivity of the aldol condensation reaction. We hope to investigate the effect of water on functionalized catalysts using MgO-OTS as a universal example and discuss how OTS alters the surface reactivity of metal oxides, which can contribute to their selectivity and activity in applications such as anti-fouling coatings, water-repellent surfaces, and catalysis.

The solvent effect has been proven to be a determined factor in the reaction activity. Water has been observed to stabilize transition states and lower the activation barrier in chemical reactions in liquid phases^{12,28,29,30}. Here we discuss a few examples of metal surfaces. For instance, Zhao et al.³⁰ observed that Pd nanoparticles supported by Al₂O₃ have enhanced hydrogenation activity for furfural in an aqueous phase and that water is attributed to the enhanced activity and the modified selectivity. Li et al.³¹ found the addition of a small amount of water promoted the carbonyl bond hydrogenation on cobalt and cobalt boride catalysts. All the findings suggest water would assist the reaction in several roles: stabilization on the free energy diagram of the reaction and direct participation in the catalysis. Many simulations have observed the water-assisted stabilization of transition states, resulting in lowered free-energy barrier on regular catalyst surfaces^{30,32,33}.

However, metal and metal oxides surface are mostly hydrophilic and Some of them would quickly deactivate in liquid phases. To improve water resistance, the modification of metal oxide surfaces with organic alkyl silanes, such as OTS, is considered a promising approach to alter surface properties. OTS is a long-chain alkyl silane that can form a self-assembled monolayer (SAM) on a metal oxide surface through a chemical reaction^{34,35}. The hydrophobicity of the alkyl chain of OTS can make the surface of metal oxides more hydrophobic. By creating a hydrophobic environment, OTS provides an extra energy barrier

on the metal oxide surface by altering the environment around the active site. The altered environment can improve the stability and durability of the metal oxides since the effect of water should be less pronounced. Besides that, the reactivity is significantly altered by OTS toward various adsorbates and reaction partners. One way is OTS can alter the surface reactivity of metal oxides by reducing the availability of surface sites for adsorption and reaction. The OTS layer forms a tightly packed monolayer, which effectively blocks some surface sites from adsorption. The change in surface acidity/basicity is altered by the OTS functionalization. Eventually, those factors would contribute to the selectivity and activity difference on functionalized surfaces, making metal oxides useful for a wide range of applications such as anti-fouling coatings, water-repellent surfaces, and catalysis.

Cyclopentanone is a significant compound in biomass conversion. As a valuable intermediate, it could be used to produce high molecular-weighted fuels via C-C bond formation^{13,28,36}. To overcome the low stability of MgO in water, OTS could be used as functionalized groups on metal oxide catalyst^{12,37}. It has been shown that functionalized MgO-OTS catalyst exhibits outstanding water resistance. We would like to address the distinct catalysis performance and promotional role of water found by Duong et al.¹³ on aldol condensation reaction over functionalized MgO catalyst. As we mentioned, the functionalized MgO surface displays hydrophobicity, and Mg sites are found to be well protected from water. When TOF is measured in varied amounts of water, surprisingly, the reaction rate was found to increase as the concentration of H₂O increased from a very small amount (up to 0.355 mL). It is Investigated that the enhancement on TOF accompanies the reaction order change and such TOF enhancements are related to the alkyl chains of OTS. The liquid environment near the catalyst surface is modified by the functionalized group which introduces a hydrophobic and size-sensitive environment. By employing simulation tools, we hope to develop a molecular understanding of catalysis in liquid media over hydrophobic catalysts. The metal-support interactions react to the water attack in a way the catalysts are protected and resulting in improved stability.

We utilized DFT calculations to investigate the effect of OTS and water on the reactivity and the kinetic performance of the aldol condensation on a functionalized MgO surface. The major results are summarized in Figure 1.1. Specifically, they analyzed a MgO surface that was grafted with an organic silane at a measured density of 3 OTS per nm². The adsorption analysis revealed that the functionalized surface had dominant repulsion due to the presence of OTS which hindered the adoption of cyclopentanone (CPO). This led to weaker

CPO adsorption on functionalized MgO surface compared to the regular surface. The effect of OTS dominated the calculated free energy diagram of aldol condensation where the C-C coupling became the slowest step under water-free conditions. This explained the reduced reaction rate and change in the reaction order on the functionalized surface. However, both surfaces display a similar energy profile of enolate formation. It indicates minimal effect from OTS on the surface site. OTS decorates the chemical environment on the MgO surface where water plays an enhancing role.

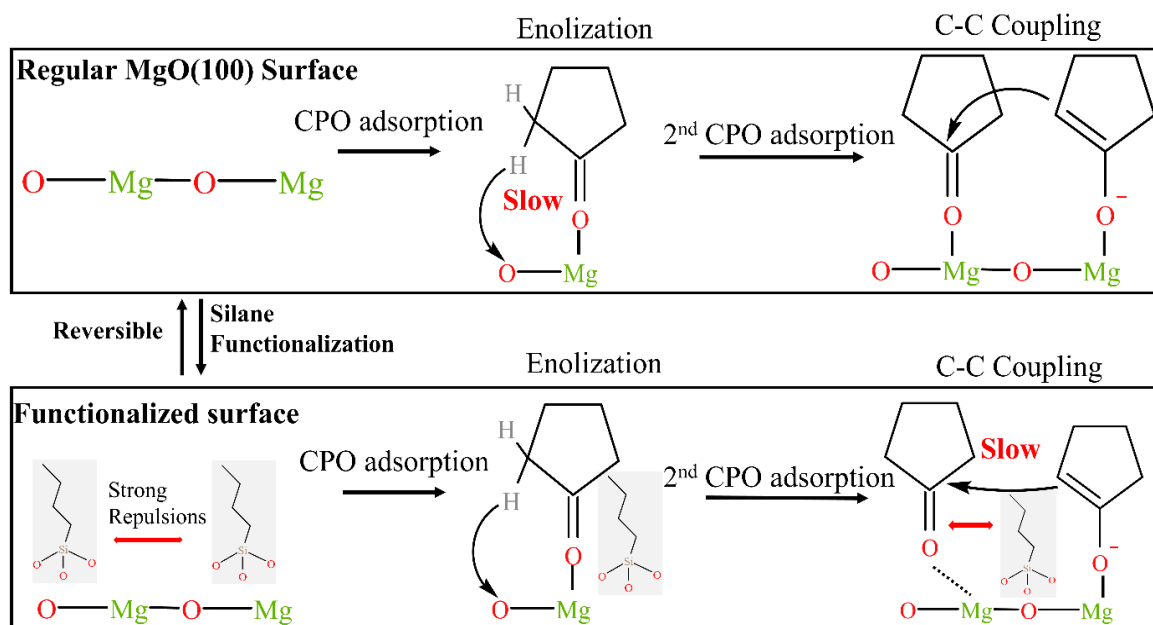


Figure 2.1 All the potential kinetic relevant steps of Aldol condensation reaction using cyclopentanone (CPO). Proton addition and dehydration are omitted. The slowest step (rate-limiting step) on each surface is labeled. The repulsion between reactant and reactant or OTS and reactant are indicated by arrows. The red color indicates the controlling factor on catalytic activity.

The addition of a water molecule was found to promote the adsorption and C-C coupling steps. The hydrogen bonding facilitated CPO adsorption with less endothermic adsorption energy and lowered the activation barrier of the following C-C coupling step. However, even with the improvement in reaction rates, the C-C coupling step remained the slowest reaction step. Thus, water was also found to alleviate the adsorbate-adsorbate interaction, resulting in lower reaction energy and barrier of the coupling step.

2.2 Experimental Results and Simulation Models

2.2.1 Experimental Results

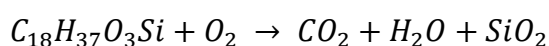
It has been found that the rate-limiting step of cyclopentanone self-aldol condensation changes from first order to second-order with the addition of OTS. This happens because the presence of high amounts of OTS makes it more difficult for cyclopentanone to adsorb onto the surface of MgO, which slows down the reaction. However, the addition of water to the reaction mixture can partially recover the catalytic activity of MgO-OTS. It is suspected that the water can help to polarize the C=O bond of cyclopentanone, making it more electrophilic and therefore more reactive. Additionally, the water can bridge the gap between the cyclopentanone molecule and the Mg²⁺ acid site, which helps to mitigate the energy barrier of the reaction.

2.2.2 Simulation methods and details.

Ab initio simulations were performed using the Vienna ab initio simulation package (VASP)^{38,39,40}. The ion–electron interaction was described through the projector-augmented wave (PAW) approach⁴¹. Perdew–Burke–Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) are used for the exchange and correlation energy⁴². The van der Waals interaction has been considered through Grimme’s DFT-D3 semiempirical method⁴³. The supercell contained four layers of (2 × 2) MgO(100) surface and 15 Å vacuum in the z-direction, with the bottom two layers fixed at the bulk positions while the top two layers were allowed to relax in all optimizations. The MgO surface is functionalized by OTS to an OTS density of 2.9 per nm² corresponding to (2 × 2) MgO surface was occupied by OTS groups with total number of 2. The built MgO-OTS structures were optimized by AIMD simulations performed in a previous publication¹³. The most stable adsorption configurations are used for the following activation barrier calculation. The aldol condensation reaction follows enolization and C-C coupling steps which are potential rate limited steps in previous findings¹³. For each reaction path, the transition state search was performed using the dimer method⁴⁴ with the initial guesses for the transition state structure and the reaction trajectory obtained through the nudged elastic band (NEB) method⁴⁵.

2.2.3 The OTS structure discussion

The OTS content on functionalized surface is determined from TGA. There is two peaks of the water mass spectrum¹³. Upon heating beyond 250 °C, the OTS anchor proceeds with the following reaction.



Where the monodentate molecule proceeds with combustion, burning out and producing CO_2 and H_2O , which are detectable in TGA signal. The measured density of OTS on MgO -OTS is 3 OTS anchors/ nm^2 . Since we are using 2×2 MgO surface, the actual OTS concentration in our simulations is set as two.

As we introduced before, the bonding of OTS molecules with a surface would end up with Si silane -O-Si and Si silane -O-Si substrate cross-linking type covalent bonds with the surface Mg atom. To simulate that, we have built up the model as the following figure shows.

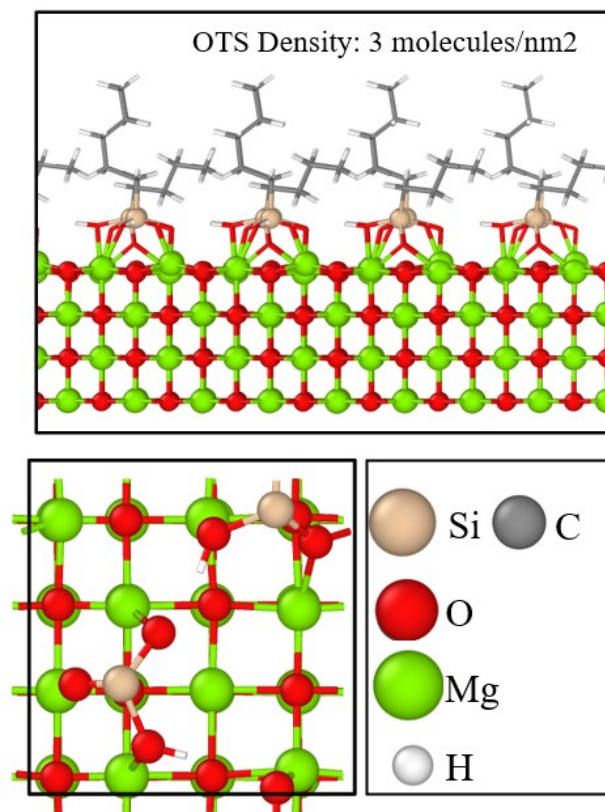


Figure 2.2 Structure of the regular MgO surface and MgO -OTS surface.

2.2.4 The solvation energy calculation

In this section, we discuss the solvation energy calculation using DFT method. Our goal was to determine the thermodynamic properties and stability of each state in the energy diagram, as well as the energy required to move from one state to another. To introduce the solvation environment, we used explicit or implicit molecule models in computational methods. Explicit molecule models involve considering the water surrounding the catalyst surface to simulate a metal-liquid phase. However, to reduce computational costs, we only considered a limited amount of water contributing to hydrogen bonding solvation. Implicit molecule models, on the other hand, account for the solvent environment using mathematical equations describing the interactions between the solvent and solute.

Although molecular approaches have become powerful tools for studying the solvation energy, few studies have investigated how the solvation environment can be tuned by functional groups or polymer molecules, despite their significant influence on reactivity. Solvent molecules surrounding the catalyst and reactant can offer additional interactions with energy states in the reaction diagram, and the solvent environment can also act as a catalyst. Also, the solvent environment can be altered by the surface topology through functionalized and polymer groups. Therefore, understanding the solvent environment is crucial in catalysis. Although few studies have examined the solvent environment in the presence of functionalized groups, we were able to determine the solvation energy for each state, which will help us understand the effect of solvation on the reaction mechanism.

2.3 Comparison of aldol condensation reaction on MgO and MgO-OTS

2.3.1 Aldol condensation pathway on MgO

MgO is a typical base catalyst for aldol condensation. Many researchers have demonstrated the effectiveness of MgO as a catalyst for aldol condensation. Aldol condensation is a reaction between aldehyde or ketone compounds to form unsaturated carbonyl compounds through new C-C double bond formation between the compounds. The mechanism of the reaction over a base catalyst involves three steps:

- (1) CPO activation by generating an enolate ion.
- (2) C-C bond formation through attack of the enolate ion on the other cyclopentanone.
- (3) C-C double bond formation through dehydration.

In the first step aldol condensation of cyclopentanone, an O anion on the MgO catalyst abstracts a proton from the α -carbon adjacent to the carbonyl group, forming an enolate ion that acts as a nucleophile. In the second step, the enolate ion attacks the carbonyl carbon of the other cyclopentanone leading to the formation of a C-C bond and the dimerization of the carbonyl compounds. In the third step, the dimer undergoes dehydration and loses a water molecule to form a double bond.

A detailed kinetic study showed that the rate-determining step on a regular MgO catalyst is the first-ordered enolate formation. However, the addition of OTS shifts the reaction order. On MgO-OTS, the total activity drops, and the reaction rate becomes second-ordered, which is limited by the second step, C-C coupling. Interestingly, the addition of a small amount of water promotes the reaction rate, but the reaction order remains second order. It is speculated that the OTS molecule alters the rate-limiting step and modifies the role of water in the reaction.

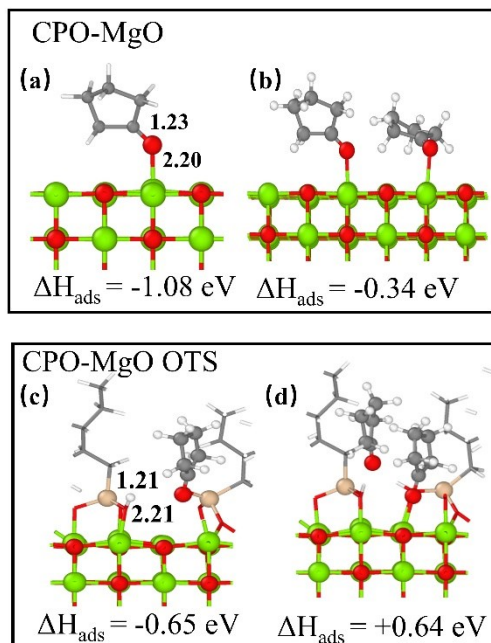


Figure 2.3 CPO adsorption on MgO and MgO-OTS surface (CPO/surface). The adsorption energy is calculated for each CPO, and the C=O and Mg-O bond lengths are indicated. (a) CPO/regular MgO. (b) CPO(ii)/regular MgO. (c) CPO/MgO-OTS. (d) CPO(ii)/MgO-OTS

2.3.2 Adsorption on MgO/MgO-OTS catalyst

In this study, we focus on understanding the adsorption of CPO on adjacent Mg sites following an LH model. Regular MgO provides a strong basic site for CPO adsorption and the dual adsorption of CPO on adjacent sites causes the energy penalty due to adsorbate-adsorbate interaction. For example, the adsorption energy of the second CPO drops from -1.08 eV to -0.34 eV. It is predicted that the functionalized surface makes subsequent CPO adsorption difficult due to the adsorbate-OTS interaction. But the first CPO adsorption releases similar adsorption energy of 0.65 eV and the measured O-Mg bond is like MgO surface. It indicates the first CPO adsorption are independent on the OTS group. OTS effect starts to play a role on the second CPO adsorption at the adjacent Mg site where, the calculated adsorption energy is +0.64 eV for the second CPO adsorption even though there was an empty Mg site on the surface. Additionally, C=O bond polarization is critical for the following reaction. Thus, we include the Bader charge study on both surfaces.

On regular MgO, the Mg site helps C=O bond polarization and a small elongation of nearly 0.01 Å was observed. Bader charge analysis revealed that the C=O was negatively charged when bonding with a MgO site. Interestingly, the first CPO undergoes a comparable amount of negative charge on both surfaces which suggests the CPO was equally activated.

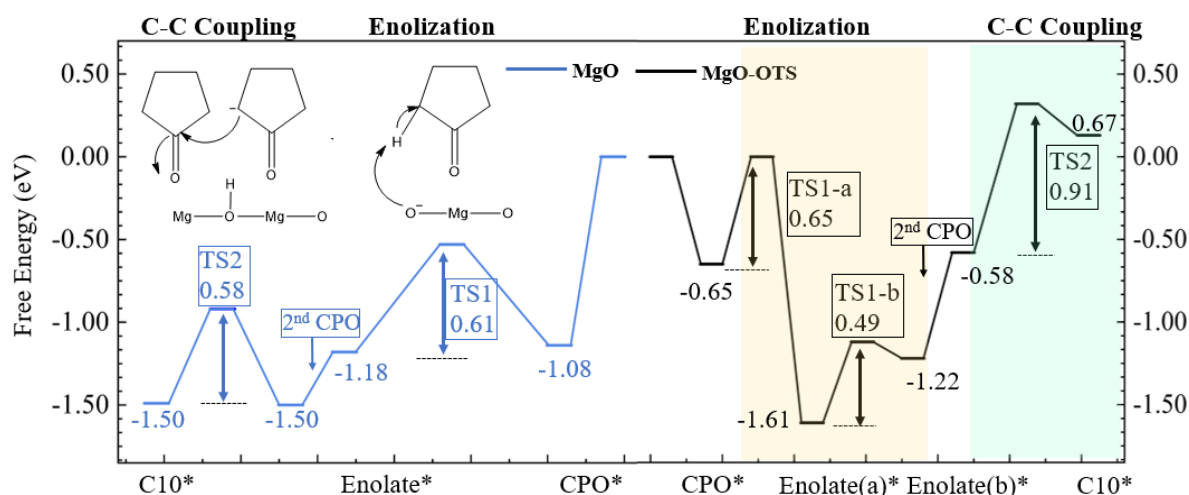


Figure 2.4 The free energy reaction diagram of aldol condensation on the MgO surface and the MgO-OTS surface. Reaction energy on each adsorption step as well as the activation barriers on each transition state are labeled in the box. CPO* stands for the first CPO adsorption. CPO (ii) is the second CPO adsorption. C10* is the C-C coupling intermediate before the proton addition and dehydration. MgO surface has only one transition state where the proton is located on the surface. The enolization occurs between two steps of adsorption (CPO* and CPO (ii)).

2.3.3 Enolization on MgO/MgO-OTS catalyst

After the CPO adsorption, the enolization step is a crucial and sensitive step for aldol condensation reaction. The deprotonation of the α -carbon of cyclopentanone generates the enolate intermediate, which is a highly reactive nucleophile. The basicity of the catalyst can have a significant impact on this step. On regular MgO, the enolization of CPO releases energy of 0.1 eV and the activation barrier is 0.61 eV. The enolization is also strongly correlated with the CPO adsorption step. The strongest adsorption with a tilted configuration always owns lower intrinsic activation barrier compared to the other configurations. Despite the decrease in surface basicity caused by the anchored OTS, the basicity strength remains totally unchanged on regular MgO. Thus, we suspected the enolate formation in the presence of OTS remains mostly the same as on a regular MgO surface. Our calculation suggests that the oxygen at anchored OTS has similar proton affinity as the surface oxygen. The first CPO is located with hindered configuration unlike the tilted one on regular MgO. The deprotonation of CPO occurs

first at the O atom of the OTS (O-OTS) and the proton transfers to the surface oxygen. According to the calculated free energy diagram, the enolization formation required two steps: deprotonation to the O-OTS and the proton transfer to oxygen in surface. The formation has an intrinsic barrier of 0.64 and 0.49 eV, respectively, similar to a regular MgO. Despite introducing another anion for H abstraction, the basicity on OTS is very similar to that on the surface, and the activation remains almost the same as on the regular MgO. Even though the reaction energy is exothermic on MgO, the enolization step is quite similar in the presence of OTS.

2.3.4 C-C Coupling on MgO/MgO-OTS catalyst

The enolization generates an enolate, which is nucleophilic. The next step in the reaction is the attack of the enolate on the carbonyl of the other cyclopentanone molecule. This step is influenced by several factors including the electrophilicity of the carbonyl carbon, the steric hindrance, and the solvent effect. The electrophilicity of the carbonyl carbon is determined by the molecule's overall electronic distribution, and steric hindrance can impede the enolate ion's attack. It has been investigated that the bulky substitution group would hinder the C-C coupling step, making the C-C coupling step highly unfavorable. The steric effect of the OTS functional group is due to the presence of its alkyl chain. This chain contains several carbon atoms, which can occupy significant space on the surface of the catalyst. As a result, when an enolate intermediate approaches the carbonyl carbon of the adjacent CPO molecule, the bulky OTS group can create a hindered environment, making it difficult for the enolate to approach the carbonyl carbon. This steric hindrance can increase the activation barrier for the C-C coupling step and make the reaction highly endothermic, as observed in the calculations. The activation barrier of C-C coupling increases from 0.58 eV on regular MgO to 0.91 eV on MgO-OTS. In addition, the reaction is highly endothermic. It is due to the steric effect from the alkyl chain of the OTS group. The second CPO adsorption is highly unfavorable and the enolate is greatly hindered. Despite the hindered C-C coupling step, the enolization step remains similar to that on the regular MgO surface, with similar intrinsic barriers. Overall, the addition of the OTS group significantly limits the C-C coupling step in the aldol condensation reaction on the MgO surface.

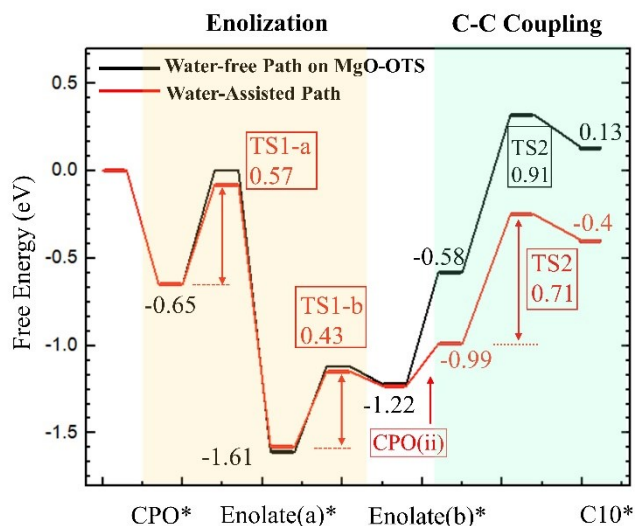


Figure 2.5 The free energy reaction diagram of aldol condensation on MgO-OTS surface with or without the involvement of water. The box labeled the true activation barriers on each pathway. The only structural difference is water on the adjacent MgO site which proceeds with CPO (ii) adsorption.

2.3.5 The role of water

The solvent can also have a significant effect on the C-C coupling step in aldol condensation. For example, in polar solvents such as water or methanol, the enolate ion is more stable due to the solvation effect, which can promote the C-C coupling step. On the other hand, in nonpolar solvents such as benzene or toluene, the enolate ion is less stable due to the lack of solvation, which can hinder the C-C coupling step.

The cations on metal oxide surfaces are very hydrophilic. Our simulation found that H₂O would strongly attach on MgO releasing 0.64 eV adsorption energy while the functionalization makes surface hydrophobic and deactivates some of the cation by anchoring. Thus, the adsorption energy of solvent decreases to -0.50 or -0.19 eV depending on cation strength. It is possible to compete with cyclopentanone with the surface site. However, given that CPO are concentrated in the solvent phase, water competitive adsorption would not be considered at the investigated concentration. However, after the first CPO adsorption, the adsorption of H₂O could occur on the weak cation site where the CPO (ii) adsorption is unfavorable.

Nevertheless, the adsorbed H₂O on the surface offers weak H bonding for the second CPO. The second CPO adsorption with the help of water increases to -0.46 eV from 1.0 eV through direct adsorption. On the functionalized catalyst, H bonding may play a significant role on offering adsorption site with less steric effects. As a smaller molecule, H₂O has less energy

penalty for adsorption after the first CPO adsorption. It modifies the steric effect by offering H bond assisting the second CPO adsorption. As found on less endothermic adsorption with +0.33 eV energy change, H bonding via water offers a more stable adsorption bond than direct adsorption on the functionalized catalyst indicated by the closer H-CPO bonding (water-CPO: 1.804 Å versus OTS-CPO: 1.858 Å). The addition of water could partly improve the [CPO] concentration on the MgO-OTS surface.

Also, Bader charge analysis found H bonding make the second CPO more electropositive which is advantageous for the C-C coupling step. Compared with the direct adsorption with less charge transfer, the whole CPO molecule is more electropositive by 0.04. The α -carbon are more electropositive, which makes it nucleophilic attack favorable.

The promotional role of water is also reflected by the calculated energy diagram where the nucleophilic attack on the second CPO underwent a lower barrier pathway. The addition of water influentially reduced the activation barrier by 0.20 eV which is attributed to activated CPO adsorption.

2.4 Discussion

Due to the bulky reactant, the aldol condensation of CPO is sensitive to the surface condition. As reported on CPO adsorption on MgO surface, the second CPO adsorption needs to overcome the adsorbate-adsorbate interaction. We suspect the energy cost brought by such interaction would be pronounced on functionalized surface. The OTS-CPO interaction originated from hydrophobic alkyl chains. Even though MgO-OTS have similar basicity strength as regular MgO surface, there are extra energy penalties on MgO-OTS to overcome the repulsion. It suggests that OTS-CPO interaction are dominant on MgO-OTS surfaces meanwhile the CPO concentration on MgO-OTS is highly limited. By looking at the adsorption, we have a hint that surface functionalization introduces repulsive adsorbate-adsorbate interaction resulting in adsorption step with high energy penalty. Thus, the reaction rate is affected by low surface coverage of reactants badly.

Also, the reaction kinetic is altered by the OTS group as well. Despite the enolization remains similar reaction energy, the intermediate proton could be stabilized by the anion at the OTS group. Other than that, OTS has displayed hindrance on the following C-C coupling step. The activation barrier on MgO-OTS has increased by 1.5 times compared to regular MgO due to multiple factors. First is the steric effect. The other is the inactive carbonyl bond on the second CPO. As mentioned, the second CPO on MgO-OTS has weaker adsorption. In other words, the weak bonding has less polarized the second CPO molecule. Less charge transfer

from surface to the carbon ring of CPO is indicated by Bader Charge analysis. Thus, the carbon is less vulnerable to the electrophile due to partly charge transfer. And the CPO on MgO-OTS displays weaker activity than it is on MgO surface resulting in much slow C-C coupling step.

The mentioned effects of OTS have been well reported on the previous report that the functionalized surface has displayed lower turnover frequency and second order kinetic. They are attributed to the slow C-C coupling step on MgO-OTS surface. Moreover, the promotional role of water is reported. We will discuss how the addition of water alters the free energy diagram producing a result explaining the experimental findings.

As investigated on many catalysis studies, solvent-reactant interaction is a significant part to consider in heterogeneous catalysis. Water, as a solvent, will contribute hydrogen bonding to the surface intermediate. Such hydrogen bonding could facilitate the reactant adsorption reflected on the energy diagram. Moreover, water as a universal solvent has been proved to play a catalytic role in the reaction. Water alters the turnover rate by acting different stabilization role on reactant and intermediates. It has been pointed out that water has different stabilization on the reactant and intermediate in the other research. Thus, to quantitatively measure the solvent effect, simulations are valuable. We believe, through simulations, the thermodynamic properties could be predicted successfully.

Similarly, to the forementioned phenomenon, water exhibits a reaction rate promotor. However, by measuring the reaction with increased water pressure, water serves as a promotional role at low pressure and switches to a negative effect on the MgO-OTS surface. Given that MgO has poor water resistance and OTS provides certain amount of hydrophobicity on the surface, the negative role of water is attributed to the large amount of water penetrating the OTS group and deactivating the Mg surface sites like regular MgO. OTS is insufficient to large amount of water. Concerning the promotional role of water, the amount of water is insignificant to form liquid cluster. In simulations, we apply the molecular water in the calculation to investigate the effect of water that is not competitive for the surface sites.

The result shows that water have stabilization on serveral reactant. The MgO-OTS always preserve a CPO molecule adsorbed on the surface since H₂O concentration is low and has a relatively weaker adsorption than CPO. Due to the limited amount of molecular sites, the adsorption of water prevails over the second CPO which is inhibited by OTS group. It is assumed that the covalent bond between Mg and O is strong enough to transfer electrons. In the Bader charge analysis, on both MgO and MgO-OTS surfaces, there is insignificant charge detected in the Mg-O covalent bond. However, water offers H bonding to the second CPO

molecule which brought significant stabilization. It is suspected that water acts as the bridge between CPO and Mg site. Mg site brought stabilization through the H bonding to the CPO which is located slightly higher than the usual adsorption. Also, higher location means less adsorbate-adsorbate interaction since OTS occupied the surface through three Si-O bond which is considered bulky adsorbate.

With the stabilization of H bonding, the second CPO is successfully absorbed with the enolate species. The C-C coupling is promoted not only by the increased converge of CPO but also by stabilized transition state with water. The transition state of C-C coupling consists nucleophilic attack to the carbonyl carbon on second CPO producing CPO dimer. As the simulation free energy diagram shows, surprisingly, transition states and the final products are stabilized by the water adsorption. Given the adsorbate-adsorbate interaction dominated the energy diagram, the alleviated effect of water is indicated by H bonding and interaction between O and the surface to reduce the adsorbate-adsorbate interaction. In such a mechanism, a molecular water is sufficient to display such an effect. It has been investigated that the elongated H-bond with several water molecules could serve as a similar effect. We don't see the H bonding stabilization could pass along water chain of two water molecules or more than that. Our CPO adsorption shows that 1 water offers vertical height of 2 Å for CPO is sufficient for the C-C coupling reaction since the enolate species are closely attached to the surface. Thus, our simulation successfully reproduces the promotional role of water and explains the increased turnover frequency.

It is noted that the addition of water doesn't change the reaction order since the overall barrier on MgO-OTS is limited by C-C coupling step which is hindered by OTS group. The increased reaction rate is due to the increased concentration of CPO and more energetically feasible transition state and intermediates.

Overall, the functionalized group OTS acts as a steric molecule, applying a steric effect on the surface adsorbate, and has hindered the CPO adsorption and the C-C coupling step except for the enolization. OTS hindered the reaction by introducing extra energy cost on C-C coupling and destabilizing the second CPO absorption and the dimer product. As the result, MgO-OTS is limited by the second-ordered C-C coupling reaction and displays much lower reaction rate than regular MgO surface. Also, the rate promotion role of water is verified on the the enhanced CPO adsorption and stabilization of the condensation product by offering a favorable nucleophilic attack. Overall, the simulation results is well agreed with the experimental findings in kinetic¹³.

Conclusion

In conclusion, these DFT calculations have provided valuable mechanistic insights into the reaction pathway of CPO aldol condensation. Through our calculations, we have determined the energy barriers and intermediates involved in the adsorption step, enolization step, and C-C coupling step and identified the key factors that govern the reactivity of the catalyst. The role of functionalized group and water are revealed in the calculated reaction. The major finding is listed below:

- 1) The bulky and hydrophobic nature of the OTS group introduces repulsive adsorbate-adsorbate interactions which hinders the adsorption and stabilization of reactants and products on functionalized surface. The hindrance effect is calculated on the CPO adsorption. The concentration of CPO is limited on functionalized surfaces since there are not enough active sites at the given coverage of OTS.
- 2) The functionalized group doesn't affect the overall barrier of enolization but the later C-C coupling step. The transition state of C-C coupling is greatly destabilized by 0.38 eV. Combined with the effect on CPO adsorption, OTS includes lower turnover frequency and second-order kinetics since OTS introduces additional energy costs on various kinetic steps, particularly the C-C coupling step. Also, less charge transfer from the functionalized surface to the carbon ring of the reactant, making it less susceptible to electrophilic attack.
- 3) Water promotes CPO adsorption by offering H bonding, and it facilitates the concentration of CPO. Moreover, water stabilizes the transition state and the product of the C-C coupling step. The activation barrier is observed to decrease by 0.20 eV. Based on the activation energy calculated, the aldol condensation activity ranks from high to low is $\text{MgO} > \text{MgO-OTS (water)} > \text{MgO-OTS}$.
- 4) The second-ordered kinetic and the effect of the water molecule are in agreement with the experimental measurement. The TOF ranks from high to low is $\text{MgO} > \text{MgO-OTS (water)} > \text{MgO-OTS}$ and the reaction order shift to the second order with the introduction of OTS.

In this chapter, we demonstrate the intricate interplay between electronic and steric effects on the functionalized surface and have helped to understand the origin of the observed experimental trends. Moreover, we investigated the role of water in the reaction by measuring the stabilization effect on each elementary step and the molecule activation. The aldol condensation reaction involved in water has been successfully observed and explained in the

previous research results. Overall, our findings pave the way for future studies on functionalized catalysts aimed at improving the efficiency of aldol condensation. We highlight the importance of theoretical studies in guiding the catalyst surface functionalization and optimization of catalytic systems.

Chapter 3

NO REDUCTION ON METAL NANOPARTICLES: UNDERSTANDING THE FUNDAMENTAL KINETIC AND MECHANISM

3.1 Introduction

3.1.1 Catalytic Hydrogenation for water treatment

Hydrogen has developed as an important energy source as well as significant chemicals^{46,47,48,49,50}. For the catalytic use of hydrogen, reaction hydrogenation, and hydrolysis are significant fields. They are used to convert unsaturated molecules into saturated ones and break down the molecules into small ones which could be used as building blocks of synthesized chemicals⁵¹. To find out the hydrogenation catalyst with the highest activity and best economical expense, a thorough understanding of fundamental energy and kinetic is crucial. Hydrogenation is used in many places such as pollutant removal^{46,51,52}.

Denitrification reactions have gained renewed interest due to the leakage of nitrogen-based fertilizers from intensive agricultural activities into natural aquifers. Nitrite, originating from excessive fertilizer use, accumulates and converts into nitrate over time^{51,52}. The reaction has gained renewed interest primarily due to the leakage of nitrogen-based fertilizers from intensive agricultural activities into natural aquifers. while the removal of one of the micropollutants, nitrite, has significant meaning in preventing the serious health risks to humans caused by the micropollutant in the underground water^{51,53}. Thermal denitrification using thermal energy on metal surfaces has been revealed as a potential way. However, fundamental work is lacking to distinguish the detailed mechanism and apparent reaction activity^{53,54,55,56,57}. Moreover, as most nitrite reduction occurs in the aqueous phase, the solvent environment must be considered.

3.1.2 Catalytic hydrogenation on metal

Metal surfaces, particularly noble metals like platinum, palladium, rhodium, and copper, exhibit excellent catalytic activity and selectivity in converting nitrogen compounds into harmless nitrogen gas^{52,54,55,56,57}. Understanding the kinetics of NO reduction plays a crucial role in advancing this technology while the exact reaction mechanism remains under debate due to measurement didn't perform on a wide range of concentrations. The involvement of multiple intermediates, including NO, impacts selectivity and activity. Researchers were observing NO adsorption as an intermediate species during nitrite hydrogenation^{58,59}. Determining the rate-determining step(s) and the adsorbate(s) controlling the activity and

selectivity is challenging, leading to ambiguity in the reaction order interpretation. Therefore, comprehensive research is needed to explain the rate-determining steps and selectivity in NO reduction.

Furthermore, extensive studies revealed the role of water on metal. Water has been reported to promote catalysis on metal surfaces by participating in the reaction^{60,61,62,63,64,65}. We will explore the interaction between water and metal sites supported by nanoparticles using computational methods. As indicated by the Solvent, H₂O is one of the local environments in the catalyst, it could serve as a site blocker to the active site while stabilizing the reactant in a confined environment. Moreover, research has reported H₂O to participate in a reaction and alter the free energy diagram for hydroegnation^{60,62,63,64,65}. It remains an open question whether H₂O could promote nitrite reduction.

3.1.3 The Scope of nitrite removal

The reduction of NO on metal surfaces is of great significance, not only for fundamental research but also for addressing the removal of nitrate and nitrite contaminants in drinking water. Another interesting topic on solvent effect could be altered by the environment introduced by polymer-coating on the catalyst^{15,16,66,67}. Temperature-dependent polymers, such as p-NIPAM, will be examined for their fine-tuning properties to water, which can be controlled by temperature-induced swelling and shrinking states. The transition temperature, known as the LCST, determines the hydrophilic or hydrophobic behavior of p-NIPAM. Growing temperature-dependent polymers on Al₂O₃ catalyst supports alters the solvent phase near the catalyst surface^{16,66}. Controlling the reaction temperatures, the swelling and collapsed states of p-NIPAM are suspected to influence the reactive water layer on the active site. The details and relevant discussion are in the next chapter.

It is significant to investigating an alternative energy and energy-friendly source such as electrocatalytic approaches to efficiently remove and convert nitrite^{46,51}. However, limited by low selectivity and efficiency on noble metal nanoparticles, we have an additional effort on fine-tuning the coordination structure to electrocatalytically remove NO on Chapter 5 and this chapter hopes to address the fundamental acknowledge required for electrocatalytic removing N-compound.

Understanding the effect of water and the role of temperature-dependent polymers on metal surfaces further enhances our knowledge of catalytic processes^{16,66}. The hydrogenation of nitric oxide (NO) holds significant importance not only for fundamental research but also for addressing the catalytic reduction of nitrate (NO₃⁻) and nitrite (NO₂⁻) contaminants in

drinking water. This chapter aims to fill up the lack of fundamental study on the basics but important denitrification reaction.

3.1.4 Research objectives

This study aims to elucidate the kinetic rule and mechanism for nitrite reduction on palladium surface at a wide range of reactant concentration. DFT calculations and experimental measurement are collaborated to provide atomistic-level insights into the reaction energetics and pathways. The rate limiting is associated with hydrogenation and hydrolysis steps of NO and HNO species. These calculations enable the identification of rate-limiting steps and the prediction of reaction kinetics under different conditions. Also, we find water flattens the overall free energy diagram and leads to accurate mechanistic study and kinetic model fits with the experimental finding. Both DFT results and experimental observations contribute a comprehensive understanding of the nitrite reduction process and provide the fundamental acknowledge for the following investigations.

3.2. Simulation Methods and details

The plane-wave DFT calculations were carried out using VASP^{39,40}. The Perdew-Burke-Ernzerhof (PBE) functional⁶⁸ within the generalized gradient approximation (GGA)⁶⁸ was used for the exchange-correlation energy. Electron-ion interaction was described by the projector augmented wave (PAW) approach^{41,42} and the van der Waals (vdW) interaction was included using the DFT-D3 method⁴³. All electronic energies in calculations were converged within 10^{-5} eV, and the force on each atom was converged to below $0.02 \text{ eV } \text{\AA}^{-1}$. We calculated a close-packed 5×5 graphene surface with $20 \text{ \AA}$ vacuum in the z-direction.

The simulated Pd bulk has lattice constant of $3.89 \text{ \AA}$ which on agreement with measured crystallographic properties of Pd. The Pd (111) facet was optimized and used to build a close-packed 3×3 Pd(111) surface with thickness of 4 layers and a vacuum layer of $15 \text{ \AA}$ along z direction as the previous research⁵⁶. The reactant adsorbed on Pd surface has 1 nanometer distance which is long enough to avoid the interaction from periodic surface. The $3 \times 3 \times 1$ Monkhorst-pack k-point mesh was used to sample the first Brillouin zone during structural optimization. In calculations, two NO adsorbates were positioned on the Pd surface, equaling to $2/9$ surface coverage. Two different solvation models were compared. The implicit solvation effect was computed by VASPsol⁶⁹. The explicit model was investigated by incorporating different numbers of water molecules near the NO molecules and the most stable local configuration was used for activation barrier calculations. Total energies of several initial geometries of explicit water were compared, and the most stable one was adopted for

calculations of activation barriers and transition states. The transition state searches were performed using the dimer method with the initial guesses obtained through the (NEB) method^{70,71}. The transition states were further confirmed by calculating the vibrational frequencies. The adsorption energy E_{ads} was calculated by Eq. 1.

$$E_{ads} = (E_{slab-ads} - E_{slab} - nE_{ads-gas}) / n \quad (1)$$

Where $E_{slab-ads}$, E_{slab} , and $E_{ads-gas}$ are the total energy of adsorbate/slab system, clean metal slab, and the isolated adsorbate in gas phase, respectively, and n is the number of adsorbates in the calculations. The adsorption free energy of liquid-phase NO_2^- on Pd surface is obtained by thermodynamic cycle. For hydrogen adsorption calculations, the residual H entropy upon adsorption was assumed to be the value reported for adsorption of H over Pd black. The discussion on H entropy is covered and shown in Fig. S6 on appendix. We validate the micro-solvation model (1, 2, 3 water molecules) and investigate the entropy and enthalpy contribution on activation free energies as well as loss of water entropy in proposed mechanism.

3.3. Results and Discussions

3.3.1 Nitrite reduction mechanism on clean Pd surface

As previously mentioned, many reaction mechanisms have been proposed for nitrite reduction in aqueous solutions using Pd-based catalysts^{53,54,55,56,57}. These reaction mechanisms commonly start with nitrite adsorption and dissociative adsorption of hydrogen to form H^* , followed by hydrogenation of nitrite to form adsorbed NO^* , which has been claimed as a crucial intermediate^{54,55,57,58,59}. The N–O bond could dissociate directly to form N^* and O^* ⁵⁵ or assisted by hydrogen via hydrolysis of HNO^* , NOH^* and HNOH^* species. The NO^* direct dissociation is hindered by its high activation barrier on Pd(111)^{55,57}. Instead, NO^* hydrogenation is favored. The N–O dissociation barrier in HNO^* , NOH^* , and HNOH^* were calculated to be higher than those of the sequential hydrogenation steps^{54,56}. Therefore, in the following DFT calculations, we follow the hydrogenation of NO^* to form NHOH , hydrolysis of which produces NH^* , another surface dominant specie. The N–N bond could form between NH^* and another surface species to form N_2 . Instead, NH^* can also proceed with two more hydrogenation steps to form NH_3 . The free energy profile is plotted in Fig. 3.1.

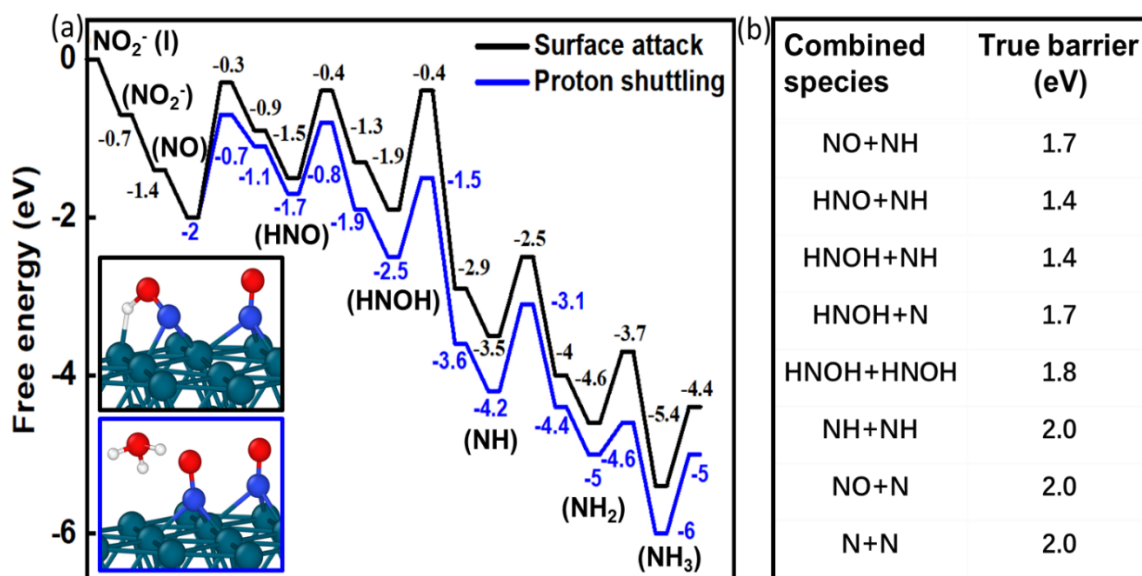


Figure 3.1 (a) Free energy diagram of NO_2^- reduction on a Pd(111) surface. Black line: hydrogen directly attacks surface species. Blue line: proton shuttle through H_2O to the surface species illustrated in solvent effect and Figure S7. The atomic structures of transition state for the first hydrogenation reaction with and without proton shuttling are shown as insets. (b) The true barriers for possible N-N coupling species. The H adsorption is shown in each step that requires H-insertion with a free energy of c.a. 0.6 eV.

The adsorption energy of NO_2^- from liquid phase onto the Pd surface is -0.7 eV, and its conversion to form NO^* is exothermic by 0.6 eV. It suggests the NO_2 favors the adsorption on Pd surface and converts to NO^* easily, agreeing with a previous report^{72,73}. NO^* adsorbs strongly on Pd with an adsorption energy of -2.8 eV, much stronger than hydrogen adsorption (-0.6 eV). This energy difference between NO^* and H^* suggests NO^* likely covers the Pd surface and competes for sites, in line with the experimentally measured negative reaction order in nitrite at low hydrogen pressures. The first hydrogenation can happen at either the N or O in NO^* . Our results show the formation of NOH^* is slightly favorable than HNO^* (see comparison in Fig. 3.1). However, the kinetic barrier of HNO^* toward HNOH^* is feasible by difference of 0.7 eV compared to the barrier of NOH^* . Thus, Fig. 2.1 shows the most favorable pathway following the sequence of NO^* , HNO^* , HNOH^* , NH^* and NH_2^* . Among all the elementary steps, the transition states (TS) of the first, second, and third steps to form HNO, HNOH and NH have a similar energy with the highest values. The RDS should thus be within the first three steps. Given the polar nature of the surface species the transition state energy of these steps will be very sensitive to the presence of water molecules via so-called “solvation effects”.

3.3.2 Solvent effects on the hydrogenation and hydrogenolysis

We consider the solvent effect in two approaches: an implicit model, which includes the effect of electrostatics, cavitation, and dispersion on the interaction between a solute and reactant, and the explicit model, where the actual H_2O molecules are included in the calculations. Our result¹⁴ shows the free energy profile of NO^* hydrogenation towards HNOH^* using either the implicit model or the explicit model. Here, one could notice that a similar change in the free energy of the TS and chemisorbed species has been observed for the steps of NO and HNO hydrogenation in two solvent models. In the following section, we focus on the explicit solvent model to include the proton shuttling mechanism where explicit water needs to be present to participate in the reaction. Strikingly, the results indicate that the proton shuttling has a pronounced effect in promoting the first three hydrogenation/hydrogenolysis steps, i.e., lowering their intrinsic activation barriers by 0.4, 0.2, and 0.5 eV, respectively, in comparison to the explicit solvent model (Fig. 3.1). Such an enhancement is because H_2O shortens the hydrogenation path, reducing the energy of the TS by stabilizing the positive charge at H_3O^+ (refer to the published results¹⁴). As a result, this shuttling mechanism lowers the apparent barriers. This flattening of the energy landscape leads to similar barriers for the first two hydrogenation steps.

The proton shuttling path was investigated with extra water molecules to test the convergence of the explicit model (see Fig. 3.2). The results with more than one H_2O molecule shows a comparable stabilization of the TS, very similar to the model with one water molecule, suggesting that the key chemistry required in this model has been captured with just one water in the proximity. The true barriers for each hydrogenation, listed in Fig. 3.1, shows the most pronounced water promotion on the NOH^* formation. When the O atom in NO^* is targeted for hydrogenation, the true barrier of shuttling is reduced by 1.0 eV, almost independent on the number of water molecules. NO^* adsorbs on Pd with N, leaving the O interfacing with the solvent. The H_2O molecules open a favorable shuttling path for the surface hydrogen to attack O as observed in other hydrogenation of oxygenates⁴⁸. Yet, such a promotion effect is strictly limited for hydrogenation of O in HNO^* , because in the tilted configuration of HNO^* , the hydrogenation path from the surface is already shortened and facilitated. Different from the O hydrogenation, hydrogenation of N in NO^* is promoted moderately by 0.5 eV, because of the extra energy cost for water to approach the surface and hydrogenate the N that is strongly bonded with Pd. A similar effect is shown for hydrogenating N in NOH^* ; the water enhancement for hydrogenating N in NOH^* is minor. While these results might indicate that

H-insertion on the O of NO* should be the most preferable pathway in the explicit water model (red curve in Fig. 3.2a i-iv), the barriers obtained for this mechanism are significantly larger than those obtained in the H-NO* pathway. Furthermore, the hydrogen addition to the O of NO* would result in reaction orders for hydrogen that vary between 1 and 1.5. That is, 1.5 hydrogen insertions occurred on the system before the RDS. Such a mechanism, however, would not explain the low reaction orders in hydrogen herein observed (Fig. 3.1). Instead, it is more likely that hydrogen is inserted at the nitrogen atom of NO* leading to similar apparent barriers in the two subsequent hydrogenation steps, resulting in two co-limiting rate limiting steps with reaction orders varying from 0 to 1.5 (blue curve in Fig. 3.2a i-iv).

It is also worth noting the reactions mediated by different number of waters at the interface require the disruption of hydrogen bonds and displacing water molecules from the bulk to the interface, which can add up as an additional free energy change. Thus, we quantitatively estimate the free energy change of water reconstruction (e.g., move a cluster of water (1-3 molecules) from the bulk to the interface) at room temperature. The enthalpy and entropy change result from breaking hydrogen bonds between the water clusters and the water bulk during the reconstruction. Previous studies showed that such disruption of hydrogen bonds could lead to a noticeable free energy cost (~ 1 kJ/mol per hydrogen bond), which includes the enthalpy loss and entropy gain by breaking one hydrogen bond^{48,72}. Such a free energy cost associated with large water clusters at the interface was also discussed in olefin epoxidation, though the exact entropy change is different as in the latter case water is partitioned from organic nitrile rather than bulk water⁷⁴. Formation of large water clusters at the interface, which requires breaking multiple hydrogen bonds, is thus less likely than the model with one interfacial water molecule.

Overall, presence of water molecules does not change the reaction mechanism as the hydrogenation of NO* still follows the HNO path. However, there is a subtle but noticeable change of the relative difference between TS1 and TS2. That is, the second hydrogenation has either a larger (by 0.2 eV) or comparable apparent barrier, as compared to the first hydrogenation. This finding is in good agreement with our further kinetic fitting analysis.

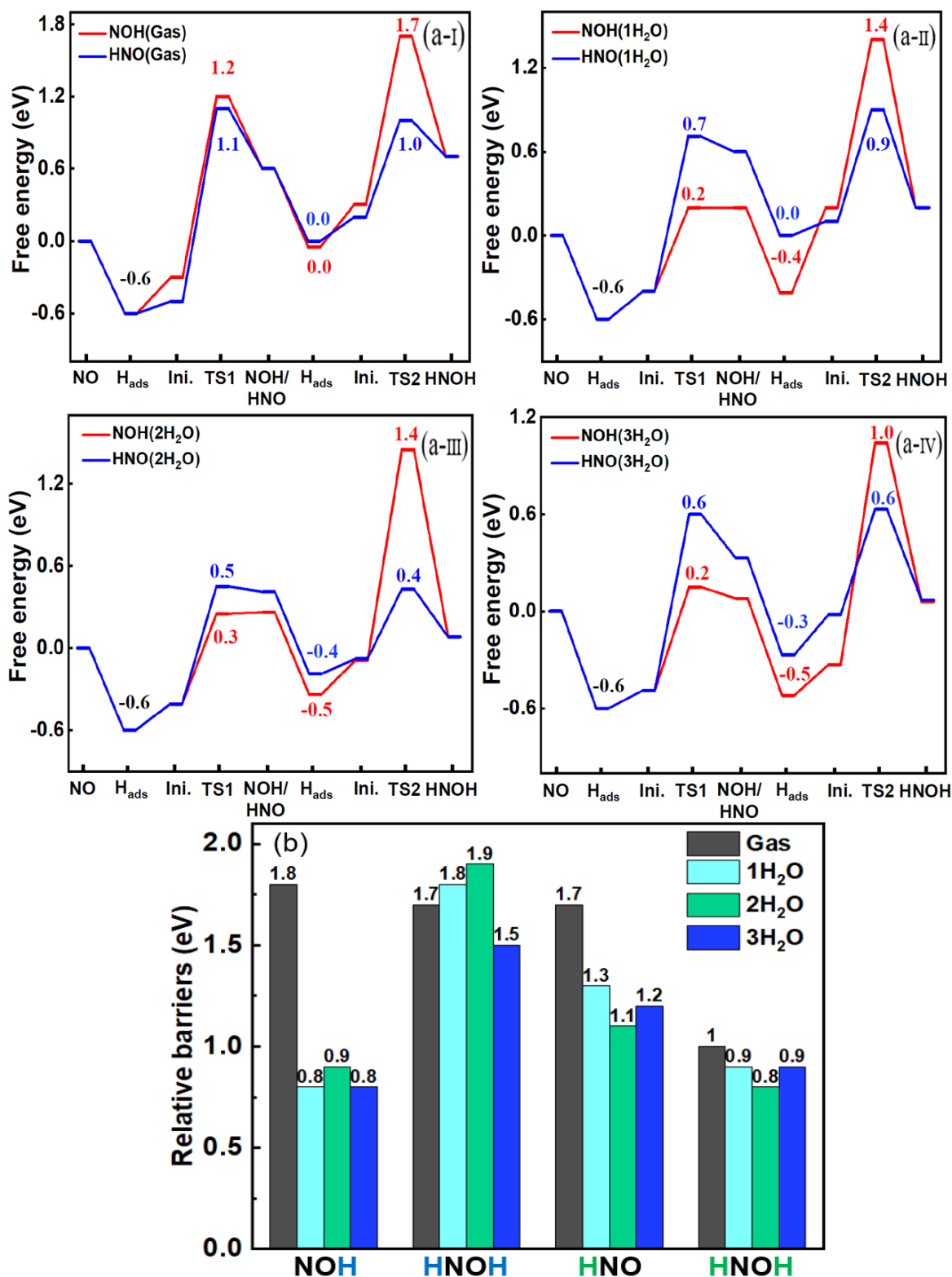


Figure 3.2 Free energy diagram for NO reduction on the Pd(111) surface with different molecules (a-I) Gas; (a-II) 1 H₂O; (a-III) 2H₂O; (a-IV) 3H₂O.(b) The relative barriers for each hydrogenation step via NOH to HNOH or via HNO to HNOH.

Finally, we want to briefly discuss the selectivity to N_2 and NH_3 based on the DFT calculations. Fig. 3.1 suggests that the N-N coupling barriers between different surface species (N^* , NO^* , NH^* , HNO^* , HNOH^*) are all higher than the corresponding hydrogenation barriers, indicating NH_3 formation to be more favorable. However, it should be noticed that NO^* and its reaction intermediates bind stronger with Pd than hydrogen does. The prominence of the N_2 product observed in experiments could be due to the high coverage of NO^* and its intermediates on the Pd surface, which leads to a competitive coupling reaction toward N_2 over the hydrogenation. This explains the high selectivity of the catalyst towards nitrogen ($> 98\%$) for the different reaction conditions employed. This interpretation is in good agreement with the observation that at the end of a batch experiment, the Pd surface is almost completely covered with remarkably stable N atoms⁷³.

3.3.3 Kinetic measurements

A comprehensive analysis is conducted on the activation barrier and reaction order for the reduction of nitrite on a Pd surface. These results and analysis were performed by Dr. P. Huang from U. Twente. We included this information here to compare with our DFT calculations. The major findings that are relevant to this chapter are summarized here. The apparent activation energy barrier is determined for the reduction of nitrite in aqueous phase on a Pd catalyst. The obtained value, as shown in Figure 3.3, was $29 \pm 1 \text{ kJ mol}^{-1}$. This falls within the range of values reported in the literature for Pd catalysts under similar reaction conditions¹⁴, which range from 22.6 to 35.3 kJ mol^{-1} .

Additionally, the reaction orders for nitrite and hydrogen were measured over a wide range of concentrations and at both low and high temperatures. The summarized overall reaction orders can be found in Table 3.1. The results, depicted in Figures 3.3, showed that regardless of the reaction temperature (25°C and 50°C), the apparent reaction orders for nitrite varied from 0.7 to 0 at high hydrogen partial pressures (0.8 bar). Notably, when the hydrogen partial pressure was reduced to 0.05 bar, there was a drastic change in the reaction order to -0.9 and -0.2 at 25°C and 50°C, respectively.

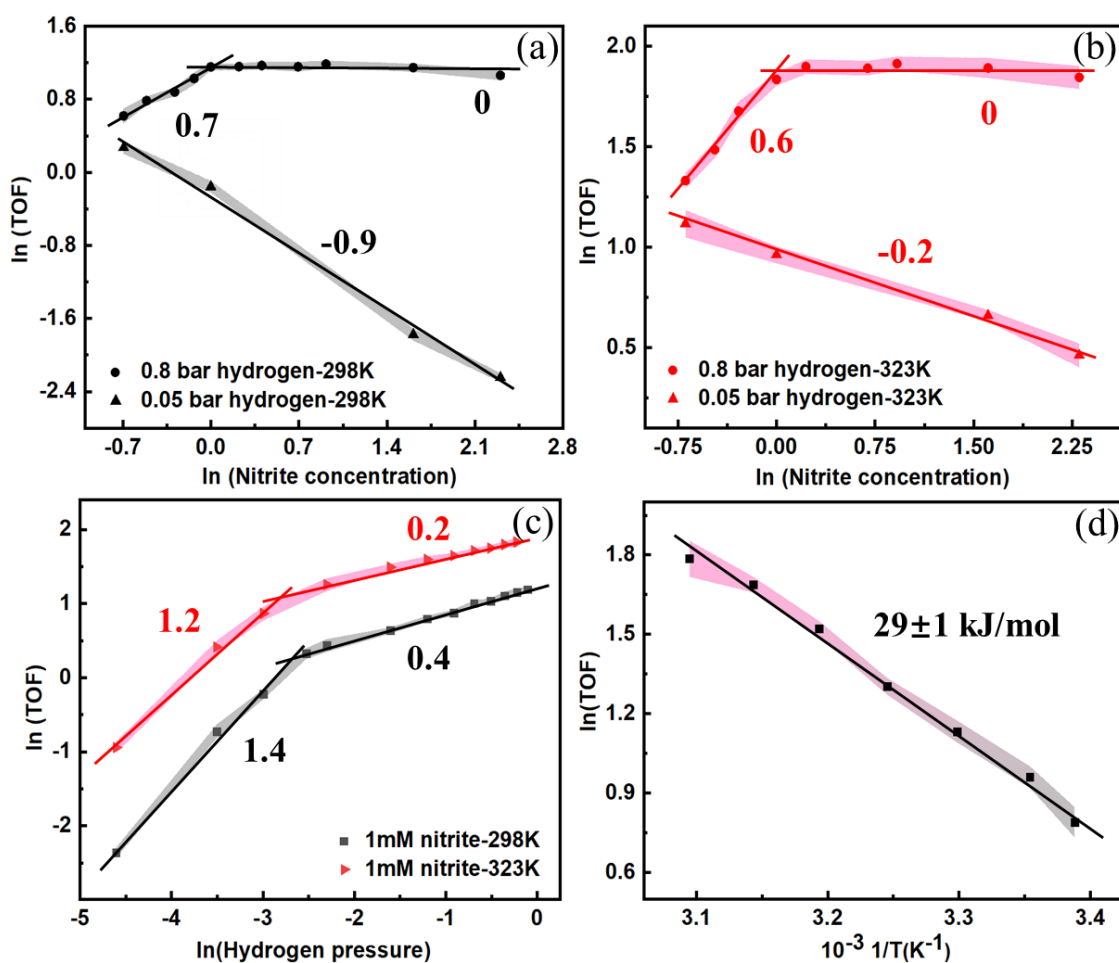


Figure 3.3 (a) and (b) effect of nitrite concentration on reaction rate for 0.05 and 0.8 bar hydrogen pressure at 25°C and 50°C. (c) Effect of hydrogen pressure on reaction rate for 1 mM nitrite concentration at 25°C and 50°C, (d) Temperature dependence of TOF over temperature. The shadow shows the error margin.

Table 3.1. Overview of the apparent reaction orders in nitrite and hydrogen information in all ranges of the nitrite and hydrogen concentrations

Temperature (°C)	Low hydrogen pressure		High hydrogen pressure	
	Hydrogen order	Nitrite order	Hydrogen order	Nitrite order
25	1.4 ± 0.1	-0.9 ± 0.1	0.4 ± 0.1	0.7 ± 0.1
50	1.2 ± 0.1	-0.2 ± 0.1	0.2 ± 0.1	0.6 ± 0.1

These significant reaction orders observed at high hydrogen partial pressures suggest that nitrite chemisorption occurs via molecular adsorption. On the other hand, the strong inhibition of nitrite observed at low hydrogen partial pressures indicates competition between hydrogen and nitrite for the same active sites on the Pd surface. This contrasts with the previously proposed mechanisms by Rosca et al.^{75,76} which claimed that the rate-determining step involves breaking the N-O bond followed by hydrogenation of the dissociated fragments. Huang's results suggest that the rate-determining step only requires one N-containing surface species, as the highest apparent reaction order is significantly lower than 2 even at low nitrite concentrations.

In the ¹⁵N-labelling experiments (Table 3.2), isotopically labelled NaNO₂ with ¹⁵N was used while keeping all other reaction conditions constant. The observed turnover frequency (TOF) for the reduction of labelled NaNO₂ was found to be similar to that of unlabeled NaNO₂ reduction. The small values obtained in this study suggest that there is no significant primary KIE, further supporting the idea that the rate-determining step is not related to N-N bond formation or N-O cleavage, as previously proposed.

In the hydrogen-deuterium isotope effect experiments (Table 3.2), kinetic experiments were conducted using deuterated hydrogen (D) and water. These experiments aimed to investigate the role of hydrogen insertion in nitrite hydrogenation. At 25°C, a primary kinetic isotope effect was observed, with a K_H/K_D value of 2.4. This indicates that the rate of reaction involving deuterium (D) is 2.4 times slower than that involving hydrogen (H) at room temperature. When the temperature was increased to 50°C, the K_H/K_D isotope effect decreased to 1.5 (Table 23.2). The kinetic isotope effect clearly indicates the involvement of the hydrogen atom in the rate-determining step of the reaction.

Table 3.2. Kinetic isotope effect

	KIE(K _H /K _D) ¹	KIE(K _H /K _D)	KIE(K ¹⁴ _N /K ¹⁵ _N)
	25°C	50°C	25°C
Pd/SiO ₂	2.37 ± 0.1	1.51 ± 0.1	1.04 ± 0.02

Note: 1. using D₂/D₂O to replace H₂ and H₂O. 2. using Na¹⁵NO₂ to replace Na¹⁴NO₂.

3.3.4 Rate expression development

As previously explained, the mechanism for nitrite hydrogenation involves barrier less formation of NO^* on the palladium surface from chemisorbed NO_2^- and H_2 , followed by sequential hydrogenation reactions to form HNO^* , HNOH^* , and HN^* . The only possible mechanism that would lead to reaction orders for hydrogen that vary from 0.5 to 1.5, and thus fitting our results, is that involving co-limiting hydrogenation of NO^* and HNO^* . Choosing a single RDS would unavoidably lead to variations of the reaction orders for hydrogen that vary between 0-1 for NO^* hydrogenation or 0.5-1.5 for HNO^* hydrogenation, which would be inconsistent with experimentally measured values. In this scenario, the elementary steps are as follows:

1. $\text{H}_2 + 2 * \rightleftharpoons 2\text{H}^*$ (*dissociative hydrogen adsorption*, $\mathbf{K}_1$)
2. $\text{NO}_2^- + * \rightleftharpoons \text{NO}_2^{*-}$ (*molecular nitrite adsorption*, $\mathbf{K}_2$)
3. $\text{NO}_2^{*-} + \text{H}^* + \text{H}^+ \rightleftharpoons \text{NO}^* + \text{H}_2\text{O} + *$ (*barrierless NO * formation*, $\mathbf{K}_3$)
4. $\text{NO}^* + \text{H}^* \rightarrow \text{HNO}^* + *$ (*hydrogenation of NO **, $\mathbf{k}_4$) **TS1** RDS
5. $\text{HNO}^* + \text{H}^* \rightarrow \text{HNOH}^* + *$ (*hydrogenation of HNO **, $\mathbf{k}_5$) **TS2** RDS
6. $\text{HNOH}^* + \text{H}^* \rightleftharpoons \text{HN}^* + \text{H}_2\text{O} + *$ (*hydrogenation of HNOH **, $\mathbf{k}_6$) **TS3**

The underlying assumption in this mechanism is that protons are readily available in this system and that chemisorbed hydrogen on Pd is required to provide the electrons for the reduction reactions. As a result, hydrogen atoms have been included in the site balance equation. This results in the following rate expression (Eq. 3.1).

$$r_{\text{NO}_2^-} = \frac{k_5 k_4 K_1^{3/2} K_2 K_3 [\text{H}_2]^{3/2} [\text{NO}_2^-] [\text{H}^+]}{\left[k_{-4} + k_5 K_1^{1/2} [\text{H}_2]^{1/2} \right] \left[1 + K_1^{1/2} [\text{H}_2]^{1/2} + K_2 [\text{NO}_2^-] + K_1^{1/2} K_2 K_3 [\text{H}_2]^{1/2} [\text{NO}_2^-] [\text{H}^+] + \dots \right]^2} \quad (3.1)$$

If one considers that the concentration of the $[\text{H}^+]$ is low and constant (about $10^{-5} \text{ mol L}^{-1}$) in comparison to NO_2^- and H_2 concentrations ($\sim 10^{-3} \text{ mol L}^{-1}$), then it is possible to neglect the influence of protons in this buffered system. In this sense, the expression above can be simplified to Eq. 3.2.

$$r_{\text{NO}_2^-} = \frac{k_5 k_4 K_1^{3/2} K_2 K_3 [\text{H}_2]^{3/2} [\text{NO}_2^-]}{\left[k_{-4} + k_5 K_1^{1/2} [\text{H}_2]^{1/2} \right] \left[1 + K_1^{1/2} [\text{H}_2]^{1/2} + K_2 [\text{NO}_2^-] \right]^2} \quad (3.2)$$

In this rate expression (Eq. 9), one can immediately recognize that the reaction order for hydrogen and nitrite vary from 0 to 1.5 and -1 to 1, respectively.

Conclusion

A DFT study was performed on nitrite reduction on the Pd surface. By calculating the possible intermediates, the most favorable pathway, and the detailed reduction mechanism for NO conversion into products are elucidated. We find water solvent displays a promotional effect on the hydrogenation steps, in which the activation barrier is reduced via the proton shuttling mechanism. Thus, the flattened free energy diagram suggests nitrite reduction and the hydrogenation on NO and HNO are controlling the overall reaction rate. It is in good agreement with the kinetic measurements from the collaborator. The details are listed below:

- 1) On a clean Pd surface, the comparable hydrogenation kinetic barrier was found on intermediate NO, HNO, and HNOH*. The overall reaction rate is controlled by the activation barrier of 1.3 eV. The kinetic-relevant species are identified as well as the sequence of the hydrogenation.
- 2) Implicit and explicit are employed on the reaction pathway and show unnoticeable stabilization on the mechanism. Instead of acting as an observer, the role of water was found to participate in the reaction. Water forms a hydronium ion and shuttling proton to the N-species, which significantly reduces the activation barrier by 0.5eV. The rate-limiting step and the relevant pathways to products N₂ and NH₃ are elucidated. Instead of solvent stabilizing the reaction in the last chapter, the other effect of solvent was found to promote the hydrogenation step via new pathway proton shuttling.
- 3) The proton shuttling energy diagram suggests the new rate-limiting step, which is both the hydrogenation step of NO and HNO. Based on the detailed kinetic study, the predicted reaction orders are in good agreement with the measured reaction orders.

After all, this study provided theoretical and experimental evidence on the nitrite reduction mechanism. Our results reveal the importance of considering the Gibbs free energies of activation (rate and adsorption constants) in analyzing the seemingly simple nitrite hydrogenation reaction on palladium.

CHAPTER 4

THE EFFECT OF LOCAL CHEMICAL ENVIRONMENT ON POLYMER-BASED STIMULI-RESPONSIVE RECYCLABLE CATALYTIC SYSTEM

4.1 Introduction

Based on previous research, palladium has been proven to be effective in hydrogenation and hydrolysis reactions. The fundamental understanding is significant for the catalytic processes based on Pd. For an advanced process, the complexity of the system needs to be considered. The local environment would significantly influence the activity and selectivity-inducing factors such as solvent effects and coordination numbers. Recognizing the potential of polymers to modify the local environment on metal catalysts, our research focuses on investigating the interplay between water, polymers, and catalytic reactions. In this chapter, we present the use of polymers to modify the local environment on metal catalysts and how polymers can be employed in the water structure and influence reactivity. This work builds upon our previous investigations into MgO and Pd catalysts, where water was observed to play a crucial role.

The solvent water is a significant part of the local environment of catalysts^{77,78}. As mentioned in previous work, we observed the profound influence of water on catalytic reactions^{60,78,79,80,81}. However, we also recognized that the introduction of functionalized groups on the MgO surface altered the role of water, highlighting the importance of surface modifications in controlling the local environment. Beyond the specific effects on water structure, polymers offer a versatile approach to modifying the local environment on metal catalysts. It could not only block sites but also altered the electronic structure of the metal atoms by adsorption on the surface. Another significant effect of polymers on metal catalysts is their hydrophobicity or hydrophilicity. Polymers with hydrophobic properties can create a more confined environment around the metal catalyst, which can promote specific reaction pathways.

To further understand and control the local environment, we turned to N-isopropyl acrylamide (NIPAM), a temperature-responsive polymer^{16,82,83,84}. Our collaborators present a new approach to influence the selectivity and activity of the metal-catalyzed hydrogenation reaction of nitrites in the aqueous phase using a catalyst containing NIPAM polymer coatings which can induce fully-reversible solvation effects on the surface reaction kinetics^{82,85,86,87,88,89,90}. It is assumed that the water behavior has been influenced by NIPAM¹⁶. The theory predicts that as the p-NIPAM environment becomes more hydrophobic above the

LCST the partition of molecules into the polymer matrix increases exponentially for the more hydrophobic reactants, while the opposite occurs for the hydrophilic substrates. And the results from experimental observation indicate that polymer-reactant interactions are key for both reactions of molecules on p-NIPAM functionalized catalysts.

Through collaboration efforts from computational and experimental studies, we demonstrated that NIPAM influenced the water structure, particularly through its hydrophobic properties^{16,84,91}. The altered water structure, in turn, impacted the reactivity of water, with the nitrogen atom on nitrite becoming more favorable for hydrogenation due to the favorable distribution of water molecules¹⁶. Noble metals, especially, are commonly dispersed on support materials with high surface areas to ensure a significant fraction of atoms on the particle surface are exposed. However, a crucial issue arises in many applications due to particle growth at high temperatures, leading to a decline in catalytic activity. The stabilization of the dispersion has been achieved for certain systems through optimized interactions with additional agents such as a polymer. The stimulus-responsive polymer could be used to design a stimulus-responsive polymer. The temperate-responsive polymer hopes to guide tailoring the micro-solvation environment of catalysts.

In this study, we demonstrated that the water structure over the metal surface can be modified by the polymer. The interface between metal and water is characterized by computational study. Molecule dynamics are used to generate the radial distribution of water to describe the metal-water interface in the presence and absence of NIPAM. It has been revealed that two types of water in terms of coordination. The second one is located further away from the surface but is still within the solvation shell of the metal ions. The presence of NIPAM restricts the mobility of water molecules near the surface, as they are confined by the micro-environment created by NIPAM. The mobility of water molecules is investigated by analyzing the MSD of water molecules. Overall, this suggests the presence of NIPAM does not drastically alter the water structure but instead influences the location of the second water peak.

4.2 Introduction and computational details

4.2.1 Experimental details

The functionalized group always introduces liquid-solid transport limitations. Our collaborators have tuned the reaction condition to verify the absence of any mass transfer limitation. An efficient gas-liquid reactant exchange is ensured by a high mixing rate. Under such conditions, a rigorous measurement on kinetic is performed on the p-NIPAM-catalyst.

The reaction is performed on liquid environment containing p-NIPAM. The analysis of reaction rate and kinetics at different temperatures identifies two distinct apparent activation barriers. They are relating the swelling/shrinking state of p-NIPAM. At temperatures below the LCST, low activation energy barriers were obtained. Increasing the temperature, however, led to activation barriers like those observed on the conventional catalyst. This indicates the swollen state of p-NIPAM is associated with the change in apparent barriers. The apparent barriers to NO reduction are associated with the protonation step facilitated by water molecules. Thus, the state of p-NIPAM is directly associated with the liquid phase and the water environment over Pd catalyst. In transition state treatments and solvent effect analysis suggests the stabilization on barrier are attributed to the enthalpic stabilization induced by NIPAM which is believed to be the strong hydrogen bonding of the p-NIPAM. Also, it is assumed that the confined degrees of freedom of the chemisorbed species.

The interaction between water and the polymer over the catalyst surface plays a crucial role in the catalytic system^{60,77,78,79,81}. The water-metal interface refers to the region where water molecules encounter the catalytic metal surface. In this context, the interplay between water and the polymer, such as p-NIPAM, is related to how these components influence the water-metal interface and affect the transition state of reduction. Understanding this interplay is important for elucidating the mechanisms and behaviors of the catalytic reaction.

Also, water has been shown to have a significant impact on the catalytic mechanism. Water molecule could participate in the reaction as competitive adsorbates or as reactants^{60,78,81}. As we introduced in the last chapter, water molecules may participate in key reaction steps by facilitating protonation or deprotonation processes^{60,81}. Thus, in this context, understanding the polymer effect on the reaction is significant.

Polymers, including p-NIPAM, can influence the reaction in various ways. On Pd-p-NIPAM, we assume polymer can provide a favorable environment of solvent affecting the reaction kinetics. Understanding the polymer's effect on the reaction is important for optimizing the catalytic performance and designing efficient materials for catalytic separation.

4.2.2 computational details

Next, we proceed to the methodology section, where we elucidate the computational techniques and procedures employed in this study to investigate the metal-water interface in the presence and absence of p-NIPAM. Instead of using implicit or explicit solvent models, to better express the effect of p-NIPAM, we performed ab initio MD simulations on the model to describe the metal-water interface.

Ab initio simulations were performed using the Vienna ab initio simulation package (VASP)^{38,39,40}. The ion–electron interaction was described through the projector-augmented wave (PAW) approach⁴¹. Perdew–Burke–Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) are used for the exchange and correlation energy⁴². The van der Waals interaction has been considered through Grimme’s DFT-D3 semiempirical method⁴³.

The construction of Pd (111) surface follows previous work¹⁴. To construct the Pd-water phase, the Pd bulk surface and ice-like water bulk phase was pre-equilibrated. An additional 15 Å vacuum is built in the Z direction above the water bulk in Pd-water phase. To test convergence, different sizes of water bulk were used over the surfaces, with the water density calculated as 0.700 and 0.999 g/cm³ in the bulk cell. To better simulate the effect of NIPAM on metal-water interface, NIPAM monomers were first introduced to the water phase and produce well-mixed solution phases which are added to the Pd surface later. One NIPAM monomer is positioned near the surface to simulate the collapsed structure above LCST. After equilibrium is reached at room temperature, the NIPAM monomer is in water at vertical height of 3 Å and 7 Å Pd surface. The location of NIPAM above the surface is indicated in Figure 4.1 potential energy diagram. It suggested the system reaches an equilibrium state after 10 ps. The data analysis is performed over the last 5 ps. The structures visualization and density analysis were performed using the VMD software.

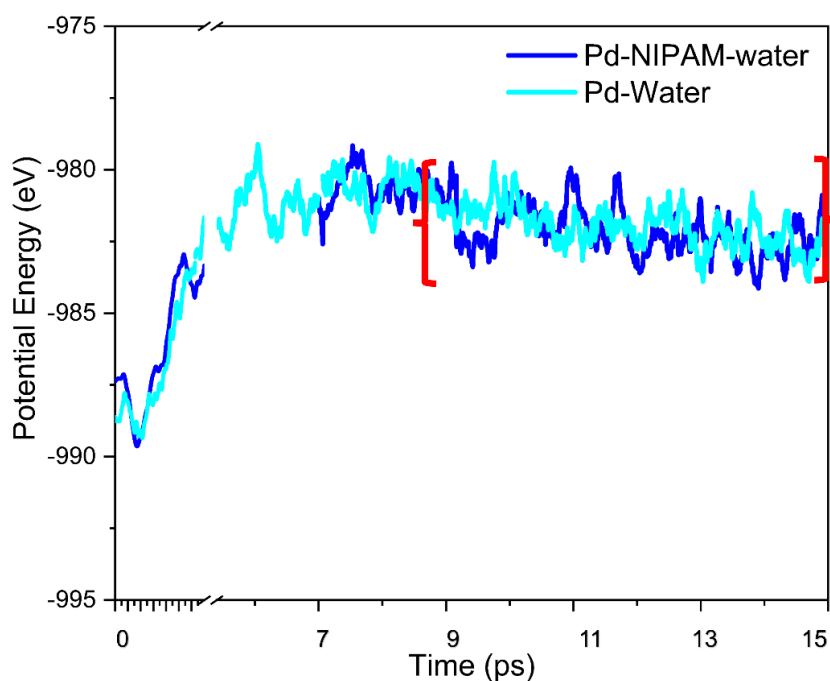


Figure 4.1 Variation of potential energy during the initial phase of the simulation. The red bracket highlights the energy fluctuations within a specific range, indicating that the structure

remains dynamically equilibrated, representing an equilibrium state. The first 15 ps are shown to verify the system's reaching of equilibrium, and data collection and sampling were performed based on an additional 15 ps of simulation time.

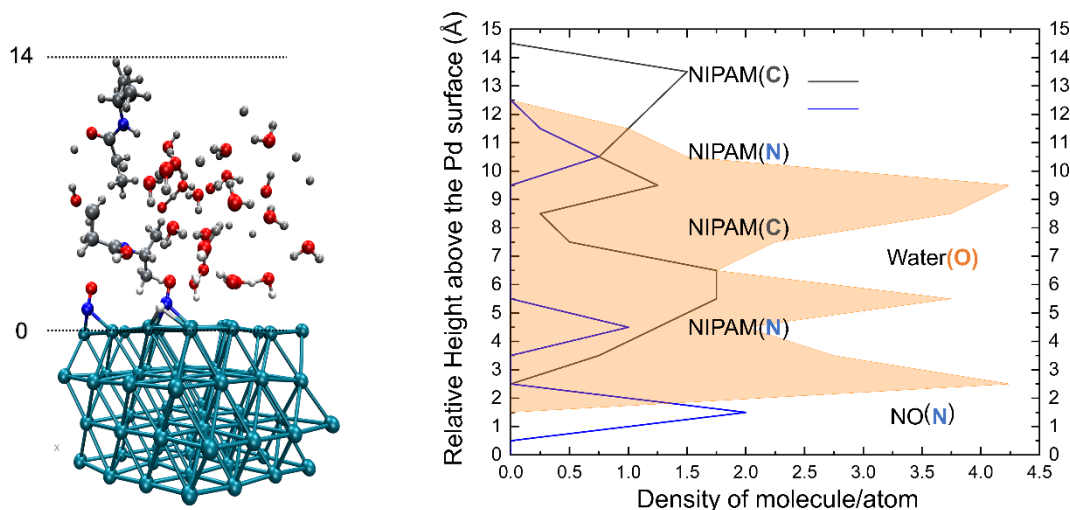


Figure 4.2 Equilibrated structure of the Pd-p-NIPAM system presented in atomic structure and atom density profiles along the surface. The left panel illustrates the atomic structure of the system, highlighting the interaction between Pd and p-NIPAM molecules. The right panel displays the atomic density profiles of p-NIPAM, H₂O, and reactant NO along the surface. Atomic densities were measured at 0.5 Å intervals.

Pd-water interface is attributed to the interaction between Pd and water. The Pd surface merely influences the water layer above as far as 5 Å. The water structure within 5 Å is considered catalysis-relevant^{11,77}. This study is particularly focused on the Pd-water interface in the presence of NIPAM. Figure 4.2 demonstrates the simulated metal-water interface are fully surrounded by NIPAM species. The NIPAM species locates around the range of 5 to 14 Å and influences the water bulk in the similar range. The water layer near the metal surface is below one of the p-NIPAM species. No attraction is observed between H₂O molecules and the amide group or the NIPAM chain which is consistent with many findings that NIPAM gains more hydrophobic properties above the lower critical solution temperature (LCST).

The calculation of water coverage is included. The profile of water density as well as the fluctuation of the distance between the oxygen atom and metal surface are plotted in Figure 4.2. The equilibrated water profile is defined as the vertical distance(height) of a water molecule along the surface normal. Water profile and diffusivity analysis were formed using the coordination of water molecules from the first water layer. The water profile was evaluated using vertical height along the surface normal of oxygen on each water molecule. The vertical

height is calculated as the difference between each water molecule and Pd surface in the Z direction. The water distribution diagram displays the possibility of each water location counted in the samplings. Around 7 or 8 water molecules are detected during the equilibration time which is roughly equal to 0.8 ML of water converge suggested in literatures^{77,92}. The ensemble average is calculated as the average of each water molecule found on the first water layer (vertical height below 5 Å). The H₂O diffusivity was evaluated by calculating the mean square displacement using the coordination along X, Y and Z directions according to the following equation:

$$\text{MSD}(\Delta t) = \langle [x, y, z(t - \Delta t) - x, y, z(t)]^2 \rangle \quad (1)$$

$$\text{MSD}(\Delta t) = \sum_{i=1}^N \text{MSD}_i(\Delta t) \quad (2)$$

where x, y, z represents the position of water molecules at each dimension at each given time t. The mean square displacement is calculated by the moving position of each H₂O molecule on each given time Δt .

The mean square displacement (MSD) is a measure of the average squared distance that water molecules move from their initial positions over a given time range. To calculate the MSD, the displacement of each water molecule is calculated at the time intervals of 0.5 fs, and the average of the squared displacements is determined. The MSD provides insights into the mobility and diffusion behavior of water molecules in the system with or without p-NIPAM.

Also, to quantify the effect of NIPAM on the catalyst, we tried to look at the surface-adsorbate binding and intermolecular bonding. H₂O are absorbed on the top site on the surface while NO₂⁻ and H are favorable to be located on the FCC site as previous finding. To investigate the adsorbate surface binding energy, the bond length between surface and the adsorbate are measured. The adsorbate binding strength are measured in the AIMD simulations.

4.3 Molecule dynamic simulations on Water-Pd-p-NIPAM interface

4.3.1 AIMD results about water-Pd interface

The water-water interface is usually shown in the atom density profile since it provides insights into the arrangement and distribution of water molecules along the palladium surface. It also helps understand the interactions between water and metal surface on each layer of water.

Water would form a layered distribution near the surface shown in the atom density profile. At the interface, the first layer of water molecules forms a tightly packed structure, commonly referred to as the "adsorbed" or "bound" layer. This layer is characterized by a high atom density, indicating a strong interaction between water and the palladium surface. The

bound layer existed at the height of 2 to 5 Å above the surface. For Pd surfaces, we identified two distinct peaks on water distribution. Both are bound layer, which locates at 2.3 and 3.5 Å, respectively.

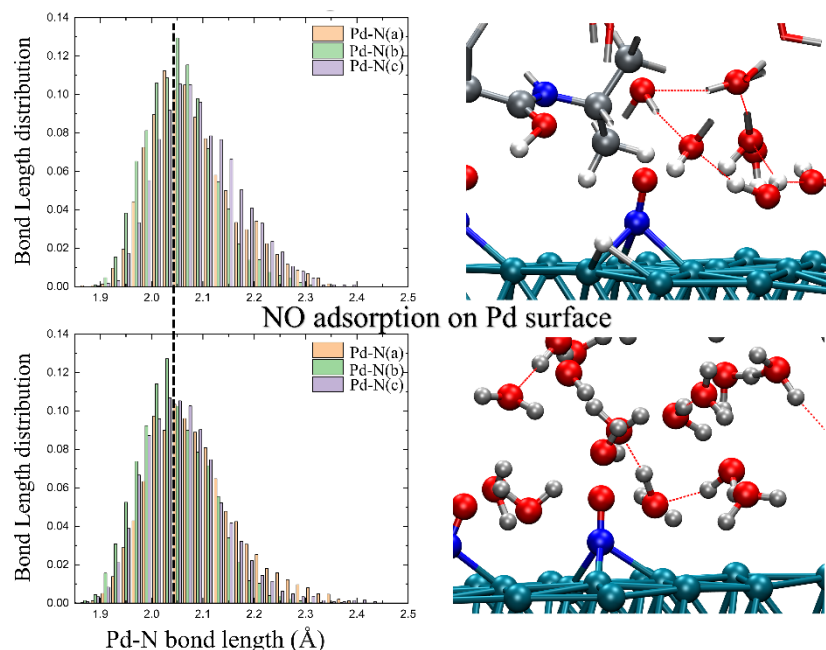


Figure 4.3 Variation of bond length along the simulation time. The right panel shows the Pd-N bond lengths, reflecting the NO binding energy. Each NO molecule interacts with three palladium atoms on the surface, resulting in similar bond lengths. The values shown in the graph represent the ensemble average. The left panel illustrates the vibration of Pd-N bond lengths during the 5 ps simulation time. The dotted line represents the ensemble average value for the Pd-N bond length.

Beyond the first layer, there is a transition from the bound layer to the bulk water region. As the distance from the metal surface increases, the water density approaches the bulk value, indicating a more typical water structure. This transition suggests that the influence of the metal surface diminishes with increasing distance, and the water molecules behave more like those in the bulk solution.

Normally, the bound layer is more relevant with the reactivity since the reactive site and the reactant adsorption are on the surface. Thus, we examine the atom density profile induced by the presence of polymer on the next section.

4.3.2 The water distribution over Water-Pd interface in the presence of p-NIPAM

The atom density profile also provides information about any structural changes induced by the presence of polymers or other surface modifiers. In the presence of polymers, the water distribution may be altered, leading to changes in the atom density profile. Here, we

investigate the effect of NIPAM on the bound water layer which normally existed within the height of 2 to 5 Å. By the comparison between the absence and presence of NIPAM, we noticed the difference occurred within the tails of the bound water layer. NIPAM exists at the height of range of 3 to 6 Å which overlaps with upper part of the bound layer. It resulted in narrow distribution of water layers. However, the centered position of the peaks remains very similar. It indicates the interaction between metal and water doesn't influence much by p-NIPAM. Overall, the effect of NIPAM on water layer are mild that the water layer is constrained by the NIPAM species. The structure of water layer is revealed on the following analysis where MD simulates the water diffusivity.

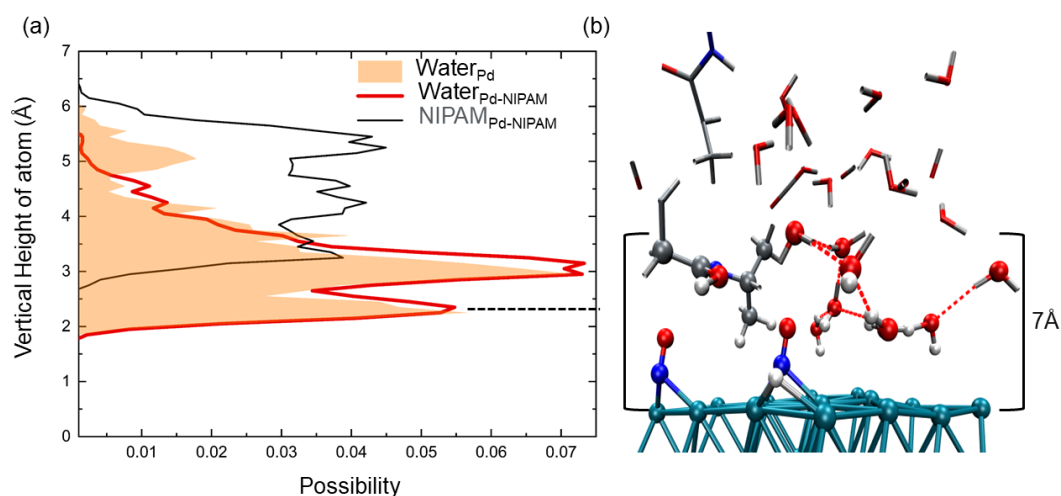


Figure 4.4 Water distribution above the metal surface in Pd-water interface (shaded area) and Pd-NIPAM-water interface (solid lines). The distribution is approximated by the relative vertical height of Oxygen to the Pd surface plane. (b) The computed structure of Pd-NIPAM-water interface showing the water layer within the height of 7 Å. showcasing Different water layers. The red dash line indicates the possible hydrogen bond in the interface. Element colors (Pd: light Blue; C: Grey; H: white; O: Red; Nitrogen: Blue.)

4.3.3 The water diffusivity over water-Pd interface in the presence of p-NIPAM

To investigate the effect of NIPAM on water diffusivity and its implications for the reactive environment, we examined the water distribution and mobility over time using molecular dynamics simulations. Figure 4.5 illustrates the water distribution along with simulation time, providing insights into the dynamic vibrations of water molecules at the Pd-water interface. Strongly bound water molecules near the Pd surface exhibit restricted mobility due to the strong binding forces, leading to a localized distribution close to the surface. Interestingly, the introduction of NIPAM does not directly affect the Pd surface but interacts with the water layer located approximately 3 Å from the surface. NIPAM's hydrophobic nature

causes it to repel water molecules, resulting in altered water structure and dynamics within its vicinity. This is evident in the confinement of the dynamic water distribution by the carbon chain of NIPAM, as shown in Figure 4.5.

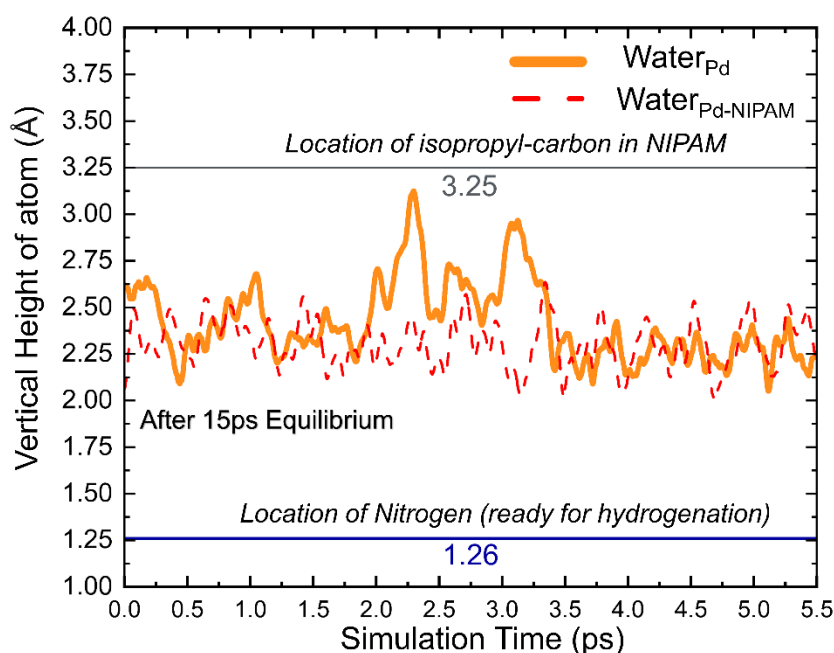


Figure 4.5 The varied position of H₂O molecules at the vertical height of 2.3 Å within 5 ps in simulation time. The distribution is shown for the specified time, while the water molecules at different heights and the distribution over a longer time is provided in the Supplementary Information (SI). The locations of NIPAM and reactant NO are depicted with solid lines, indicating their average values.

To further analyze the impact of NIPAM on water mobility, we examined the mean square displacement (MSD) of water molecules. The MSD provides information about the extent of particle or molecule mobility and diffusion within a system. The slope of the MSD plot as a function of time correlates with the diffusivity of the particles. By investigating the water layer located at 2.5 Å from the surface, we observed that the presence of NIPAM restricts the mobility of water molecules near the surface, as evidenced by smaller vibrations in the water distribution. This observation suggests that NIPAM hinders the movement of water molecules at that height. Although the water diffusivity in the presence of NIPAM shows a comparable value to the absence of NIPAM, the combination of the smaller vibrations and slight diffusivity difference indicates that NIPAM influences the mobility of water molecules within the confined region.

Furthermore, we observed intriguing dynamics in the upper layer of the binding layer. The Pd-O bond length exhibited a significant jump, indicating a sudden change in the

interaction between palladium and oxygen atoms in water molecules. This jump coincided with the time when water molecules typically exhibit dynamic diffusion behavior in the lower layer. The hydrophobic nature of NIPAM likely plays a crucial role in this phenomenon, as previously explained. Additionally, our analysis of diffusivity revealed higher diffusivity in the upper part of the water layer compared to the lower part, consistent with our observations. This asymmetry can be attributed to the dynamic nature of water molecules at the Pd-water interface, with fewer binding sites and lower interaction with the Pd surface in the upper layer, allowing for greater mobility and diffusivity.

Remarkably, the effect of NIPAM on water diffusivity is consistent across both the upper and lower layers. The minimal difference of $0.1\text{E-}05$ in diffusivity between the absence and presence of NIPAM suggests that NIPAM has a limited impact on the overall diffusivity of water in both layers. This similarity in the effect of NIPAM on diffusivity indicates that NIPAM primarily influences the local solvated environment rather than specifically altering water dynamics. The presence of NIPAM leads to a more confined and structured water environment, resulting in a similar reduction in diffusivity in both the upper and lower layers. Overall, these findings demonstrate that NIPAM causes structural changes in the water layer, leading to a more enthalpically favorable environment for reactions on the Pd surface.

Overall, the combination of strong binding forces between water and the Pd surface and the hydrophobic interactions between NIPAM and the surrounding water layer result in a complex interplay of water dynamics and confinement. Our study on the effect of NIPAM on water diffusivity at the Pd-water interface has provided valuable insights into the modification of the reactive environment. Interestingly, we found that the presence of NIPAM leads to a confined water environment without significantly impacting the overall diffusivity of water in both the upper and lower layers. This suggests that NIPAM primarily influences the local solvated environment rather than directly affecting water dynamics.

The confined and structured water environment created by NIPAM has important implications for the reactivity of hydrogenation on NO. The dynamic vibrations and spatial arrangement of water molecules play a crucial role in facilitating or hindering reactions on the surface. The restricted mobility of water molecules near the surface due to strong binding forces limits their ability to participate in reactions. Additionally, the confinement of water molecules by NIPAM affects their solvation and orientation, potentially favoring specific reaction pathways and facilitating the formation of more stable intermediates.

In our subsequent discussion, we will delve into how the dynamic vibrations and spatial arrangement of water molecules, influenced by the presence of NIPAM, contribute to the enthalpic favorability of reactions at the Pd-water interface.

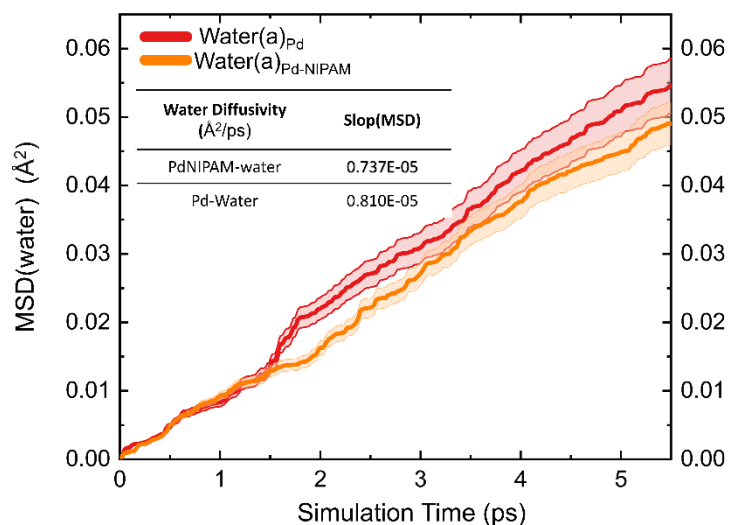


Figure 4.6 The mean square displacement of water (a) along the vertical direction of the metal surface. The error bar values are estimated to be 5.0% and shown in the shaded area. The calculated slope is listed in the table. The difference in the diffusivity with and without NIPAM is within the error bar of calculations.

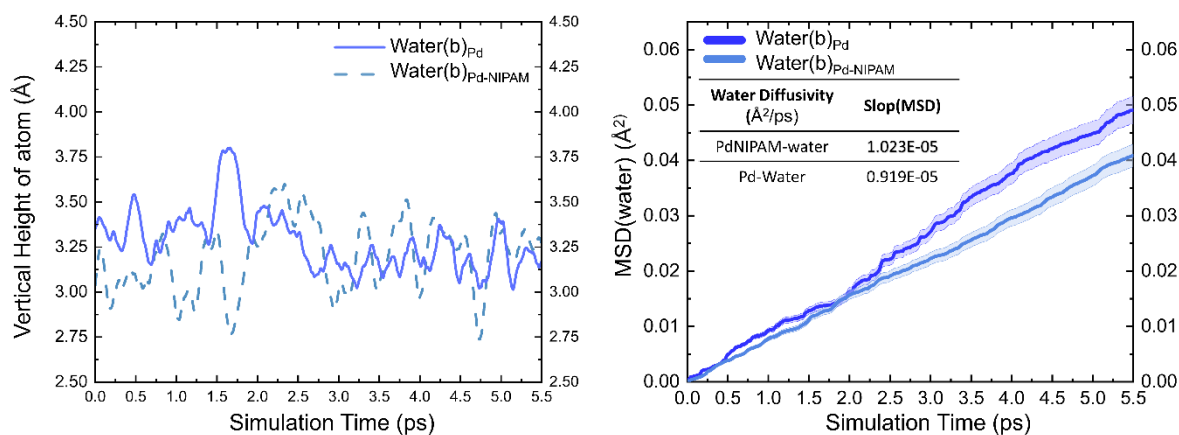


Figure 4.7 Left panel - Varied positions of H_2O molecules at a vertical height of 3.2 Å within a 5 ps simulation time. Right panel - Mean square displacement (MSD) of water (a) over the simulation time, along with the diffusivity along the vertical direction.

4.4 Discussion

4.4.1 The nature effect of NIPAM on the bounding layer

The hydrophobic nature of NIPAM is a key factor influencing the alteration of the metal-water interaction on the Pd-NIPAM surface. Molecular dynamics simulations provide evidence that at a height of 5 Å from the Pd surface, no hydrogen bonding occurs between

water layers and the hydrophobic isopropyl groups of NIPAM. This indicates that the isopropyl groups play a crucial role in repelling water molecules and driving the NIPAM-water interaction.

The overlap between NIPAM and the water layer is observed within the range of 3 Å, where the isopropyl groups are located. The presence of NIPAM creates a confined environment for the water layers above and below it. This is evident in the sandwich-like structure observed, with the water molecules tightly confined between NIPAM and the Pd surface. Observed from the water position change along with time, the impact of this confinement is further supported by the observation that without NIPAM, water from the bounding layer exhibits the ability to diffuse to the upper layer. However, in the presence of NIPAM, this diffusion is hindered due to the water-repelling properties of NIPAM on the adjacent water layers. This phenomenon is clearly illustrated in the observed confined water diffusion.

Overall, the hydrophobic properties of NIPAM significantly influence the structural changes in the surrounding water layers, leading to a more structured lower water layer at a height of 2.3 Å, which forms stronger covalent bonds with the Pd surface and restricts the vertical motion of water molecules. These findings provide compelling evidence of the water-repelling effects of NIPAM, which effectively modify the solvated environment around the metal surface.

4.4.2 The effect of NIPAM on NO reduction reactivity

The experimental results provide evidence that the introduction of hydrophobicity NIPAM leads to a reduction in the apparent activation barrier for nitrite reduction, indicating a change in the reactivity of the system. We attribute this reduction to the altered solvated environment of water caused by NIPAM. Water molecules play a crucial role in facilitating proton transfer and reshaping the energy profile through a proton shuttling mechanism. In the case of nitrite reduction, water promotes the hydrogenation of the N=O bond, which typically exhibits a relatively low activation barrier.

The inclusion of NIPAM in the system enhances this hydrogenation process, suggesting that it creates a structured water layer that facilitates favorable proton shuttling. The transition state of proton shuttling involves the water molecule pick adsorbed H atom to form hydronium ion (H_3O^+), a step that requires water molecule diffusion. Our previous results indicate that water molecules located at a height of 2.5 Å from the surface are crucial for the reactivity, as

they are strongly bound to the surface adsorbate, enabling efficient hydrogen transfer to water to form H_3O^+ .

In the presence of NIPAM, the water layer above the bound layer likely undergoes reconstruction, creating a confined micro-environment that facilitates the proton pickup process. The catalyst surface attracts H_2O molecules from below, while NIPAM, located above the bound layer, repels them, resulting in a localized water structure favorable for proton pickup. Although these changes in the water structure may not significantly affect water diffusivity, they contribute to a reduced apparent barrier for nitrite reduction by facilitating the energetically favorable proton pickup process.

In summary, the structured water environment created by NIPAM, with its hydrophobic nature and spatial arrangement, modifies the solvated environment and influences the reactivity of hydrogenation on NO. This alteration of water structure and dynamics plays a crucial role in facilitating the proton shuttling mechanism and reducing the apparent activation barrier for nitrite reduction.

4.4.3 To manipulate the local environment of solvent

In our current simulation, we focused on a low concentration of NIPAM added to the water bulk. However, it would be interesting to investigate the effects of higher concentrations of NIPAM on the water structure and dynamics. Increasing the concentration of NIPAM may lead to a more pronounced disruption of the water structure, providing further insights into the interaction between NIPAM and water molecules.

Additionally, incorporating temperature effects in our simulations would be valuable. By studying the dynamic transformations of NIPAM around its LCST (critical temperature), we can observe how changes in temperature influence the behavior and structure of NIPAM and its interaction with water molecules. This can provide a deeper understanding of the temperature-dependent effects on the confined water environment. It's worth noting that our current simulations were conducted on a relatively small scale using DFT. To investigate the phenomenon at a larger scale and better manipulate the local environment, advanced computational tools, and techniques, such as classical molecular dynamics simulations, can be employed. These methods allow for the simulation of larger systems and longer time scales, enabling a more comprehensive study of the effects of NIPAM on water dynamics and reactivity.

By understanding and controlling the local environment, we can effectively tune and enhance the reactivity of chemical processes. This concept extends beyond the modulation of

water structure in the presence of the chemical reactions, the local environment plays a crucial role in influencing reaction kinetics, thermodynamics, and selectivity. By manipulating factors such as temperature, pressure, pH, solvent composition, catalyst design, and surface properties, we can effectively modify the local environment to optimize reaction conditions.

Additionally, selecting appropriate solvents or solvent mixtures can create specific microenvironments that facilitate desired reaction pathways or promote the stabilization of reactive intermediates. The design and modification of catalysts can also be employed to tailor the local environment, optimizing catalytic activity and selectivity.

Furthermore, advances in nanotechnology and surface science have enabled the manipulation of the local environment at the molecular scale. As revealed on the MgO site, the surface modifications, OTS, can decorate the surface sites thereby influencing reaction mechanisms and selectivity. Overall, developing strategies to manipulate the local environment for chemical reactions is a promising avenue for improving reaction efficiency, selectivity, and sustainability. By understanding the interplay between the local environment and reaction dynamics, researchers can design innovative approaches to tailor the chemical environment and achieve desired outcomes.

Conclusion

Understanding and modifying the local environment of metal catalysts is pivotal for advancing catalytic processes. Through our investigations, we have shed light on the crucial role of water as a local environment modifier and demonstrated the potential of polymers to finely tune water structure and influence reactivity. Our major findings are listed below.

- 1) **Hydrophobic nature of NIPAM:** NIPAM exhibits hydrophobic properties, which affect the interaction between NIPAM and adjacent water layers. It repels the bound water layer and modifies the metal-water interface.
- 2) **Water structure:** The presence of NIPAM creates a more confined and structured water environment. Water molecules near the Pd surface experience restricted mobility due to strong binding forces. The dynamic vibrations of water molecules play a crucial role in the reactivity.
- 3) **The water diffusivity:** The altered water structure and dynamics induced by NIPAM influence the solvated environment around the metal surface.

By comprehending and manipulating the interplay between water, polymers, and metal catalysts, we open new possibilities for catalyst design and development. Our work paves the way for the rational design of polymer-modified catalysts with enhanced activity, selectivity,

and stability. Continued research in this field such as studying enhanced disruption of water structure and incorporating temperature effect provides insights into controlling a dynamic local environment on the catalyst. It holds promise for fine-tuning catalytic performance and enhancing the realization of sustainable and efficient chemical processes.

CHAPTER 5

LOCAL ENVIRONMENT ON DISPERSED METAL SITE OF CATALYST

5.1 Introduction

5.1.1 The dispersed atom site by varying coordination structure

Single-atom catalysts (SACs) are an emerging class of heterogeneous catalysts that have been gaining significant attention in recent years due to their unique properties and potential applications in a wide range of catalytic processes^{93,94,95}. Dispersing the efficient metal site into dispersed has proved to increase catalyst efficiency and avoid coke formation. Single-atom catalysts (SACs) have a significant advantage over the normal metal surface. SACs consist of a single atom of metal or other element dispersed on the surface of a support material, which can be tailored to enhance the catalytic activity and selectivity of the dispersed atom^{50,93,96}.

5.1.2 The single-atom catalyst used for electrical reaction

SACs offer several advantages over conventional catalysts, including higher surface area, increased stability, and tunable electronic and geometric properties^{96,97,98}. SACs have more exposed active sites and stronger metal-support interaction leading to the highly activated reactant^{93,94,95,97,99}. By dispersing the single-atom catalyst, the reaction could be precisely controlled when the size of an atom is controllable in the reaction. Also, the maximum atom utility is reached.

In the case of hydrogenation and hydrolysis, tens of thousands of palladium atoms could be replaced by one atom^{22,94,96}. The advantage of SAC over metal nanoparticles is that SAC has 100% atom utilization efficiency, which means all metal atoms are exposed as active sites, and no metal atoms are wasted in the bulk or covered by ligands. The local environment is tailored to reach the more exposed active site, low atom coordination^{25,26,27}. Strong metal-support interactions, well-defined bonding with the support based on the charge transfer and the electron influence²³. Such interactions are essential in optimizing the reaction kinetics and maximizing the catalytic performance.

5.1.3 Background of nitrite reduction using electricity

Compared to using thermal energy to supply catalytic reaction happen, alternative energy sources are using electricity as a supply. Unlike the thermal energy produced at the cost of carbon output, electricity could be generated in a clean and green way. They could be produced from renewable resources: solar, wind, and tides. Thus, applying electricity produced

from renewable resources to replace thermal-dependent conversation is a promising direction^{94,97}. Compared with metal particles, SAC has the advantage of fine-tuning the support and metal site for various properties. SAC is an active form of the metal catalyst. They offer strong adsorbate-surface bonding and target reaction for the conversion^{93,95,96,100}. Based on the previous study on metal surfaces, we know the N=O bond is potentially the most table bond in the reaction diagram. It requires an excessive amount of energy to hydrogenate the bond. In other words, it determines the activation energy.

5.1.4 Research objective

The objective of our study is to investigate the NO reduction mechanism on metal-based SACs, specifically focusing on the La-based SAC. We aim to provide a comprehensive understanding of the reaction pathways, intermediate species, and the advantages of using La-based SAC compared to Co based catalysts. By elucidating the fundamental aspects of NO reduction on SACs, we contribute to the development of efficient and selective single atom catalysts for the reduction of NO_x pollutants. Also, we demonstrate SAC has distinct electronic structure which is favored for the hydrogenation on NO molecule.

5.2. Research Approaches

5.2.1 The Metal selection on Single atom catalyst

Co-SACs feature a flexible, well-defined atomic geometry and superior electrical conductivity^{93,94,96,98,99,101}. We will focus on applying carbon material as the metal substrate due to the high surface area and the good electron capability. Also, it is relatively easy for single atom catalysts synthesis using carbon with defects and space.

The emerging application of rare-earth (RE)-based SAC has been developed with great potentials in several electrocatalytic reactions^{27,102,103,104,105,106} because of the distinct electronic properties of RE from d-block element; this includes the more localized 4f atomic orbital, large atom radii, pronounced spin-orbit coupling, high oxophilicity¹⁰⁷, and low electronegativity^{27,102,107}. The unique electronic structure of 4f orbitals is also reported to promote charge transport^{102,103,105}. Although many research have been performed to incorporate RE elements into nanostructured materials in the form of atomically dispersed single-atom site^{103,104,105,106,108,109}, a systematic study on the unique property of RE and its involvement in the electrocatalytic reduction in NO is still lacking. Thus, we select La-SAC as our prototype of RE element which have relatively high oxophilicity among the metal family.

The SAC catalyst synthesis is developing extensively along with the catalyst research. Unlike the metal nanoparticle with cluster size of 1-100 nm and finite number of active sites

the SACs have a large surface area but limited number of active sites^{18,110,111}. Thus, a short paragraph to describe the deposition of single atom on substrate are included below. Synthesizing single atom catalysts on carbon substrates, such as graphene, can be achieved through various methods, each resulting in catalyst surfaces with different loadings, atomic structures, and catalytic performances^{93,94,95,100}. Three commonly used methods for synthesizing single atom catalysts on graphene are atomic layer deposition (ALD), graphene quantum dots, and electron beam-assisted atom deposition.

- 1) Atomic layer deposition (ALD) is a technique that enables the uniform deposition of metal atoms on the graphene surface¹¹². Different metals can be used by utilizing specific precursor molecules. In the ALD process, the precursor is introduced into a chamber, where it adheres to the graphene surface until no more room is available. Typically, metal deposition selectively occurs at the line defects of graphene due to their higher metal reactivity. Subsequently, the excess precursor is removed, leaving only the metal atoms on the graphene surface. This process can be repeated through multiple ALD cycles to achieve the desired metal loading and distribution.
- 2) Graphene quantum dots offer another approach to depositing metal atoms, such as cobalt or other noble metals, onto graphene¹¹³. This method involves using small pieces of graphene with numerous edges and defects as a support for metal atoms. These few-nanometer-sized graphene quantum dots are capable of binding with metal atoms. The resulting hybrid material, consisting of graphene quantum dots with metal atoms, can be mixed with a larger piece of graphene to achieve a high metal loading and favorable catalytic activity. However, the high loading of metal atoms may present challenges related to aggregation.
- 3) Electron beam-assisted atom deposition utilizes an electron beam to assist in the deposition of single atoms onto the carbon substrate¹¹². This technique involves the ejection of lattice atoms from the graphene surface, creating vacancies. Single metal atoms are then precisely placed onto these vacancies. Similar to the previous methods, a precursor is required for this process.

It is important to note that each of these synthesis methods has its own advantages and limitations, and the choice of method depends on the specific requirements of the desired single atom catalyst. Further references and research can provide more detailed information for it^{112,113,114,115,116,117,118,119}. Thus, we are studying the computed ideal structure of the single atom site using computational tool to investigate its electrocatalytic reactivity.

5.2.2 Computing Electrocatalysis

CHE and CEP model. As we mentioned in Chapter 1, the activation barrier is a common factor for both thermal catalysis and electrocatalysis. In electrochemistry, the electrolyte provides protons that differ from the H_2 dissociation reaction in thermal catalysis. Proton transfer and diffusion are assumed to be barrierless in the electrolyte. Therefore, in computational studies of electrocatalysis, we use an approximation based on the computational hydrogen electrode (CHE) model. The details are explained in Chapter 1. Thus, the reaction energy profile is predicted by the thermodynamic difference, which is the reaction energy. The electric input on the catalyst is represented by the surface potential. The applied potential drives the reaction of the reactants. However, the CHE model has some limitations. Considering that the electrode undergoes a certain potential input for the catalysis to occur, it is not accurate to assume that the energy state of the reactants remains the same at different potentials. A modified method based on the CHE model has been developed, which provides a correction for the energy state at different potentials. The details are given in Chapter 1.

5.2.3 The effect of solvent on SACs

The solvent plays a similar role on single atom catalysts (SACs). However, the competitive adsorption is less significant since the surface has a limited number of sites. In this study, we will focus on the interaction between the SAC site and water molecules. We also believe that the interaction between water and the catalyst support is critical for catalysis research.

5.3. Results and Discussions

5.3.1 The electronic structure of Co and La-SAC

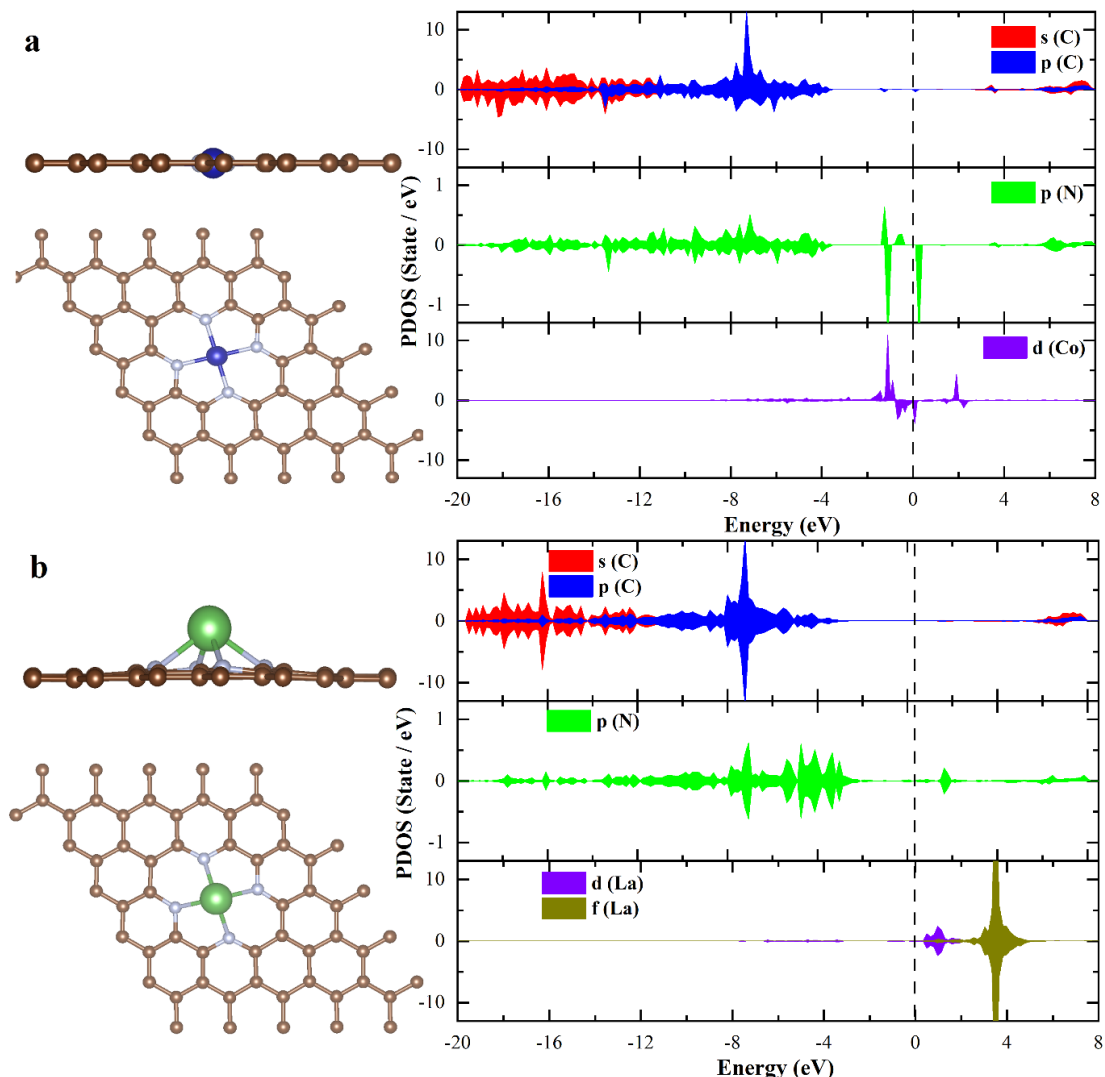


Figure 5.1. Comparison of the atomic structures and electronic properties of the Co- and La-SAC. (a) The optimized adsorption configuration of Co-SAC and PDOS of the substrate and the metal; (b) The optimized configurations and PDOS of La-SAC. Brown, silver, blue, and green balls represent C, N, Co, and La, respectively.

The formation energy was calculated for Co or La incorporated into N₄-Graphene. The values of E_f represent the thermodynamic trend for single atoms to aggregate into clusters versus binding to the substrate as single atoms. We find that the Co atom is attached to the center of the vacancy (Figure 5.1) with a formation energy of -2.5 eV, while the La atom strongly adsorbs above the surface with a formation energy of -3.3 eV. It shows that both metals tend to be atomically dispersed on the substrate rather than aggregation to form the metal clusters. The projected density of states (PDOS) analysis is then used to analyze the

hybridization state between the single atom and the substrate. The Co single atom hybridizes with metal d orbitals and nitrogen p orbitals of N₄-graphene close to the Fermi energy. The CoN₄ moiety carries a magnetic moment of 0.69 μ_B , as shown by the asymmetric spin-up and spin-down states close to the Fermi energy (Figure 5.1a). In contrast, La-SAC does not carry any magnetic moment. The Bader charge analysis shows that La is oxidized to form La²⁺, indicating a pronounced charge transfer between La and the substrate. The more localized La electronic states indicate weaker hybridization with the substrate, and its larger atomic size results in vertical displacement from the graphene plane. Similar electron transfer was reported on single La atom on graphitic carbon for the CO₂ reduction¹⁰⁵. The different electronic occupation in La compared to Co leads to unique chemistry when interacting with oxygenates as discussed below.

The reactant NO adsorbs with two possible configurations: side-on with both N and O atoms involved in the bonding and end-on with only N atom forming a bond with the metal. We find that only the end-on configuration is accessible on the Co-SAC, like most transition metal-based SACs^{120,121}. The adsorption energy is -1.9 eV (Table 5.1). The activation of NO on Co-SAC is manifested by the elongated N-O bond, which increases to 1.19 Å from 1.17 Å in the gas phase. Bader charge analysis in Figure 5.2 shows that 0.24 negative charge is accumulated in the NO molecule. Instead, NO adsorbs on La in both the end-on and side-on configurations, with the same adsorption energy of -1.8 eV, comparable to NO adsorption on Co-SAC. The La-N bond length is 2.43 and 2.61 Å in the side-on and end-on configuration, respectively. The N-O bond is elongated to 1.22 or 1.26 Å and is observed on La-SAC, indicating a more pronounced NO activation than it on Co-SAC. In addition, we find a more enhanced charge transfer for NO adsorption on La-SAC. That is, side-on NO gains 0.71 electrons in total. Compared to gas-phase NO, the N and O atoms upon adsorption carries 0.12 and 0.59 negative charges, respectively, transferred from the La-SAC. The NO adsorbed via the end-on configuration on La-SAC shows a very similar trend in charge transfer and bond length with the side-on configuration. Both the intensified negative charge and longer chemical bond imply a more activated NO and a feasible NOER activity over La-SAC.

Table 5.1. Adsorption energy and bond lengths upon NO adsorption on Co- and La-SAC.

SAC (Configuration)	Eads (eV)	Bond Length	
		N-Co/La (Å)	N-O (Å)
Co (End-on)	-1.9	1.80	1.19
La (Side-On)	-1.8	2.61	1.26
La (End-On)	-1.8	2.43	1.22

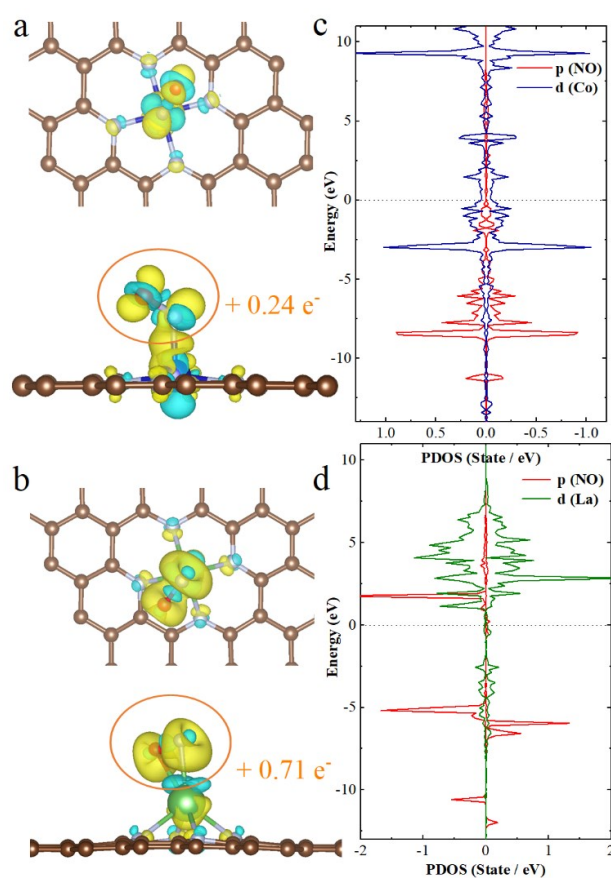


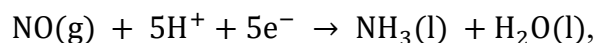
Figure 5.2. Comparison of the NO adsorption on the Co- and La-SAC. Charge density difference of NO adsorption on (a) Co- and (b) La-SAC. Bader charge on the NO is shown. The iso-surface value is set to $4 \times 10^{-3} \text{ e}/\text{\AA}^3$. The positive and negative values in yellow and cyan show electron accumulation and depletion, respectively. The PDOS of NO adsorbed on (c) Co-SAC and (d) La-SAC. Brown, silver, red, blue, and green balls represent C, N, O, Co, and La, respectively.

5.3.2 NO adsorption and activation on La and Co-SACs

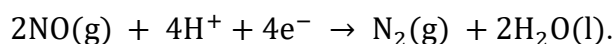
Further insight into NO adsorption on SACs is revealed in the PDOS analysis on NO p orbital and the metal d orbital (Figure 5.2). NO on Co-SAC with more hybridized and delocalized p-states suggests a covalent adsorbate-catalyst interaction. The magnetic moment on Co-SAC disappears upon NO adsorption because the two unpaired electrons at Co-SAC and NO are now paired, leading to degenerate states. Instead, the NO p states remain localized on La-SAC, evidenced by the narrower states in Figure 2d. This analysis suggests an ionic bonding on La-SAC. The NO-La-SAC carries a magnetic moment of 1.9 μ_B , which results from the unpaired electron in P_y of NO and an addition electron transferred from the La-SAC to the P_z orbital of NO (Figure 5.2d). Thus, the La single atom in SAC can be considered La^{3+} upon the NO adsorption. The La-SAC has strong interactions with NO and water due to its strong oxophilicity, which was reported in the literature¹⁰⁷. Thus, there is pronounced NOER activity difference as discussed below.

5.3.3 NO monomer electrical reduction

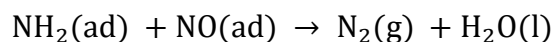
The mechanism of NOER has been studied extensively on metal catalysts and SAC. It is known that the product of NOER depends on the NO coverage. At a low coverage, the NO molecules adsorb on metal sites and follows sequential protonation to form NH_3 following



where the first protonation is the potential-limiting step in DFT studies^{120,122,123}. When the NO coverage increases, NO may adsorb as a dimer and be reduced to N_2 through an N_2O intermediate following the equation.



N_2 can also be produced through the N-N coupling between adsorbed NO and partially hydrogenated species NH_x described by the equation.



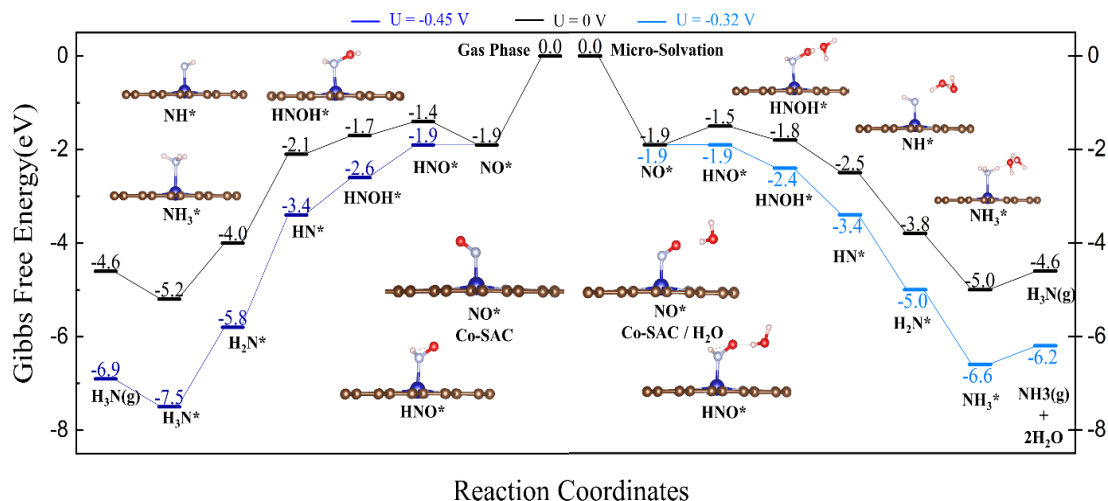


Figure 5.3. Calculated free energy diagram for NOER toward NH_3 over Co-SAC. The profile on Co-SAC following the most favorable reduction pathway at pH=0 in a gas-phase model is shown on the left panel and in a micro-solvation model on the right.

In the following, we first study the NOER initialized by NO unimolecular adsorption on Co- and La-SAC. We find that in the absence of water solvent, the key intermediate HNO^* is more thermodynamically stable than NOH^* , in good agreement with literature studies^{120,121}. The NOER reaction follows the sequence of NO, HNO, HNOH, NH, NH_2 , and NH_3 . We also tested the species H_2NO^* and H_2NOH^* but found they were less energetically favorable. The complete NOER diagram on Co-SAC is shown in Figure 5.3; the NOER on Co-SAC is limited by the first protonation step, which demands an electrode potential of -0.45 V to eliminate the uphill energy difference. Meanwhile, the desorption of NH_3 is energetically difficult in the gas phase, similar to molecular desorption over many noble metal-based SAC¹²³, requesting 0.6 eV desorption energy on Co-SAC. The desorption is much easier in the water solvent as discussed later in the text.

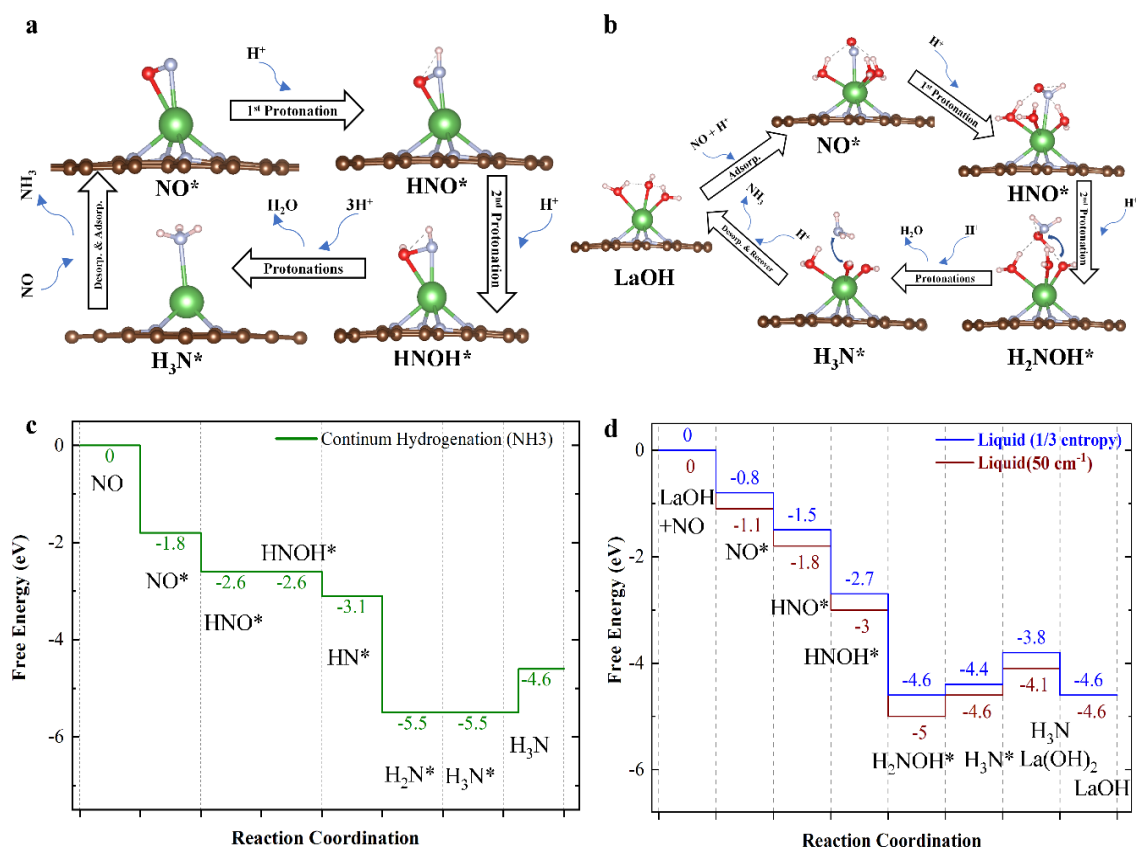


Figure 5.4. Calculated free energy diagram for NOER toward NH₃ over La-SAC. (a) and (c) The configuration of NOER species on La and free energy diagram of NOER toward NH₃ on La-N₄-graphene catalyst without considering water. (b) and (d) NOER configurations and free energy diagrams using micro-solvation. Two different methods to calculate the entropic contribution are compared in (d).

A similar NOER path was investigated on La-SAC (Figure 5.4a). No obvious uphill step was observed on the formation of HNO* or other steps, except the last desorption of NH₃ (Figure 5.4c). This trend in NO reduction is distinct from Co-SAC. The feasibility of HNO* on La-SAC can be attributed to the intensive charge transfer to NO from La. As evidenced in the PODS and magnetic moment calculations in Figure 5.2, the adsorbed NO molecule is electron rich on La, driving the occurrence of protonation. On La-SAC, the sequential hydrogenation follows HNO, HNOH, NH, NH₂, and finally NH₃, which then desorbs. No uphill steps were observed for the overall path in the absence of an electrode potential. Despite the desorption step of NH₃ with an energy cost of 0.6 eV energy cost, the solvation energy of NH₃ may reduce the energy cost, similar to it on Co-SAC.

5.3.4 The role of solvent on Co and La-SACs

In heterogeneous catalysis, the role of waters is critical in many different ways and in a variety of reactions^{7,11,14}. For example, the interaction between surface species and water could be responsible for lowering the activation energy of the rate-limiting step and enhancing the catalytic activity. Here, we investigated the interfacial reaction in NOER by introducing an explicit water molecule. On Co-SAC, it is found the water is weakly bound to Co-SAC; the adsorption energy is -0.23 eV. Since NO adsorption is strongly favored at Co-SAC, the pre-adsorbed H₂O is thus replaced upon NO adsorption. This water is then tightly bind with the NO adsorbate, forming a H-bond, and other reactive intermediates formed along the pathway. We find that this H-bonding stabilizes each intermediate in NOER to a similar extent. As shown in Figure 5.3, the solvent brings 0.1 to 0.3 eV energy gain in the NOER elementary steps on Co-SAC. The limiting potential (i.e., to form HNO) is reduced by 0.13 V when water forms a H-bond with HNO* in this micro-solvation model. Also, the energy cost of NH₃ desorption decreased by 0.5 eV when the solution was applied.

The role of water is particularly pronounced over La-SAC. On La-SAC, the water solvent has a strong interaction with the La-SAC. Multiple H₂O molecules co-adsorb at La-SAC because of the high oxophilicity of La and open space for adsorption. We found that three H₂O could attach to La-SAC, forming La(H₂O)₃ with adsorption energy for each H₂O around -0.8 eV. Besides, the water dissociation to form La-OH is favorable under zero external potential. The first water dissociation in La(H₂O)₃ forms La(OH)(H₂O)₂ with an additional energy gain of -0.59 eV. However, deprotonation of the second and the third water is endothermic, requiring 0.58 and 1.74 eV reaction energy, respectively. The Bader charge analysis show more positive charge localized at the hydrated La center than the pristine La-SAC, due to the formation of this hydroxide group.

On the hydrated La-SAC site, NOER follows a similar reaction path shown in Figure 4b. NO is reduced to HNO* followed by HNOH*, similar to the NOER mechanism on the pristine La-SAC. Once the HNOH* species is formed, it simultaneously abstracts a proton from a La-bonded water, forming H₂NOH*. The remaining H₂O considerably stabilize the H₂NOH species, different from the NOER intermediate on a clean La-SAC. The exothermic reaction indicates that formation of the H₂NOH intermediate is feasible. This new intermediate observed on hydrated La suggests a prevalent solvent effect that provides an excellent stabilization for certain polar chemical species. Upon another protonation step, the N-O bond in H₂NOH dissociates to form NH₂.

Before moving on to discuss the solvent effect and reactions to form N₂, here we briefly discuss the entropic contribution and the effect of constant potential. Using two ways to include the entropy effect, the NOER free energy profile on La(OH)(H₂O)₂ is displayed in Figure 5.4d. In one method, the low frequency (< 50 cm⁻¹) modes were all rounded up to a particular value (50 cm⁻¹), while in the other, 1/3 entropy loss of gas-phase molecule was assumed upon adsorption. Using the second approach assuming adsorbed NO maintains 2/3 gaseous translational and rotational entropy, the adsorption energy of NO is -0.8 eV. The NO adsorption is more feasible in the first approach with an additional 0.3 eV energy gain. In the NOER free energy diagram, this is generally true that all the surface species are stabilized by 0.3 eV with the first approach. Therefore, the reaction energies remain the same for all the elementary steps, except adsorption and desorption.

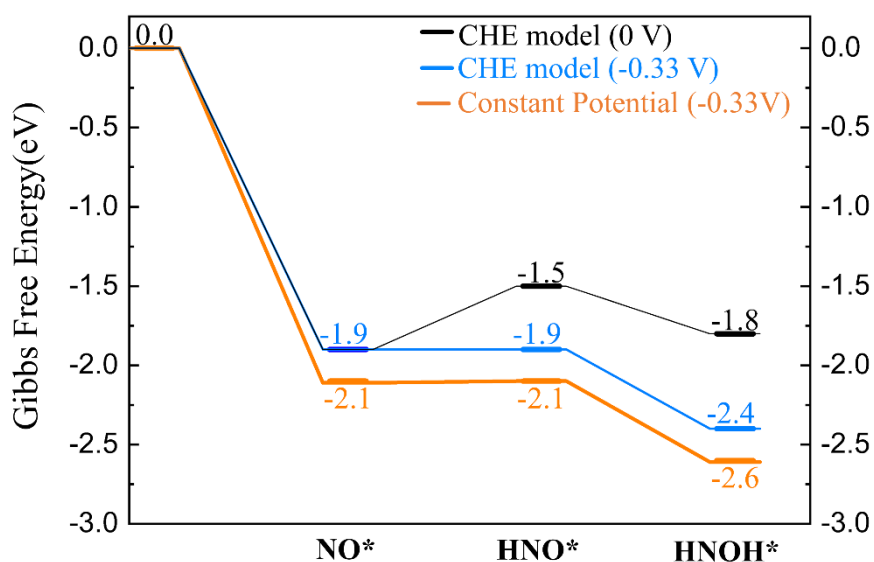


Figure 5.5. The free energy diagram of NO reduction toward HNOH on CHE model and constant potential approach.

The first two protonation steps are included since NO protonation step is calculated to be potential determined step based on CHE model. When the calculation is performed on constant-potential, it gives very similar results in term of potential determined step. It is noted that each intermediate in NO reduction are stabilized to the same extent at constant potential.

5.3.5 NO bimolecular electrical reduction

The hydration on La-SAC offers a strong driving force on this sequential hydrogenation mechanism. We find that the LaOH(H₂O)₂ favors transferring one more hydrogen to NH₂*, producing NH₃*. The hydrated La-SAC undergoes another protonation step to close the catalytic cycle, recovering the active site to LaOH(H₂O)₂. This step is slightly endothermic with an 0.2 eV energy cost. In the presence of water, in addition to stabilizing the reactive

species on $\text{LaOH}(\text{H}_2\text{O})_2$, the solvent saturates the hydration of La and participates in the reaction acts as a proton source. There are no uphill elementary steps observed in NOER on La-SAC in this micro-solvent model.

We further calculated the hydrogen binding energy over Co-SAC, La-SAC, and hydrated La-SAC (i.e., $\text{La}(\text{OH})(\text{H}_2\text{O})_2$). Over the La-based SAC, the hydrogen binding energy is more positive than it on the Co-SAC, which suggests La-based SACs show improved selectivity toward NOER.

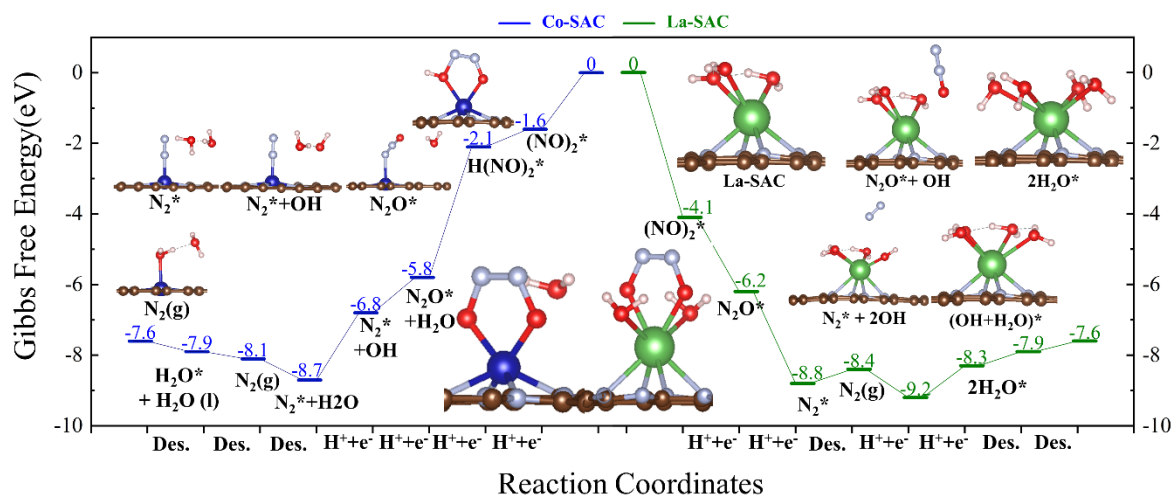


Figure 5.6. Free energy diagram of NOER toward N_2 at $\text{pH}=0$. The profile on Co (left half) and La (right half) are compared.

In the following, we discuss the alternative reaction path of NOER toward N_2 . In the proposed mechanisms on Pt, highly feasible N_2 formation could result from N-N coupling between N-containing surface species.¹²⁴ The NOER mechanism on SAC toward N_2 starts with NO bimolecular adsorption. $(\text{NO})_2$ has a weak bond between two N atoms within the molecule. The metal site interacts with the two O atoms in the NO dimer, forming a five-membered ring. The structure of $(\text{NO})_2$ adsorption and its reduction on Co- and La-SAC are displayed in Figure 5.6. The dimer $(\text{NO})_2$ is highly stabilized over La-SAC. The adsorption energy per NO is -2.1 eV, about the same as the single NO adsorption. Such strong binding can be attributed to the strong oxophilicity of La-SAC. The bimolecular adsorption energy on Co-SAC is -0.8 eV per NO, which is weaker than single NO adsorption (-1.6 eV). Due to this less favorable $(\text{NO})_2$ adsorption on Co, the bimolecular adsorption on Co-SAC could only be observed when the NO concentration is very high. The reduction of $(\text{NO})_2$ to N_2 includes four proton-electron steps. The protons are added to O sequentially, forming $\text{H}(\text{NO})_2$, $\text{N}_2\text{O} + \text{H}_2\text{O}$, and $\text{N}_2 + 2\text{H}_2\text{O}$. Each N-O bond cleavage produces a water molecule at the end. The catalytic cycle is completed with the desorption of N_2 and water molecules. The free energy diagram of

(NO)₂ reduction on Co-SAC shows no uphill steps except the desorption step. It is anticipated that NH₃ is still the major product as co-adsorption of two NO is less likely on Co-SAC.

Over La-SAC, La starts with a hydrated configuration LaOH(H₂O)₂. To allow the NO bimolecular adsorption, a protonation to the OH on La is needed to desorb a water molecule to accommodate (NO)₂ adsorption. The adsorption is still exothermic even though it replaces one water molecule. The dissociation of N-O bonds in (NO)₂ is favorable on La after a protonation step to N. The N-O bond dissociation produces N₂O and OH directly. N₂O is not fully attached to La. We find that reduction of N₂O to N₂ is feasible in the protic environment and easily desorb from the SAC with an almost neutral energy profile. This hydrated La-SAC thus promotes both NH₃ and N₂ production.

5.3.6 The mechanism on different SACs

It should be noted that the SAC defects, such as those generated during pyrolysis, may affect the electronic structure of the graphene and performance of the catalyst. For example, presence of the structural defects can tune the charge localization on the carbon and also the coordination between the metal center and the carbon host^{105,125,126}. The exact local bonding configuration and coordination of La can be tuned by enlarging the vacancies in graphene, which provides more flexibility for introducing additional functional groups^{105,125}. In addition, the reaction mechanism may vary depending on the active sites, as the latter determine the stability of different species over the surface, such as NOH on metal-free but defect-rich graphene¹²⁶ and HNO over metal and Co-SAC^{32,123,127}. The exact reaction mechanism (and the dominate surface species) is thus determined by the active sites; It will be valuable to compare the calculated results with experiments over well-controlled samples. This versatile tunability can in principle be leveraged to control the electronic structure of the single atoms in experiments.

Conclusion

In this study, we are exploring the tuning of the binding energy between metal and NO by varying the coordination number of the active site as well as the type of active site. Co and La are selected and compared on NO reduction. The detailed findings are listed below:

- 1) Co and La SACs are selected and compared for their performance in NO reduction. LA-SAC exhibits enhanced electron transfer to adsorbed NO, facilitating the potential-limiting step of NO protonation compared to Co-SAC.

- 2) The current computational results on free energy calculation on each state are proved valid after considering a few corrections on the energy state including entropy correction and the potential correction.

After all, the study reveals the unique mechanism of NO reduction over rare-earth-based catalysts, highlighting the potential application of atomically dispersed f-block elements in electrocatalytic reactions. The dispersion of metal atoms in SACs significantly promotes the hydrogenation reaction, suggesting broader applications for metal atom dispersion.

CHAPTER 6

INVESTIGATE THE POTENTIAL OF CATALYTIC SEPARATION.

6.1 Introduction

To cut down energy consumption, pressure-driven and solution-diffusion separation by membrane have been one of the promising processes¹²⁸. The EPA estimates \$4 billion/year and 100 million tons of CO₂ emissions could be saved when the use of membrane-based separation increases. To improve the membrane design, we investigate gas separation to develop our understanding of molecules in a confined environment. iptycene units are the ones that exhibit extraordinary permeability on gas separation.

To use porous material as the platform for the catalyst, we focus on utilizing the polymer as a matrix or support material. Previous research has demonstrated the potential of dispersed metal sites for catalytic separation^{88,89,90,129}. However, challenges persist in finding suitable substrates and structures with high stability and understanding the principles of polymer designing¹³⁰.

One crucial factor influencing the separation efficiency of porous materials is the distribution of free volume. To improve separation capabilities, we investigate the impact of tuning the content concentration on the distribution of free volume within the porous polymer¹³¹. Our research is particularly focused on amorphous polymers, where designing the polymer structure holds promise for enhancing separation efficiency¹³².

The reaction micro-environment near the active site offers a variety of tunability for metal clusters¹³³. The transition between swollen and de-swollen states can be tuned by modifying the chemistry of the polymer vesicle. These complex polymeric environments can exert on the surface reaction intermediates and, consequently, transition state energetics of catalytic reactions. It is critical to understand the adsorbate adsorption in a complex polymeric environment.

In this study, we present a computational approach to design and optimize a porous material for catalytic separation. We propose a computational investigation to achieve a molecular-level understanding of small-molecule sorption and transport in free volume. Atomistic simulations are used to elucidate the underlying transport mechanism in polymers with configuration-based free volume and the effect of nano-confinement. We demonstrate the potential of dispersing metal sites on the substrate and apply it to the reactive process. In this

chapter, we aim to maximize the exposed surface area of the catalyst while ensuring its stability by embedding catalytic sites within a polymer matrix.

By employing molecular dynamics simulations, we investigate the structure-properties relationship associated with varying concentrations of the triptycene compound. Specifically, we examine the formation of free volume within the triptycene-containing chains and explore their potential application for gaseous reactant separation^{88,89,131,134}. Our objective is to enhance the performance of catalytic separation by leveraging the unique properties of triptycene and providing guidance for the design of efficient and sustainable material processes.

6.2 Computational & Analytical method

6.2.1 Membrane model construction

The simulation of triptycene-based TPBO was performed to investigate the properties of the free volume responsible for the gas molecule transport mechanism. The molecular model is based on the thermally rearranged polymer investigated in the experiment. All the simulation work was done at the OU Supercomputing Center for Education and Research (OSKER). Details for the membrane construction and simulation method are described below.

The triptycene-based polyimide was constructed with the repeated unit of triptycene-containing poly(benzoxazole-co-imide)s (TPI-PBO) with varying PBO content. Based on the fraction of triptycene-containing repeat unit(s), the poly copolymer was named TPI-PBO-x ($x = 0.25, 0.5, \text{ and } 0.75$). The x ratios are adjusted by varying the molar ratio of the monomer. The monomer unit contains custom-synthesized triptycene-1,4-diamine monomer in varying feeding ratios and 2,2'-bis(3-amino-4-hydroxyphenyl) hexafluoro propane (6FAP). The initial configuration was constructed with a Para-linked connection in agreement with lab synthesis. The degree of polymerization of the membrane model was not considered in this simulation to obtain a balance between the cell dimension and calculation time. The TPI-PBO-0.25 is constructed by the Packmol package^{135,136} using the repeated unit of the polymer. The polymer chains with 100 repeated units are optimized with the cell with a molar ratio of 6FAP-trip and 6FAP of 5:5. The gas adsorption model is based on the Packmol structures as well. For the packing procedure, a general methodology was used for generating a realistic structure of triptycene-based polyimide:

- 1) A total of 100 units were uniformly distributed in an amorphous cell at a lower density using the Packmol. The cubic computational cell runs with periodic boundary conditions. In gas adsorption simulations, gas molecules are introduced at the same time. The simulation cell reaches energy minimization by running at NVT-MD at 10 K for 100ps.

- 2) The polymer packing simulation starts with increased temperature. The system runs at NVT-MD for 100 ps at a simulation temperature from 10 to 100 K. The simulation time is enough for the polymer to pack and reach the energy equilibrium. Similarly, the simulation temperature increases by 100 K per 100 ps until it reaches 300 K. To reach thermodynamic equilibrium, the polymer runs at 300 K for a longer period before studying any properties of the polymer. The density of the system during this process remains very low.
- 3) Compression of the cells was performed after the system reach equilibrium at 300 K. The simulation box runs at NPT. The cell was compressed in three directions until the density of 1.38 g/cm^3 is attained which is similar to the polymer synthesized in the lab.
- 4) For pore size distribution analysis and gas transport study, the polymer continues to run at NVT-MD for an extra-long time. During this period, the screenshots are studied for the properties of the polymer.

6.2.2 Pore Size Distribution

Pore size distribution was measured on the optimized polymer structure using the program PSDsolv¹³⁷. This is a rough estimation of the pores within the polymer. At each point inside the pore, the point is called P. The pores size is measured by the largest diameter of the sphere which can pass through point P without overlapping the pore wall. And the pore size is equal to the largest diameter. For a realistic polymer model, we used this rough estimation of pore size to analyze the distribution of TPI-PBO and investigate the effect of iptycene on the free volumes inside the polymer.

In gas transport simulation, we looked at the adsorption of gas molecules with different kinetic diameters. Entropic adsorption is sensitive to the molecule size, and so is enthalpic-dominant adsorption. Similar to the experimental result, we selected CO₂, methanol, ethanol, 1-propanol, and iso-propanol in our simulations. We introduced the gas molecules in very small concentrations (10 gas molecules) into the cell at the same time as the polymer monomer. After similar NVT and NPT processes, the adsorption of gas molecules would be measured by their distance to the central carbon in triptycene structures. The distance would be plotted along the simulation time for our future analysis.

6.3 Results

6.3.1 Computational free volume distribution and thermal equilibrium

To simulate the experimental finding, we decided to use pore size distribution to validate the accuracy of the model. The free volume in the polymer usually represents pores with different size. They are usually sensitive to temperature. Thus, the structure of pores in

300 K are studied. Also, the total energy along with the simulation time are displayed showing the snapshot of polymer are in thermal equilibrium.

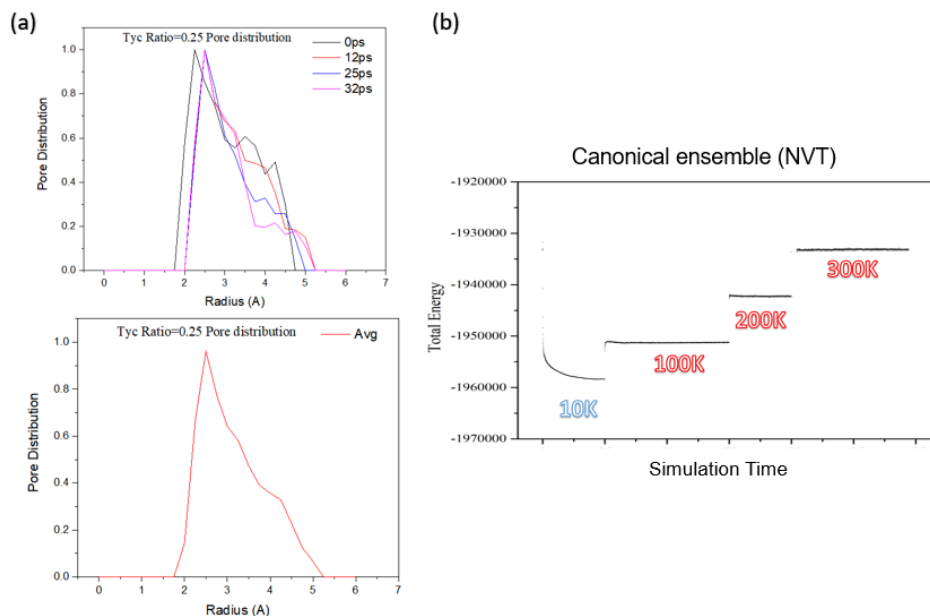


Figure 6.1 (a) The “free volume” exited in each snapshot using the analytic method on the structure of every 12 ps in equilibrium calculation. (b) The total energy diagram from NVT ensemble calculation. The constant total energy indicated in the snapshots are particularly in thermal equilibrium after NVT simulation at 300K.

Here, we use a simple method to simulate the gas adsorption process. A similar simulation was performed on polymer along with some gas molecules. The structure starts from polymer monomers and a few gas molecules and are calculated along the same process: NVT, NPT and NVT. The snapshot after equilibrium at 300 K is used for structural analysis. In our adsorption assumption, we assume triptycene units are responsible for gas adsorption. Thus, the bond length between the central carbon in triptycene structure and the oxygen atom in gas molecules are analyzed. After equilibrium calculations, each molecule found their local minimum states. They end up staying in different free volume in the polymer. Adsorbed molecules rarely leave free volume.

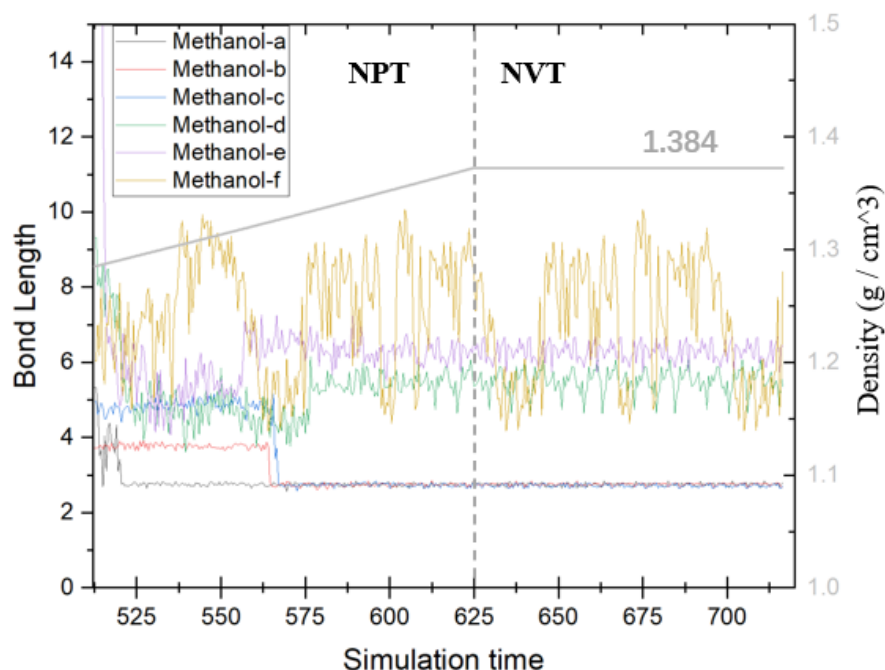


Figure 6.2 The movement of molecules and the density of the polymer during NPT and NVT process. Bond length are shown in unit(Angstrom). Simulation temperature are 300 K.

Their movement within the “volume” are estimated by the bond length we measured. The movement of gas molecules could be simply translational, rotational, and vibrational. The information including the significant part of the translational and rotational movement are shown in the distance. Also, to precisely distinguish rotational movement, we have measured two different bond lengths. The carbon atom and oxygen atom in molecule move away the triptycene functional group.

It is observed that based on the distances, methanol molecules could be divided into categories. The obvious trend is the longer the distance is, the more fluctuation the data would be. The fluctuation is due to the molecule diffusing inside the free volume. It is clear evidence for enthalpy argument. The longer distance the molecule has, the more freedom the molecule processes. The molecule is stabilized by the van der Waals interaction provided by triptycene.

6.3.2 Free Volume measurement on pore size distribution

The bulky units enable superior molecular sieving capability in triptycene-containing glassy polymer. The internal free volume provided by triptycene units is not related to the non-equilibrium conformation, but to the molecular configuration.¹³⁸ Such configuration-based free volume is intrinsic to the polymer structure and, as such, it is non-collapsible, similar to the case of inorganic molecular sieves. However, it is not clear how configurational free volume regulates small molecules sorption and transport.

Here we investigate the free volume where each adsorbed gas stayed. There is multiple triptycene contents near the gas molecule. The bond length is measured in a similar way. The anti-correlation is shown in the measured bond length. The anti-correlation indicates the methanol molecule have a certain degree of translational freedom within the triptycene units. Further evidence is still needed to prove the free volume is created by triptycene units.

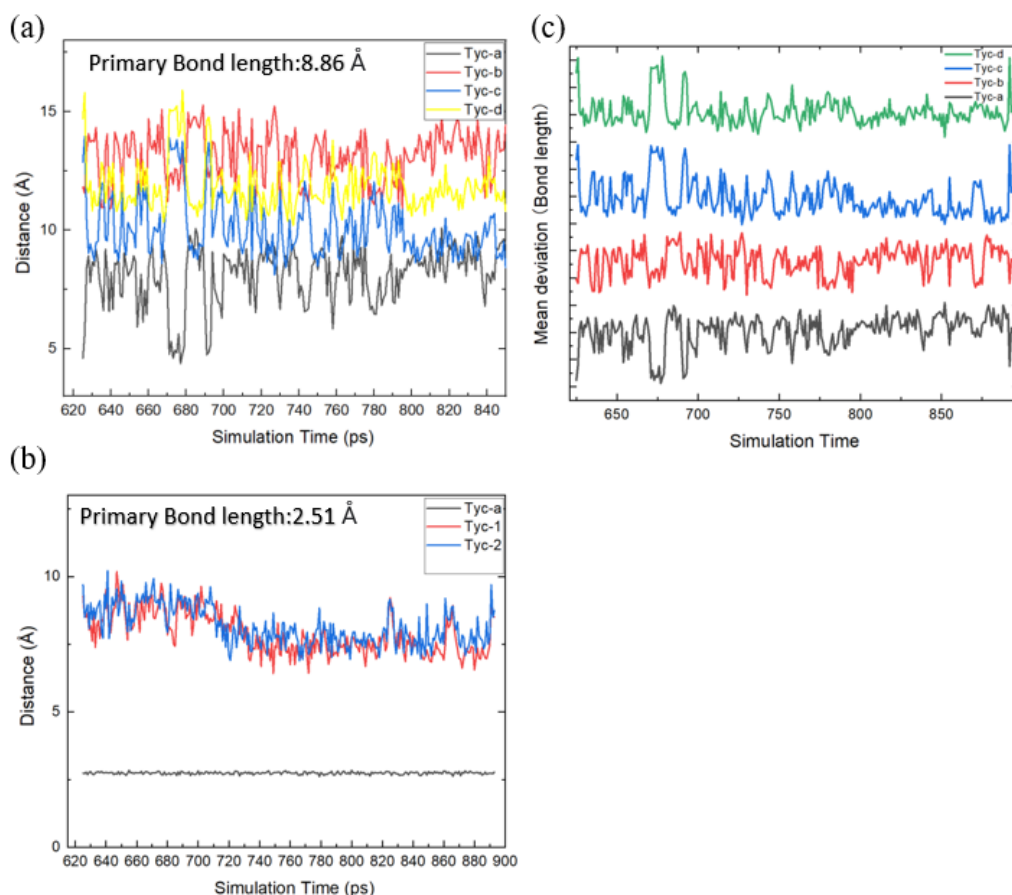


Figure 6.3 The bond length between each methanol molecule in different range and the triptycene unit nearby. (a) The methanol with the shortest distance 8.86 Å to the unit. (b) The methanol with the shortest distance 2.51 Å to the unit and its distance to the nearby unit. (c) The mean deviation analyzes on the methanol with bond length of 2.51Å. Mean deviation defines bond length as the average bond length.

6.4 Discussion

We have successfully simulated the triptycene-based polymer with experimental density. At 300 K, the pore size analytic method shows bimolecular peaks are existing in the polymer with a 0.25 ratio of triptycene. Also, methanol adsorption is performed with polymer monomer. After simulating a similar temperature ensemble, the adsorption structures are obtained for analysis. The local environment of each methanol is shown in the bond length to triptycene content. The methanol adsorption falls into several categories of distance from 3 Å to 6 Å. As

the distance increases, the degree of translational freedom is increasing indicated by the fluctuation of the distance. As the methanol is in a range of 3 Å, the fluctuation of the data is unnoticeable as compared to those molecules 6 Å away. To better simulate the actual free volume of gas molecules, we show there is anti-correlation between the distance to primary triptycene and the other triptycene nearby indicating the relative location of triptycene contents remains unchanged. The distance represents mostly the movement of the molecule within the confined environment formed by polymers.

FUTURE WORKS

The future work aims to focus on the development of a catalytic membrane with specific objectives in mind. Firstly, it is crucial to establish an active site supported by porous structures. This involves designing and optimizing the membrane's structure to provide a suitable environment for the deposition of catalytic materials. The porous structure should facilitate efficient mass transport and ensure accessibility to the active sites for catalytic reactions.

Additionally, the interaction between water and the porous structure plays a significant role in catalytic membrane performance. Understanding and characterizing the water-porous structure interface is essential for enhancing the selectivity and activity of the membrane. This involves studying the adsorption and diffusion of water molecules within the porous structure, as well as their effect on catalytic reactions and separation processes. By elucidating the water-porous structure interface, we can design membranes that effectively utilize the presence of water for improved performance.

Furthermore, the application of the catalytic membrane extends beyond gas-phase separations to liquid-phase separations. Investigating the membrane's performance and optimizing its design for liquid-phase separations is a crucial aspect of future work. This includes studying the transport properties of liquids through the membrane, exploring the selectivity of the membrane towards different liquid components, and assessing its stability and efficiency under liquid-phase separation conditions.

By addressing these subjects in future research, we aim to advance the development of catalytic membranes that possess active sites supported by porous structures, capitalize on the water-porous structure interface, and demonstrate effectiveness in liquid-phase separation applications. This work holds great potential for enabling innovative solutions in various fields, including wastewater treatment, chemical processing, and environmental sustainability.

CONCLUSIONS

This dissertation focuses on catalytic processes combined with separation techniques in an energy-efficient manner. Based on insightful ideas derived from computational studies, we focus on understanding the chemical environments controlling the performance of catalysts and separation. Additionally, I'll propose an innovative application of catalytic membranes in water purification, specifically focusing on the denitrification reaction which is NO_2^- reduction. By leveraging the well-defined structure of catalysts, we can deposit active sites onto the porous structure of the membrane, creating a catalytic membrane. This catalytic membrane plays a crucial role in the denitrification process, where the active sites facilitate the efficient reduction of nitrite (NO_2^-) into nitrogen gas (N_2) and other products, which automatically are separated into a different phase.

This dissertation focuses on catalytic processes combined with separation techniques that demand a catalyst design specific for selective denitrification and the material design of the porous structure as catalyst support and liquid filter. The fundamental of catalyst design for a high selectivity reaction is discussed along with two examples aiming to understand and manipulate the local chemical environment.

Firstly, we show how nitrite reduction occurs on conventional catalysts and studied the influence of solvents. We found that the key intermediate NO controlled the overall activity and selectivity, and the mechanistic study on NO reached agreement with the experimental finding. Also, solvent as a local environment has profound effects on the denitrification shown in further activation energy drop via the proton shuttling mechanism. On the other hand, the stabilization effect from the solvent as polar molecules shows obvious effects on the metal oxide surfaces. Computational tools give quantitative measurements of the solvent effect and provide insight into the solvent-assisted mechanism and the role of water on the catalytic surface. An ongoing project on the NIPAM-turned solvent environment on a Pd surface indicates the potential of manipulating the solvent environment to reach higher activity and selectivity.

As the other example of running a local environment, we have some effort into tuning the coordination number of the metal and the solvation environment. By tuning the coordination number of metal centers, we believe a single-atom catalyst is one of the candidates for the catalytic membrane design. It has pronounced activity and selectivity showing that it is promising for catalytic membrane design due to its catalytic performance and well-defined atom structure.

Lastly, finding an appropriate matrix as an active site holder and liquid filter is significant. We studied some established membrane that uses triptycene-based polymer for gas separation. We characterized the free volume and proposed to tune the polymer system via changing molecule structures. It provides a fundamental understanding of the membrane system although it might not be the best platform to serve as a catalyst support.

Overall, we hope this piece of work provides an elementary idea of the catalyst design and separation design with the aim of denitrification membrane.

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