

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL

**QUANTUM CHEMICAL INVESTIGATION OF METHANOL
DECOMPOSITION ON COPPER EMBEDDED BORON NITRIDE
TO BE USED IN A FUEL CELL**

GÖKBERK ÇELİKEL

**A THESIS OF MASTER OF SCIENCE
DEPARTMENT OF CHEMICAL ENGINEERING**

ADVISOR: ASSOC. PROF. DR. MURAT OLUŞ ÖZBEK

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LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

**YAKIT HÜCRESİNDE KULLANILMAK ÜZERE BAKIR KATKILI
BOR NİTRÜR ÜZERİNDE METANOL DEKOMPOZİSYONUNUN
KUANTUM KİMYASAL İNCELENMESİ**

GÖKBERK ÇELİKEL

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ABSTRACT

This study was carried out as part of the ongoing search for non-precious metal catalysts for sustainable methanol oxidation reactions, aiming to computationally assess the catalytic performance of selected surfaces for direct methanol fuel cell technologies. In this study, catalytic performance in methanol decomposition on copper-doped boron nitride surface as potential methanol fuel cell catalysts, following $\text{CH}_3\text{OH}^* \rightarrow \text{CH}_3\text{O}^* \rightarrow \text{CH}_2\text{O}^* \rightarrow \text{CHO}^* \rightarrow \text{CO}^*$ mechanism was investigated via computational modeling using periodic Density Functional Theory (DFT) and slab based surface models. Copper was selected as the active site due to its proven catalytic performance in methanol industry and cost efficiency compared to conventional PGM-based fuel cell catalysts. Boron nitride was selected as 2D support material for its resemblance to graphene, offering structural stability and chemical inertness.

Relative energies of intermediate reaction steps were estimated to construct a complete energy profile as well as to analyze intermediate steps individually. Ground and transition states were analyzed via geometric relaxation and climbing image nudged elastic band (CI-NEB) methods using Quantum ESPRESSO software. Results were compared to literature on previous theoretical studies on Cu(111) and copper-doped graphene surfaces. Zero-point energy (ZPE) and thermodynamic corrections were included to raw DFT-based findings to obtain results that are more comparable to experimental literature.

Both Cu/B and Cu/N variants of Cu-doped BN surfaces, where a copper substituted a boron and a nitrogen atom, respectively, exhibited affinity towards methanol and atomic hydrogen at the copper and the surface. Cu/B and Cu/N surfaces showed relatively low methanol adsorption energies (-54 and -99 kJ/mol), slightly outperforming the Cu(111) reference. Cu/B surface exhibited significantly larger activation barriers for most of the remaining reaction pathway, peaking at 207 kJ/mol, indicating slower reaction kinetics compared to reference studies. Cu/N surface showed a smooth energy profile with highest activation barrier observed at 157 kJ/mol, which makes it comparable to copper-doped graphene and pure copper. As a result, it was concluded that methanol decomposition on Cu-doped BN surfaces following this route may be feasible on Cu/N surface but within the scope and settings of this study, Cu/B surface showed rather poor catalytic performance. Our results showed that Cu/N would be a viable candidate for the use in DMFC as an anode side catalyst. Further studies exploring alternative pathways, computational parameters or in-depth analysis of individual states may yield promising outcomes as Cu-doped BN possesses desirable surface properties and exhibits promising catalytic characteristics.

Keywords: Cu-BN, DFT, Methanol, Heterogeneous Catalysis, Fuel Cell, Computational Catalysis

ÖZET

Bu çalışma, sürdürülebilir metanol oksidasyon reaksiyonları için platin grubu metal içermeyen katalizörlerin geliştirilmesine katkı sağlamak amacıyla, seçilen yüzeylerin direkt metanol yakıt hücresinde katalitik performansını hesaplamalı yöntemlerle değerlendirmeyi amaçlamaktadır. Bu çalışmada, $\text{CH}_3\text{OH}^* \rightarrow \text{CH}_3\text{O}^* \rightarrow \text{CH}_2\text{O}^* \rightarrow \text{CHO}^* \rightarrow \text{CO}^*$ mekanizmasını takip eden potansiyel metanol yakıt pili katalizörleri olarak bakır katkılı bor nitrür yüzeyinde metanol ayrışmasının katalitik performansı, periyodik Yoğunluk Fonksiyoneli Teorisi (DFT) ve yüzey modelleri kullanılarak hesaplamalı modelleme yoluyla araştırılmıştır. Bakır, metanol endüstrisinde kanıtlanmış katalitik performansı ve geleneksel PGM bazlı yakıt pili katalizörlerine kıyasla maliyet verimliliği nedeniyle aktif bölgeyi oluşturan element olarak seçilmiştir. Bor nitrür, grafene benzerliği, yapısal kararlılığı ve düşük kimyasal aktivitesi nedeniyle 2B destek malzemesi olarak seçilmiştir.

Ara reaksiyon adımlarının bağıl enerjileri, tam bir enerji profili oluşturmanın yanı sıra ara adımları ayrı ayrı analiz etmek için hesaplamalar yoluyla elde edilmiştir. Temel (GS) ve geçiş halleri (TS) geometri optimizasyonu (relaxation) ve Climbing Image Nudged Elastic Band (CI-NEB) yöntemleri ile analiz edilmiştir. Sonuçlar Cu(111) ve bakır katkılı grafen yüzeyleri üzerine yapılan önceki teorik çalışmaların sonuçlarıyla karşılaştırılmıştır. Deneysel literatürle daha karşılaştırılabilir sonuçlar elde etmek için ham DFT tabanlı bulgulara sıfır nokta enerjisi (ZPE) ve termodinamik düzeltmeler uygulanmıştır.

Cu katkılı BN yüzeylerin hem bakırın bor atomu yerine geçtiği Cu/B hem de azot atomu yerine geçtiği Cu/N varyantlarında da metanolün bakıra oksijen tarafından tutunduğu, ayrıca metanolden ayrılan atomik hidrojenlerin hem yüzeyde hem de bakır üzerinde tutunduğu gözlemlenmiştir. Cu/B yüzeyi, reaksiyon esnasında çoğunlukla hem Cu/N yüzeye hem de literatüre kıyasla daha yüksek aktivasyon enerjileri göstermiş, ilk hidrojen ayrılması esnasında 207 kJ/mol ile en yüksek bariyere ulaşmış, dolayısıyla daha yavaş reaksiyon kinetiğine işaret etmiştir. Cu/N yüzeyi ise daha dengeli bir enerji profili sergilemiş, en yüksek aktivasyon bariyeri olan 157 kJ/mol değeri ile bakır katkılı grafen ve de saf (111) bakır yüzeydeki değerler ile kıyaslanabilir sonuçlar vermiştir. Sonuç olarak bu reaksiyon yolu izlendiğinde, Cu/N yüzey üzerinde metanol oksitlenmesinin mümkün olabileceği değerlendirilmiş; ancak bu çalışma kapsamı ve kullanılan ayarlar çerçevesinde Cu/B yüzey zayıf bir katalitik performans sergilemiştir. Sonuçlar göre Cu/N yapı, direkt metanol yakıt hücresinin anot tarafında katalizör olarak kullanımı için uygun bir katalizör olarak bulunmuştur. Alternatif reaksiyon yollarının, farklı hesaplama parametrelerinin veya geçiş hallerinin daha detaylı analizi ile bakır katkılı bor nitrür yüzeyler için daha umut verici sonuçlar elde edilebilir, zira bu yüzeyler yapısal olarak uygun özelliklere sahip olup, katalitik açıdan potansiyel vaat etmektedir.

Anahtar Kelimeler: Cu-BN, DFT, Metanol, Heterojen Kataliz, Yakıt Hücresi, Hesaplamalı Kataliz

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LIST OF SYMBOLS AND ABBREVIATIONS

ads	: Adsorption
$C_{p,avg}$	: Average heat capacity
Cu/B	: Boron-replaced BN surface
Cu/N	: Nitrogen-replaced BN surface
CuG	: Copper-doped graphene surface
E	: Total energy (in kJ/mol)
E_a	: Activation energy (in kJ/mol)
E_{DFT}	: Energy obtained via DFT (in Ry)
E_{gas}	: Total energy of substances in gas phase (in kJ/mol)
E_r	: Reaction energy (in kJ/mol)
E_{sub}	: Substitution energy (in kJ/mol)
$E_{surf/ads}$	: Total energy of surface and adsorbate (in kJ/mol)
h	: Planck constant (in eV.s)
hBN	: Hexagonal boron nitride
k	: Rate constant (in s^{-1})
k_B	: Boltzmann constant (in J/K)
PtRu	: Platinum-ruthenium
R	: Gas constant (in J/(mol.K))
rBN	: Rhombohedral boron nitride
Ry	: Rydberg unit
T	: Temperature (in K)
C-O	: Carbon-oxygen
CO	: Carbon monoxide
2D	: Two dimensional
2D-hBN	: Two dimensional hexagonal boron nitride
ν_i	: Vibrational frequency of mode i
ΔE_{ads}	: Adsorption energy (in kJ/mol)
ΔG	: Gibbs free energy change (in kJ/mol)
$\Delta G^\ddagger$	: Gibbs free energy of activation (in kJ/mol)
ΔG_{in}	: Total Gibbs free energy of reactants (in kJ/mol)
ΔG_{out}	: Total Gibbs free energy of products (in kJ/mol)
ΔG_{rxn}	: Gibbs free energy of reaction (in kJ/mol)
ΔH_f°	: Standard enthalpy of formation (in kJ/mol)
ΔH_{vib}	: Vibrational enthalpy change (in kJ/mol)
ΔS°	: Standard entropy (in kJ/mol)
ΔS_{vib}	: Vibrational entropy change (in kJ/mol)
BN	: Boron nitride
CI-NEB	: Climbing image nudged elastic band
DMFC	: Direct methanol fuel cell
EOS	: Equation of state

GGA	: Generalized gradient approximation
GS	: Ground state
GTÜ	: Gebze Teknik Üniversitesi
HF	: Hartree-Fock
HFC	: Hydrogen fuel cell
HK	: Hohenberg-Kohn
ICE	: Internal combustion engine
IMFC	: Indirect methanol fuel cell
KS	: Kohn-Sham
LDA	: Local density approximation
MEA	: Membrane-electrode assembly
MEP	: Minimum energy path
MFC	: Methanol fuel cell
ML	: Monolayer
NCPP	: Norm-conserving pseudopotential
NEB	: Nudged elastic band
PAW	: Projector augmented-wave
PBE	: Perdew-Burke-Ernzerhof
PEM	: Proton exchange membrane
PGM	: Platinum group metal
QD	: Quantum dot
QE	: Quantum ESPRESSO
TS	: Transition state
UHeM	: Ulusal Yüksek Başarımlı Hesaplama Merkezi
USPP	: Ultrasoft pseudopotential
SCF	: Self-consistent field
ZPE	: Zero-point energy (in kJ/mol)

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1. INTRODUCTION

In this section, general information about fuel cells, their types and operating principles will be given. Current drawbacks and a specific set of theoretical tools to simulate catalytic performance of probable fuel cell catalysts to find a more sustainable, cheaper or higher activity catalyst for future applications will also be explained.

1.1. Fuel Cells

Sustainability, eco-friendliness and energy efficiency have become major concerns in recent years. As concerns about climate change and the negative effects of fossil fuels keep increasing, cleaner and more sustainable energy alternatives are being explored to replace conventional energy sources with high greenhouse gas and pollutant emissions, such as fossil fuels [1]-[3]. One of the main applications of fossil fuels are the internal combustion engines (ICEs), providing power in mobile applications such as vehicles. The problem with ICEs is not only the type of fuel they use but also the fairly low thermal efficiency that leads to more resource being used and more pollutants to be emitted.

Considering both the low thermal efficiency and fossil fuel usage of ICEs, fuel cells emerge as an alternative, offering better performance while utilizing the chance to use more eco-friendly fuels [4]. One of the main advantages of fuel cells is that they generate electricity without causing direct pollution, thanks to their electrochemical working principle [5]. In vehicle applications, the most commonly used fuel cell type is the hydrogen fuel cells while the most common type among them are the proton exchange membrane fuel cells.

1.2. Working Principle and Types of Fuel Cells

Fuel cells operate by electrochemically converting chemical energy into electrical energy through redox reactions. A schematic representation of a typical fuel cell, highlighting its operating principle, is provided in **Figure 1.1**.

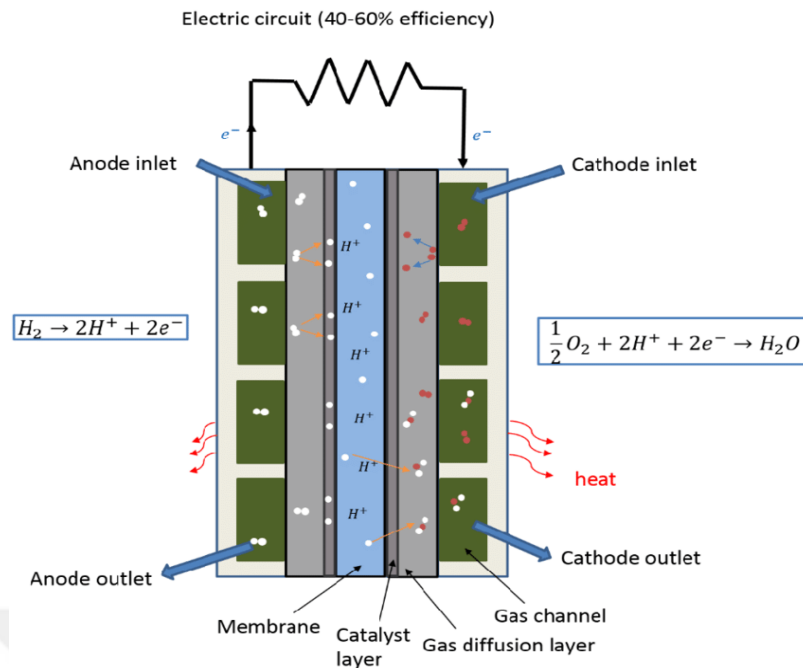


Figure 1.1: Diagram showing working principle of a Proton Exchange Membrane (PEM) fuel cell [6].

A typical fuel cell is made up of three primary components: an anode, a cathode and an ion conducting electrolyte (or membrane) which are also referred to as membrane-electrode assembly (MEA) together [7]. Anode is the negative electrode of fuel cell where the fuel is oxidized. Cathode is the positive electrode where the oxidant is reduced by accepting electrons. The membrane, or electrolyte, is a selective permeable barrier that allows the passage of specific ions but does not allow molecules or electrons through. Fuel is introduced from the anode side and the oxidant from the cathode side, therefore, they do not undergo a direct chemical reaction but instead they undergo separate half reactions on their respective sides. Specific ions move through the electrolyte from anode side to cathode side. Meanwhile, the electrons from anode side have to travel around in the same direction through an external circuit, circumventing the impermeable membrane. This movement causes a current flow between the two sides of the fuel cell and this is how the fuel cells ultimately convert the chemical energy into electrical, useful energy.

Fuel cells differ in terms of fuels, outputs and electrolyte materials. Due to these differences, other parameters such as operating temperature, power output and efficiency vary between different types. The term hydrogen fuel cell (HFC) refers to any fuel cell that operates with hydrogen as fuel. Proton exchange membrane fuel cells

(PEMFCs) are a type of HFC's that operate under relatively low temperatures such as 60-80°C, use pure hydrogen as fuel and are ideal for portable applications due to fast startup and mild operating conditions. It is also the most renowned type with the simplest reaction that uses pure hydrogen as input, converts it into water by using atmospheric oxygen and generating power through this process. However, PEMFCs are not suitable for all applications.

To meet varying performance demands and environmental conditions, other types of fuel cells have been developed, each with unique characteristics and advantages. Alkaline fuel cells (AFCs) are another type that operate under similar temperatures but their electrolytes are solid or aqueous alkaline solution such as KOH whereas PEMFCs use solid polymer membranes as electrolyte. Solid oxide (SOFC) and molten carbonate fuel cells (MCFCs) are the fuel cells that operate under high temperatures because their electrolyte materials, such as solid ceramic electrolytes or molten carbonate salts, require elevated temperatures to show adequate ionic conductivity. Moreover, high temperatures allow internal reforming of fuels other than H₂, such as CO or CH₄, which allows such gases to be fed as fuel. Both SOFCs and MCFCs are preferred in stationary uses for several reasons such as slow start up, size and weight constraints and fuel flexibility that is more feasible in stationary plants. Phosphoric acid fuel cells (PAFCs) have liquid phosphoric acid as electrolyte, operate at slightly elevated temperatures and although they can tolerate a small amount of CO as impurity, they suffer from slow start up as well and therefore are more suitable for stationary applications. **Table 1.1** compares the important characteristics of aforementioned types of fuel cells.

Table 1.1: Summary of key characteristics of various fuel cell types [8].

Fuel Cell	Fuel	Common Electrolyte	Operating Temperature (°C)	Efficiency (%)
PEMFC	H ₂	Perfluorosulfonic acid	<120	40-60
SOFC	H ₂ , CO, hydrocarbons	Ytria-stabilized zirconia (YSZ)	500–1,000	60
MCFC	H ₂ , CO, natural gas	Molten carbonate salts	600–700	50
PAFC	H ₂	Phosphoric acid	150–200	40
AFC	H ₂	Aqueous potassium hydroxide (KOH)	<100	60

Hydrogen fuel cells are the most dominant option in mobile applications but they also have several drawbacks: Hydrogen is a very small molecule that needs to be stored and transported in highly pressurized tanks or cryogenic storage, posing a safety concern. Moreover, current gasoline infrastructure would not be enough to facilitate hydrogen transportation and storage, needing a huge investment if the hydrogen fuel cells were to become more and more common. Direct methanol fuel cells can be a decent alternative in near future but there are a few obstacles to be tackled first, which will be discussed in the upcoming Section 3.1.

Although some fuel cells show comparable efficiency ranges, they differ significantly in terms of operating temperature, electrolyte material, and fuel compatibility. For instance, PEMFCs can operate not only with hydrogen but also with alternative fuels such as methanol, broadening their application potential and paving the way for variants like methanol fuel cells, discussed in upcoming subsection.

1.3. Methanol Fuel Cells

Methanol fuel cells (MFCs) use methanol as their primary fuel and are classified into two types. One type where methanol is directly fed into the anode side of MEA is called direct methanol fuel cells (DMFCs). The other variant is called indirect methanol fuel cell (IMFC) because in this type, methanol first undergoes a reforming process to produce hydrogen, which then is fed into a hydrogen fuel cell. This study focuses on DMFCs, as IMFCs involve a separate reforming step and are outside the scope.

DMFCs share the basic operating principle of PEMFCs but differ in that they use methanol directly instead of hydrogen, leading to unique challenges and performance characteristics. Also, the operating temperature of DMFCs are comparably lower than any other types of fuel cells discussed previously in Section 1.2. While there are studies that cover the effects of temperature on performance of DMFCs ranging between 60-120°C [9] and 30-90°C [10], the operating temperatures of DMFCs are commonly specified as 60-70°C [11].

In DMFC's, either pure or diluted methanol is fed through the anode side, while unreacted methanol (and water) and CO₂ leave the anode side. On the cathode side, the reactant is oxygen from ambient air, while water is the output on the cathode side.

Another possible output on the cathode side is methanol, as some methanol molecules permeate through the electrolyte from the anode without undergoing oxidation, a phenomenon known as methanol crossover. This issue significantly reduces fuel cell efficiency and will be discussed in more detail in Section 2.1. **Figure 1.2** shows a schematic, cross sectional representation of a typical methanol fuel cell.

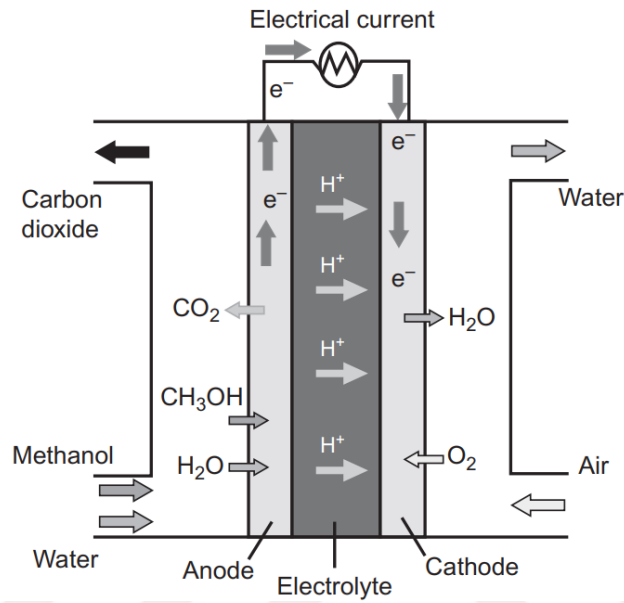
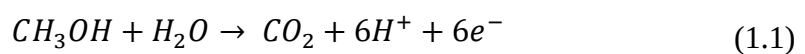


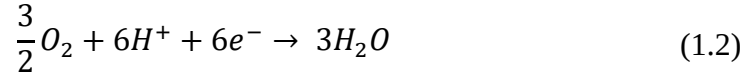
Figure 1.2: Cross sectional view of an operating DMFC [12]. Excess inputs and crossover methanol leave the system through output streams but are not explicitly shown.

On the anode side, methanol undergoes oxidation, releasing protons and electrons. Released protons go through the electrolyte, react with oxygen and form water eventually. The electrochemical processes in a DMFC can be categorized into the anodic half-reaction and cathodic half-reaction that together constitute the overall reaction.

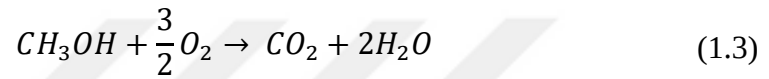
Input on the anode side is either pure or diluted methanol and on this side, methanol undergoes electrochemical oxidation. Equation (1.1) shows the anode side half reaction.



Cathode side input is ambient air which constitutes oxygen molecules that react with protons passing through the electrolyte, forming water as the output. Equation (1.2) shows the cathode side half reaction.



The overall electrochemical reaction in a DMFC is obtained by summing the half reactions occurring at the anode and cathode. Equation (1.3) shows the overall reaction as the sum of both anode and cathode reactions.



Even though the electrochemical reactions in DMFCs are fairly simple, using them in real-world applications comes with several challenges. These challenges are primarily related to fuel handling efficiency, cell performance, and catalyst durability. The challenges and problems related to DMFCs will be explained in the following subsection.

1.4. Problems of DMFCs

Methanol-powered fuel cells are more advantageous than batteries and hydrogen fuel cells in terms of high volumetric energy density, easy distribution and storage of fuel. However, DMFCs are shadowed by the hydrogen fuel cells in terms of overall efficiency. Besides, their applications are limited due to technical problems such as low performance [13]. Three main problems reducing the performance are sluggish reaction kinetics, methanol crossover and release of a large amount of CO₂ that disturbs the gas flow on the anode side [14].

Carbon-supported platinum catalysts are commonly used in methanol fuel cells. However high cost, reduced activity of the catalyst due to poisoning by carbon monoxide, and aggregation or degradation of platinum/platinum-ruthenium particles over time renders them disadvantageous [15]. A typical DMFC requires a significantly larger mass of catalyst on the anode side as compared to a HFC to overcome slow MOR, increasing the overall cost substantially [16].

Considering the aforementioned drawbacks, three key factors have been identified as major barriers to the development and widespread adoption of DMFCs. These problems were catalytic activity and poisoning, high catalyst cost and methanol crossover, all of which will be discussed in detail under next subsections of 1.4.

1.4.1. Methanol Crossover

Methanol crossover is the undesired transportation of unreacted methanol through the membrane towards to cathode side instead of decomposing at the anode side. This phenomenon is directly linked to the properties of proton exchange membrane (PEM) and is acknowledged as a major drawback of current DMFC's. Currently, fluorinated polymers with sulphonic acid based functional groups are the most common types of PEM materials.

1.4.2. Catalyst Poisoning

Catalyst poisoning can be described as the deactivation of the catalyst surface over time, resulting in less active sites and lower catalytic activity. Pt-Ru alloy is the most common anode catalyst material in DMFCs because of their resistance to CO poisoning but even this bimetallic catalyst is still susceptible to intermediate species such as CO and formate. In order to facilitate faster reaction kinetics and overall efficiency, an anode side catalyst with more resistance to catalyst poisoning would be beneficial. Given that Pt-Ru catalysts already represent a high performance standard in DMFCs, their vulnerability to poisoning highlights a fundamental limitation. Therefore, during the search for alternative catalyst systems, resilience to poisoning is a critical aspect that could improve the overall performance of the catalyst.

1.4.3. Catalyst Cost

DMFCs use Pt and Pt-Ru catalysts on cathode and anode sides, respectively. These materials are a part of platinum-group metals and are known for their high corrosion resistance and catalytic properties. Thanks to these strong properties, they are desirable elements in different sectors such as electronics, fuel cells and catalytic converters. The high demand for these elements cause high prices to be paid, which is another problem for the fuel cell efficiency. A much cheaper or accessible alternative catalyst

with a similar or slightly lower catalytic performance can be a solution to the financial side of the problem.

Given these challenges, it becomes essential to explore alternative strategies to enhance DMFC performance.

1.5. Theoretical Background and Density Functional Theory (DFT)

To improve overall performance and find alternative catalyst materials, both theoretical and practical research are available. Theoretical research is crucial in the design and optimization of new material by providing useful insights into active site behavior, surface reactions and reaction mechanisms that are often difficult to capture through experimental work. Computational modeling allows analysis of a wide range of catalyst structures, compositions and reaction pathways in a significantly more cost and time efficient manner compared to synthesis and testing in laboratories. In the context of fuel cells, especially DMFCs, computational studies can be utilized in identifying the reaction bottlenecks by modelling the structures and reactions and offer the chance to model even the intermediate steps that in real life takes only a few picoseconds to complete.

In this study, a computational approach was adopted to model and investigate Cu-doped BN that can possibly be used as a catalyst on anode side or the reformer of a MFC. The experimental methods for studying catalytic activities fall short in revealing detailed reaction mechanisms and short-lived intermediates due to the complexity and speed of the surface reactions. Density functional theory (DFT), a quantum chemical approach based on *ab initio* methodology focusing on electronic structure, is a viable tool for simulating heterogeneous catalytic reactions systematically. By computing optimized geometries of reactants based on DFT, intermediates and products; valuable insights on adsorption energies, activation barriers or probability of reaction pathways can be obtained. Within the scope of this study, a specific reaction pathway for methanol decomposition on a copper-doped boron nitride surface was investigated via modeling each intermediate step individually through computational software operating on DFT principles, determining relative energies of each step, enabling construction of the full energy profile from obtained data. Details of the applied approach and DFT are given in Section 3.

1.6. Literature Review

The literature was reviewed within the scope of computational studies that were related to this work by either through the support material, active site or any other aspect that provides insight about alternative catalysts to DMFCs. The starting point was the identification of current mainstream catalyst for low temperature fuel cell applications, which was identified as Pt catalyst on carbon support, often carbon black derivatives [17]. The resulting structure resembled large carbon spheres with platinum dots with diameter of a few nanometers scattered on its surface [17]. The search for an alternative catalyst material was carried out based on two main topics: selection of the active site and the support material.

Selection of active material was relatively easier because the constraints and expectations pointed to a specific element. One of the important drawbacks of MFC's was the high catalyst cost, which was mostly due to use of PGMs. Moreover, platinum-based catalysts were known to suffer from CO poisoning. So, in search for a non-PGM as the active material, copper emerged as a great alternative. Copper, a well-known and widely used catalyst in methanol synthesis applications [18] is also a transition metal that shows one of the closest performance to PGMs in ORR activity volcano plots [19]. In addition, compared to PGMs, copper relatively comes at a much lower cost and is found more abundantly. Besides, there has already been a study covering the copper-doped graphene surface as a MFC catalyst [20] which provided valuable insight and was selected as the main reference to compare the results found in this work.

The selection of support material was based on several criteria such as the shape/form of the material, the type of the material and the ability of the surface to be modelled or computed with a reasonable amount of computational efforts. Carbon based supports were the most common and extensively searched types of fuel cell catalyst support applications via DFT [15],[20]-[22]. Because carbon based supports were readily studied, a search for an alternative support lead to selection of boron nitride as the candidate support. Before proceeding with why it was selected, the shape factor should be discussed first. While the current mainstream catalyst is made up of many atom clusters as mentioned before, the increased number of surface or structural atoms increase the computational efforts required to model the surfaces. Consequently, DFT

studies covering such materials are expected to model the experimental surfaces in a way that achieves an optimal balance between the level of accuracy and computational cost. While the carbon based studies covers carbon nanotubes and other nanocomposite types [23], the focus on carbon based fuel cell support studies recently shifted towards 2D materials, namely graphene [24], which offers a larger surface area, low cost, high stability and high thermal and electronic conductivity [25]. Theoretical studies of BN supports for different application types include fullerene [26] and 2D hexagonal BN [27]-[29], all with different dopants. Moreover, due to hexagonal structure of graphene, the surface type selected for convenience was 2D, hexagonal boron nitride, which allows a straightforward comparison to results of copper-doped graphene, and a reasonable computation process compared to other 3D types of copper-doped boron nitride materials. Additionally, the lack of research on copper-doped boron nitride surfaces for fuel cell catalysis provided this work with novelty.

1.7. Cu-BN Synthesis

In addition to aforementioned BN studies [26]-[29], boron nitride itself offers several different forms such as amorphous or crystal structures as well as nanosheets, covering both 2D and 3D surfaces [30], [31]. Introduction of another species as dopant, namely copper, causes even more alternatives to consider when studying such material for surface catalysis. While copper was expected to offer the activity in methanol decomposition, the structure or form of the BN surface was also need to be selected for modelling the surface and the reaction.

Hexagonal boron nitride (*h*BN) and rhombohedral boron nitride (*r*BN) are the crystalline forms that are analogous to graphite, the difference stemming from how the layers stack on top of each other while both surfaces exhibit same hexagonal structure [31]. 2D BN structures can be synthesized following two different approaches: top-down approach where multilayer bulk BN is exfoliated into thinner nanosheets or quantum dots (QDs) using many different techniques and bottom-up approaches by synthesizing the 2D structure starting from boron and nitrogen-containing organic and inorganic materials and following methods such as hydrothermal approach, microwave irradiation or chemical vapor deposition [32]. Considering many alternatives readily available to produce 2D BN structures, and the convenience to model a 2D surface in computational methods, the BN surface was decided to be

modelled as a single sheet resembling graphene. But just to be safe, the preliminary computations included a 2-layer BN surface with a surface reaction on one side to see whether the number of layers affected the simulations but as expected, it did not. Thus, all subsequent computations were carried out on a single layer, as it will be mentioned in Chapter 3.

Synthesis of copper-doped BN surface was again possible through either top-down approaches, such as impregnating the BN sheet with copper; or bottom-up approaches, such as starting from ingredients containing boron, nitrogen and copper. Also for top-down approaches, two options were to first introduce copper and exfoliate the surfaces while the second method was to treat the exfoliated BN sheet with copper.

In one study, Cu-doped BN nanobelts were synthesized starting from boric acid and melamine, which resulted in a 2D structure with copper incorporated into the BN framework [33]. The experimental study showed that copper existed in the form of both Cu-N and Cu-B bonds (with possibly more Cu-N bonds than Cu-B bonds) which was determined through XPS and EXAFS results, meaning that copper had replaced a surface boron atom or nitrogen atom and raised the level of surface at that point to its larger diameter [33]. Also, there has been no XRD peaks observed related to copper species until a specific weight percentage of copper doping, which indicates that the copper is dispersed uniformly around the surface without forming detectable crystal structures on the surface [33], which aligns with single atom catalysis modelling.

In another study, a facile one-step pyrolysis method was incorporated that resulted in a copper-doped BN surface but instead of copper being incorporated directly into the surface, it was observed to form metallic nanoparticles on top of the surface with XRD patterns pointing to three distinguishable planes of Cu(0) [34].

An example for a top-down approach using chemical exfoliation for obtaining BN nanosheets and hydrothermal route for copper addition also resulted in highly dispersed copper with no peaks of metallic copper in XRD analysis [35]. HRTEM results showed dark spots that agree with dispersed incorporation of copper onto the surface while apart from the used terms *incorporation* and *dopant*, it was not mentioned in the study whether the copper was replacing a boron or nitrogen or was simply added on top of the surface. One other point that supports the copper replacing a surface atom was the change in crystallite size with the addition of copper. Addition

of copper had a significant influence on growth and crystallinity of the BN structure [35], which can be interpreted by assuming the copper had a more integrated or influential role than inert surface deposition.

Considering how different methods resulted in different variants of Cu-BN surfaces and that both variants of 2D Cu-*h*BN are synthesizable, these surfaces were utilized for modelling the catalytic surface for methanol decomposition in this work.

1.8. Introduction Summary

To conclude, as global pollution levels rise and the demand for sustainable energy solutions grows, the development of clean and efficient alternatives to fossil fuels has become increasingly urgent. While hydrogen-based PEM fuel cells are more widely utilized and studied for their low emission potential, DMFCs offer a distinct advantage in terms of fuel storage and handling, making them a strong candidate for portable and small-scale applications such as vehicles. However, the high cost and susceptibility to poisoning of Pt-Ru catalysts remain significant barriers to DMFC commercialization.

This study aims to address these challenges by investigating copper as a more abundant, cost-effective alternative, with the potential to enhance catalyst performance and reduce reliance on expensive PGMs. The findings from this research are expected to contribute to the development of more accessible, scalable, and sustainable fuel cell technologies, ultimately supporting global efforts to mitigate environmental pollution and advance cleaner energy solutions.

A theoretical approach was adopted due to its ability to reveal atomic scale insights such as ground and transition states or short-lived intermediates, which are often inaccessible through conventional experimental methods. Moreover, it facilitates reproducibility and efficient material screening, both of which are critical when evaluating potential catalyst candidates.

The content of this thesis is as follows: In the next chapter, the aim of this study is covered. Then, in Chapter 3, the theory behind and the methodology of the computational approach were explained thoroughly. In Chapter 4, results obtained through computations were listed and compared to literature, specifically in Sections 4.6 to 4.9. Lastly, reached conclusions were given in Chapter 5.

2. PURPOSE OF THE STUDY

This study investigates the methanol decomposition on Cu-doped BN surface based on *ab initio* approaches and DFT model to decide whether the proposed surface can be a catalyst alternative that can be used in DMFC's. At a broader perspective, there were several reasons linked to each other that led to this specific research, such as global need for clean energy solutions, the limitations of conventional fuel cells and their promising potential in mobile applications yet to be fully utilized.

Considering shortcomings of DMFC performance due to reasons mentioned in Introduction, two problems to tackle in order to make DMFCs more efficient and competitive were identified as developing a new PEM or a new catalyst. While methanol crossover is a significant downside of current DMFCs, catalyst selection is also important in both performance and especially in cost of the unit.

After the topic selection, the aim narrowed down to identifying an alternative material to current Pt-Ru based anode side catalyst to find a high performance and low cost solution. While copper is a known and widely used material in methanol synthesis and a study of a copper-doped graphene surface was carried out for this purpose yielding positive outcomes, a copper-doped boron nitride surface has not been researched yet. Through quantum chemical investigation of methanol decomposition on a single atom copper-doped hexagonal 2D boron nitride surface, the opportunity to assess the feasibility of this material and compare it to literature arose. The ultimate goal was to evaluate the feasibility and activity of the Cu-doped BN surface to be used in a DMFC as an anode side catalyst.

2.1. Solution Proposal

To achieve this goal, first, the decision to study Cu-doped BN was made based on a previous study where Cu-doped graphene was studied and proved feasible [20]. Same reaction pathway as the reference study [20], $\text{CH}_3\text{OH}(\text{g}) \rightarrow \text{CH}_3\text{OH}^* \rightarrow \text{CH}_3\text{O}^* \rightarrow \text{CH}_2\text{O}^* \rightarrow \text{CHO}^* \rightarrow \text{CO}^*$ was adopted; ground and transition states were recreated on *h*BN surface through computations with as many conformations as possible to ensure the selected GSs were indeed corresponding to the local minimum energy. In order to

construct a full reaction pathway to identify probable barriers or bottlenecks, relative energies of individual states were combined and compared.

Thermodynamic adjustments were incorporated into the DFT data to obtain values that better reflect experimental conditions and the operational environment of DMFCs, because pure DFT results does not take into account the contribution from temperature while DMFCs operate at mildly elevated temperatures.

Data obtained directly via simulations were compared to literature, specifically to Cu(111) [36] and Cu-doped graphene [20] surfaces on which the same reaction pathway was studied with DFT computations. The comparison covered activities of catalytic surfaces, relative energies of individual states, and activation and reaction energies observed during transition states. All of these comparisons were made with the aim to confirm that Cu-doped *h*BN surfaces resembled Cu-doped graphene in terms of catalytic performance, by showing similar results in all areas of interest as mentioned before.

3. THEORY AND METHODOLOGY

This chapter explains the theoretical background of utilized methods and describes the computational setup and parameters used in this study. DFT based computations were performed using periodic boundary conditions and plane-wave basis sets. The surface structures, adsorption geometries, and reaction pathways were optimized and analyzed through a series of ground and transition state computations. Methanol and all relevant reaction intermediates were placed on top of or near the copper active site in both Cu/B and Cu/N configurations. Geometry optimization was then carried out to obtain the most favorable adsorption structures in terms of total energy.

Details of the software, surface models, simulation parameters and methods are described under subsections of Chapter 3.

3.1. Density Functional Theory

Density functional theory is one of the most common quantum mechanical modeling approaches and a tool to study electronic structure of atoms and molecules. Nowadays, it has become a more feasible tool in theoretical physics and chemistry following advances in theory and increasing availability of computational power [37]. The foundations of quantum mechanics were laid by the Schrödinger equation [38] in 1920's. This wave-based formulation, which introduced the concept of the wave function, describes the behavior of particles such as electrons at the atomic level. Self-consistent field (SCF) method was proposed by Hartree shortly after in order to calculate energies and wave functions of many-body systems [39], which evolved into Hartree-Fock method (HF) with Fock's contributions that improved SCF by incorporating exchange interactions. At that state, HF method had accurate wave functions but neglected the electron correlations. In addition, it lacked performance in large systems, yielding poor total energies and high computational costs. Hohenberg-Kohn (HK) Theorems in 1960's offered a solution by incorporating electron density as the theory basis instead of wave functions. The electron density gives the probability of finding an electron at a given point in space, and is a function of only three spatial variables, making it far more efficient to handle computationally than the full many-body wave function. Further improvements to HK Theorems by Kohn-Sham (KS)

method that allowed a more practical application and offered a total energy functional split into four items, including the exchange-correlation energy.

Conversion from wave functions to density functions were the first steps of transition to density functional theory, and DFT methods kept growing afterwards with the continuous improvements in exchange-correlation approximations which was the limiting component. Some of the first and most important DFT functionals were Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA), which were succeeded by further developed methods such as Meta-GGA and hybrid functionals. As the methods improved in terms of accuracy, they also became more demanding in computational efforts and challenging in complexity. Perdew even introduced a metaphorical ladder, namely Jacob's Ladder, to rank the exchange-correlation functionals with respect to their chemical accuracies [40], with a visual representation given in **Figure 3.1**.

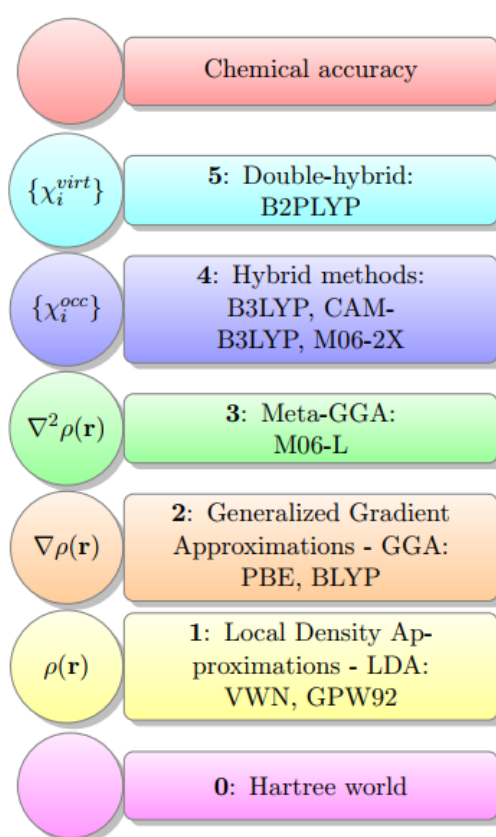


Figure 3.1: Jacob's Ladder of DFT functionals as proposed by Perdew and illustrated by Bonvicini et al. [41].

With continuous improvements over the years, DFT has become a robust computational method that is especially valuable in fields where atomic scale interactions are critical but at the same time, difficult to capture experimentally, such as catalysis or surface reactions. In catalytic reactions, DFT offers valuable information about adsorption energies and reaction pathways in quantum level, which makes it a useful tool to understand points such as how intermediates form and dissociate, which states correspond to ground or transition states and what energy barriers must be overcome. These capabilities allow efficient screening of potential catalyst materials and understanding surface-reactant interactions.

In the context of fuel cells — especially DMFCs, the exploration process for new catalysts to overcome certain drawbacks can benefit from theoretical modelling. Methanol decomposition reactions in DMFCs occur over extremely short timescales, making the detection of intermediates and transition states experimentally challenging but can be computed through DFT based computational methods. Identifying intermediates, including their ground and transition states, not only helps clarify how molecules transform along the reaction pathway, but also yields relative energy values that enable visualization of the reaction energy profile. From this, key insights such as activation barriers and step spontaneity can be extracted.

3.2. Software and Resources

All DFT calculations in this study were carried out using Quantum ESPRESSO [42]-[44], an open-source software used for *ab initio* electronic structure calculations and material modelling through DFT, plane wave basis sets and pseudopotentials. Geometry optimizations, ground and transition state searches were performed using periodic boundary conditions to simulate an environment made up of a single atom doped, two-dimensional catalyst surface and reactants that are adsorbed on one side of it. Visual representation of inputs, outputs and any geometry were obtained via XCrySDen software [45]. The simulations were executed on the National Center for High Performance Computing (UHeM) and TÜBİTAK ULAKBİM High Performance and Grid Computing Center using the core-hour and disk space allocations provided to graduate level student projects. Projector augmented wave (PAW) type pseudopotential files with *.upf* extension, were obtained from the Pseudo Dojo library [46]-[50], a curated repository of pseudopotential files developed for reliable use in

plane-wave DFT calculations. These files were based on Perdew-Burke-Ernzerhof (PBE) exchange correlations that are an extension under the GGA category. The use of PAW allowed for accurate reconstruction of wave functions near atomic cores, particularly important for transition metals such as copper.

3.3. Computational Parameters

While system parameters varied depending on the type of calculation, several key settings were consistently applied across both GS and TS calculations. In this study, number of atoms ranged between 32 and 38, including adsorbed molecules and excluding desorbed gaseous molecules although their energies were added for consistency. Type of atoms from 3 to 6, corresponding to clean surface and methanol adsorbed surface, respectively. Other important system parameter was the layout of the Cu-doped BN surface, thanks to the binary structure that allows a couple of alternatives when substituting a surface atom with copper.

Computational parameters were kept constant across same type of computations for consistency while they were readjusted for different simulations. Kinetic energy cutoff parameters for the plane-wave basis set were specified for both wave functions and charge density as 50 and 350 Ry, respectively.

To handle partially filled electronic states, Gaussian smearing of 0.02 Ry was applied. This approach stabilizes the self-consistent field (SCF) calculations by smoothing the occupations near the Fermi level, ensuring numerical stability and accuracy in systems exhibiting metallic behavior.

In order to capture long-range dispersion interactions, which are particularly relevant during physisorption steps and weakly bound intermediate states, van der Waals corrections were included using the DFT-D3 scheme proposed by Grimme [51]. This correction applied consistently across all reaction steps and all sorts of computations.

Brillouin zone sampling was performed by defining a Monkhorst-Pack grid [52] of 4x4x1 mesh, providing 16 uniformly spaced k-points in the surface plane.

3.4. Molecules in Vacuum

Total energies of gas phase molecules were computed in a supercell by isolating them from other periodic molecules. Cell vectors in all Cartesian directions were selected

greater than 10Å to create an isolated vacuum through which; energy of a single, non-interacting molecule was evaluated.

Gas phase molecules were within the scope of this study, so, energies of surface-adsorbate complex and gas phase molecules were added to assess the total energy of the surface and all atoms of a single methanol molecule at each step, to track the total energy of the 38-atom assembly consistently and comparably. Equation (3.1) shows the related expression,

$$\Delta E_{ads} = E_{surf/ads} + E_{gas} \quad (3.1)$$

where $E_{surf/ads}$ refers to the total DFT energy of the surface with adsorbed species while E_{gas} represents the sum of all gaseous molecules that originating from the initial methanol molecule. Same procedure was applied to thermodynamically corrected Gibbs free energy comparisons as well.

Geometry relaxation for gas phase molecules were treated identical to GS relaxations of surface-adsorbate complex, meaning correctional steps such as ZPE were applied. **Figure 3.2** shows the optimized geometries of gas molecules as reaction product, reactant or intermediates in vacuum.

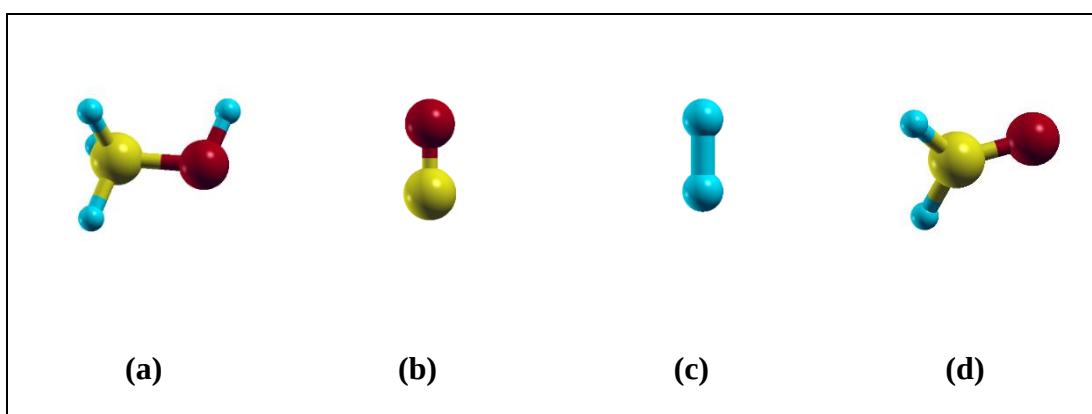


Figure 3.2: Relaxed geometries of single gas molecules: **(a)** CH₃OH, **(b)** CO, **(c)** H₂, **(d)** CH₂O. Geometric relaxations were computed through Quantum ESPRESSO, ball and stick representations were generated via XCrySDen. Light blue atoms correspond to hydrogen, red atoms to oxygen and yellow atoms to carbon.

3.5. Ground States

Ground state geometries were obtained through structural relaxation calculations by providing the initial atomic positions, relevant parameters, and input packages (see APPENDIX-A.1: DFT GROUND STATE INPUT and APPENDIX-B.1: DFT GROUND STATE OUTPUT for sample GS inputs and outputs, respectively). These optimizations yielded the most stable, lowest-energy configurations starting from the proposed geometries. Later on, the GS geometries were verified through frequency computations where all frequencies were expected to be positive except the ones that are belonging to translation and rotation.

The study aimed to investigate the reaction on a periodically repeating, non-symmetrical 2D structure. Consequently, interactions between periodically repeated surfaces along z-axis were a concern, resulting in an undesired deviancy. To eliminate spurious interaction of surfaces across neighboring cells and isolate them effectively, electric field and dipole corrections were applied.

Total electric field, is a potential simulating an electric field at a certain position of the cell that prevents the interaction of the surface with the surfaces in upper and lower cells. The axis of this field was selected as z-axis to cancel upper and lower cells whereas the position of the field within the cell was selected as (0.8) such that it would be far enough from both the particles above the surface. In addition, it was preferred to be far enough from the clean, bottom side of the surface with the aim of blocking intracellular interactions but interfering as less as possible with the molecules.

Dipole field, was another correction measure coupled with electric field to counter intracellular interactions by creating a dipole correction that cancels the artificial field stemming from periodic boundary conditions affecting electrostatic potential.

3.6. Transition States

Transition state calculations enable the identification of the highest energy point along the reaction pathway, known as the transition state, which is essential for determining the activation energy of the reaction, or intermediate reactions in this case. By optimizing the structures of both reactants and products, the Nudged Elastic Band (NEB) method, followed by the climbing image (CI) refinement, was applied to map out the minimum energy path (MEP) between selected GSs and to locate the saddle

point geometries accurately. Sample TS inputs and outputs from this work can be seen in APPENDIX-A.2: DFT TRANSITION STATE INPUT and APPENDIX-B.2: DFT TRANSITION STATE NEB OUTPUT.

Pairs of neighboring ground states along the reaction pathway were selected as initial and final geometries and the NEB method was used to interpolate the transformation between them. The NEB method divides the transition into several, evenly spaced intermediates, called images that are connected with each other by spring forces. These images are iteratively relaxed, resulting in one image converging to the highest energy point along the path, becoming a saddle point candidate while ensuring evenly distributed images.

While the NEB method creates a realistic energy profile, it is not enough to locate the transition state energy and geometry alone. One additional measure to overcome this problem is to implement the climbing image (CI) method. CI picks the intermediate image with highest energy, selects it as the image to climb upwards and allows it to proceed to saddle point by removing the spring like forces between neighboring images. This way, the CI reaches the highest energy point along the MEP, determining the true transition state energy and the geometry (see APPENDIX-B.3: DFT TRANSITION STATE NEB-CI OUTPUT for sample output). **Figure 3.3** shows a comparison between NEB and CI energy profiles.

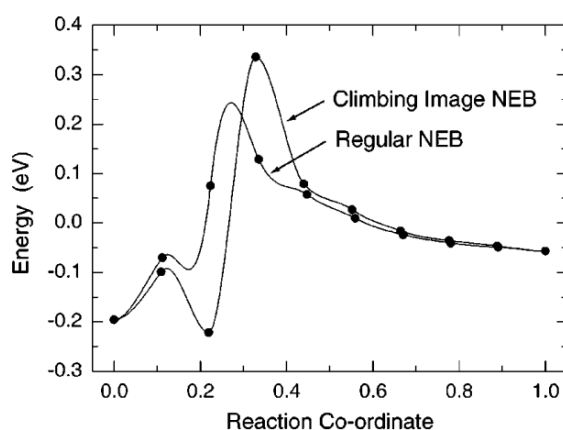


Figure 3.3: Energy profiles of CH_4 dissociative adsorption on Ir(111) surface obtained by NEB and CI-NEB methods [53]. The intermediate image with highest energy is pushed upward in CI method to reach true saddle point, which has higher energy than the saddle point obtained through regular NEB method.

In addition to common parameters across GS and TS calculations, there were several other options and parameters introduced in TS calculations. Maximum number of optimization steps to be carried out until converging varied between values such as 10, 20, 100, 300 and even 500 were used as the maximum allowed number of iterations depending on the progress. The optimization algorithm was specified as quasi-Newton Broyden's second method, which was also the suggested method in the official documentation.

The total number of images, including the initial, intermediate and final images, was set to 10 for all TS calculations. Atomic masses were included in the optimization of the reaction path by enabling the necessary option.

Also, maximum number of iterations in a self-consistent field SCF step was not specified and used as 100 in GS calculations which was the system default, but in TS calculations, it was increased to 200 as specific under the electrons subsection to better accommodate the increased complexity of TS calculations. The electron density was adjusted through density mixing during the iterative SCF process, which was controlled by ratio of the newly calculated density that is mixed with the previous one. The default mixing parameter was 0.7 while in this study, a value of 0.1 was applied. This caused a slower convergence but offered a more stable result that was required to handle the surface with the copper atom. Convergence threshold for SCF calculations was set as 10^{-5} for initial convergence and 10^{-6} for the next calculation, with the built-in units of Rydberg, for more accurate calculations before enabling climbing image method.

Self-consistent field (SCF) calculations were carried out with a convergence threshold of 10^{-5} Ry during initial relaxations, and this was tightened to 10^{-6} Ry in transition state searches and climbing image approach to ensure reliable energy barriers. To further enhance SCF stability, the density mixing parameter was reduced from its default value of 0.7 to 0.1, resulting in slower but more robust convergence, especially important for systems involving doped surfaces with transition metals.

Input coordinates, unlike ground state calculations, are made up of two geometries, namely the initial geometry of the first ground state and the final geometry that corresponds to the next ground state. During transition state calculations, surface atoms were fixed by adding three zeros next to their given coordinates to save

computational time and effort as the inspected phenomenon was the interaction around the active side.

To ensure stable and step-by-step convergence, each NEB path was evaluated through a three-stage computation process. In the first step, both the surface atoms and the copper atom were fixed, and the system was relaxed using a SCF convergence threshold of 10^{-5} Ry. Once this initial relaxation converged, a second calculation was performed in which the copper atom was freed while the rest of the surface remained fixed. This second stage used a tighter SCF convergence threshold of 10^{-6} Ry to improve energy accuracy near the transition region. In the final step, the climbing image (CI) method was enabled using the same atomic constraints and SCF parameters as the second stage, allowing the highest-energy image to accurately converge to the transition state saddle point.

3.7. Frequency (phonon) Computations

All final geometries were re-evaluated with a highly strict SCF convergence threshold of 10^{-10} Ry. These results were then used as input for PHonon module of Quantum ESPRESSO to determine vibrational frequency data with a self-consistency threshold set to 10^{-12} . During phonon calculations, only the atoms belonging to the methanol molecule were included while the surface atoms were held fixed and excluded from vibrational analysis, by setting number of atoms to match those of methanol's (except gaseous H₂ molecules) and specifying their order in the input geometry. can be seen in APPENDIX-A.4: PHONON INPUT and APPENDIX-B.4: PHONON OUTPUT shows example input and outputs for phonon computations from this work. Finally, based on vibrational frequencies, dynamical matrices were computed to visualize forces acting on each atom., 3 translational and 3 rotational ASRs were enforced specifically. The dynamical matrix file was used to analyze atomic displacements and verify whether the vibrational modes, particularly those associated with largest negative frequencies, correspond to the expected atomic movements during the transition state.

3.8. Optimization of Crystals

Energies of clean and substituted surfaces were obtained by geometric relaxation. Energies of single atom solid particles, namely copper and boron, were estimated based on their crystalline structures. For copper atom, simple FCC cubic cells were optimized (See APPENDIX-A.6: COPPER FCC CUBIC CELL OPTIMIZATION INPUT for input and APPENDIX-B.5: COPPER FCC CUBIC CELL OPTIMIZATION OUTPUT for output). Lattice parameter values ranging from 6.6 to 7.5 Bohr were scanned near the expected equilibrium to simulate the energy and volume relationship of bulk copper. A dense 12x12x12 Monkhorst-Pack k-point grid was used. Total energies obtained via SCF-based screening were fitted to Murnaghan equation of state by using the *ev.x* tool of Quantum ESPRESSO. The value corresponding to the minimum energy of a single cell was used as the energy of a single copper atom, approximating the energy of a single copper atom in a periodic bulk phase, as the unit cell had only one copper atom in it.

For the determination of energy of a single boron atom, a simple cubic cell did not suffice as it tended to exhibit complex polymorphism. A primitive 36-atom version of the most stable form of boron crystal [54], namely β -rhombohedral, was used as the crystal structure to calculate energy of a single boron atom. The geometry of the crystalline structure with the Material ID *mp-160* was obtained from The Materials Project [55]-[70], an open web-based platform for computed information. In contrast to cubic cell used in copper, screening was done by adjusting the volume of cell by adjusting cell parameters through scaling, scanning between 10% smaller and 10% larger cells than the initial volume provided in the input file. Rest of the process was identical to copper method but the energy obtained was the total energy of 36-atom bulk, so it was divided by 36 to estimate energy of a single boron atom.

Periodic boundary conditions were applied in all directions, and to prevent artificial interactions between periodic images along the surface normal (z-axis), a vacuum layer of approximately 15 Å was added above the 2D plane. Furthermore, dipole correction techniques were applied using the electric field and dipole correction options to minimize electrostatic interactions between periodic slab images. The electric field was applied along the z-direction, with the maximum potential position set at 0.8, sufficiently far from both the surface and the adsorbed species.

2D *h*BN structures and the copper-doped versions were subjected to geometrical relaxation and their relative energies were determined. The optimum structure was determined by scanning an array of cell vectors for both xy-plane and z-axis, fitting the results into Murnaghan EOS using *ev.x* tool and obtaining the cell parameters corresponding to minimum energies (See APPENDIX-B.6: *h*BN FCC FIRST AXIS OPTIMIZATION OUTPUT and APPENDIX-B.7: *h*BN FCC SECOND AXIS OPTIMIZATION OUTPUT for output files). The xy-plane fit was to determine the dimensions of the hexagonal structure while the z-axis fit was done to ensure that selected cell height was large enough to prevent interaction between two layers. **Figure 3.4** shows the parabolic curve obtained by fitting minimum energies with respect to varying lattice parameters of a single axis, which allows to determine the lattice parameter that corresponds to absolute minimum energy.

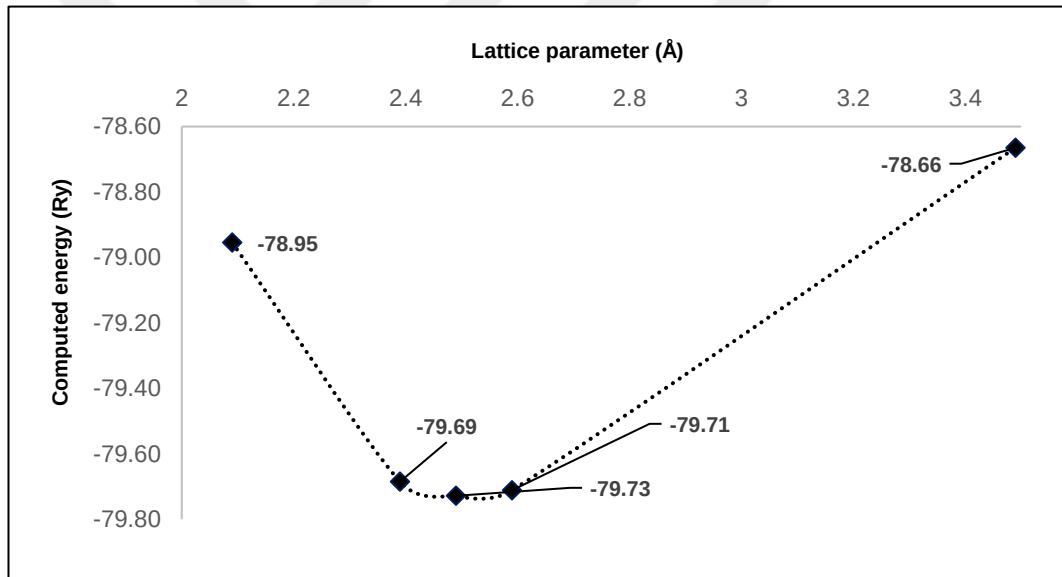


Figure 3.4: Computed energies to determine the optimum lattice parameter of *h*BN surface on xy-plane obtained by scanning a range from 2.0 to 3.5 Å. The parabola ensures the lowest energy was observed within this range.

During the optimization of hexagon dimensions, a curve showing minimum energy was needed. When determining the cell vector for z-axis, the energy graph was expected to show constantly decreasing energies. At a point, an asymptotic behavior was expected, upon passing that point it was safe to conclude that increasing the height of unit cell would have only negligible effects on interaction between two neighboring

surfaces. **Figure 3.5** shows the corresponding energy profile with aforementioned trend, which validates the selection of unit cell height.

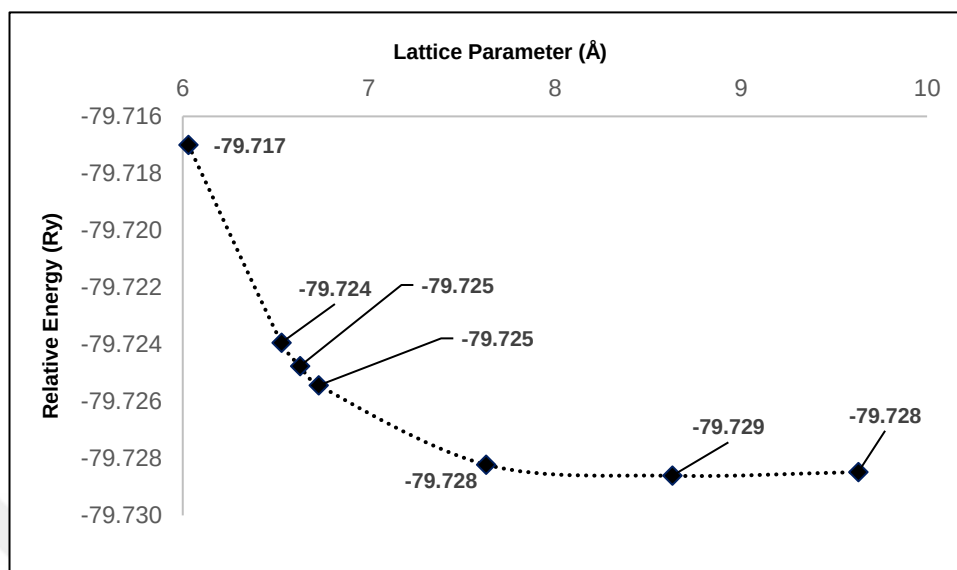


Figure 3.5: Computed energies to determine the optimum unit vector in z-axis of *h*BN surface obtained by scanning a range from 6.0 to 9.6 Å. The parabola ensures the lowest energy was observed within this range.

3.9. Surface Modeling

As **Figure 3.6** shows, the catalyst surface modeled in this study was a two-dimensional hexagonal boron nitride (h-BN) sheet chosen for its chemical stability, thermal resistance and structural similarity (i.e. hexagonal) to graphene. Upon optimizing the lattice parameters for the hexagonal 2D structure, a 4x4 supercell consisting of 32 atoms (16 B + 16 N) was constructed to represent the clean *h*BN surface. The catalytic activity was introduced by replacing a single boron or nitrogen atom from the center of surface with a copper atom, creating two alternative setups; one where copper replaces a boron atom (will be referred to as Cu/B) and a nitrogen atom (Cu/N).

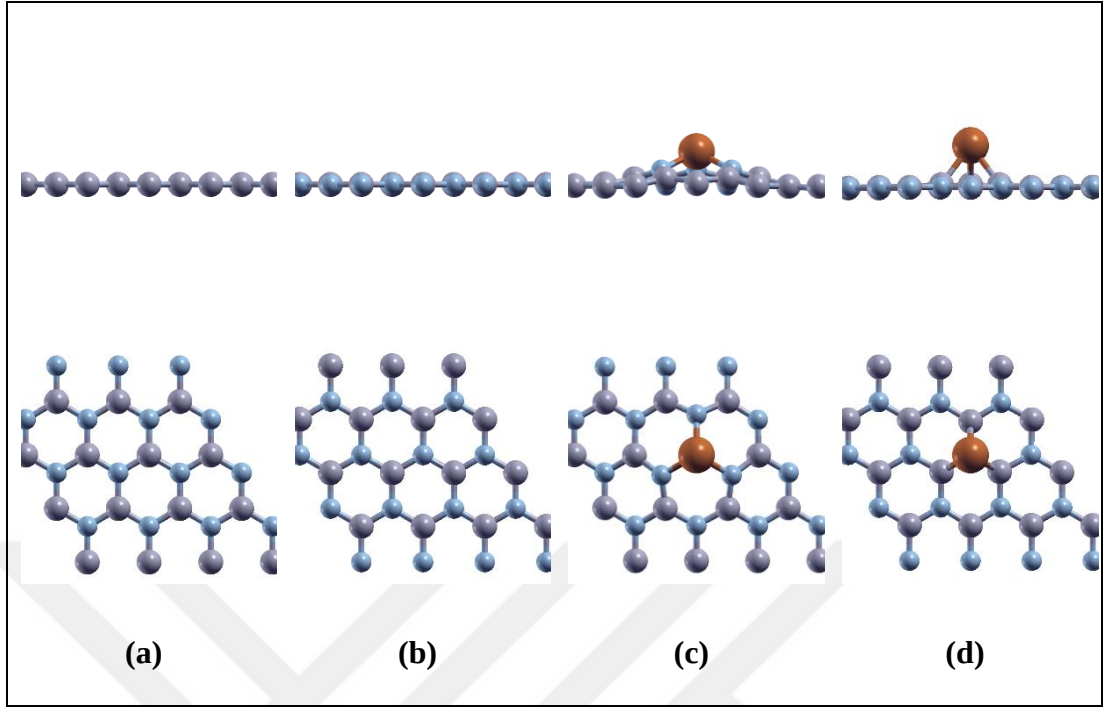


Figure 3.6: Relaxed surface geometries: **(a)** boron centered layout (B-center), **(b)** nitrogen centered layout (N-center), **(c)** central boron atom replaced by copper atom (Cu/B), **(d)** central nitrogen atom replaced by copper atom (Cu/N). Blue, gray and copper particles represent nitrogen, boron and copper, respectively.

All subsequent simulations, including adsorption, reaction, and transition state analyses, were carried out independently for both configurations to assess their comparative performance.

Substitution energies for both layouts were calculated by comparing the total energy of initial and final states based on equations (3.2) and (3.3).

$$E_{sub,Cu/B} = (E_{Cu/B} + E_B) - (E_{surf} + E_{Cu}) \quad (3.2)$$

$$E_{sub,Cu/N} = (E_{Cu/N} + \frac{1}{2}E_{N_2(g)}) - (E_{surf} + E_{Cu}) \quad (3.3)$$

The unit cell and the supercells were constructed using explicitly defined cell vectors based on the most stable geometry achieved in previous paragraph, by forming a parallelogram-shaped base with side lengths of 10 Å and an inter-vector angle of 120°

in the XY plane, and a height of 15 Å for the cell. This configuration was chosen to match the area occupied by a 4x4 h-BN supercell in the XY plane and to allow unobstructed movement of adsorbates and reaction intermediates. During simulations, the atoms forming the bottom layers of the surface were fixed to mimic the effect of a bulk-like support, while atoms near the active site were allowed to fully relax, allowing a significant benefit in terms of computational efforts.

Figure 3.7 shows several tested possibilities for Cu addition. These are **(a, b)** by replacing a surface atom, **(c, d)** attaching atop a single atom, or **(e)** occupying the center of the hexagonal gap between surface atoms. The relative stabilities of these structures were compared in two ways. First, the energetics of copper addition were determined by comparing final energies of copper and surface assembly whether it was an addition or replacement. When replacing a surface atom, this energy was evaluated through the equations (3.2) and (3.3). **Table 3.1** shows the relative energies obtained for this comparison.

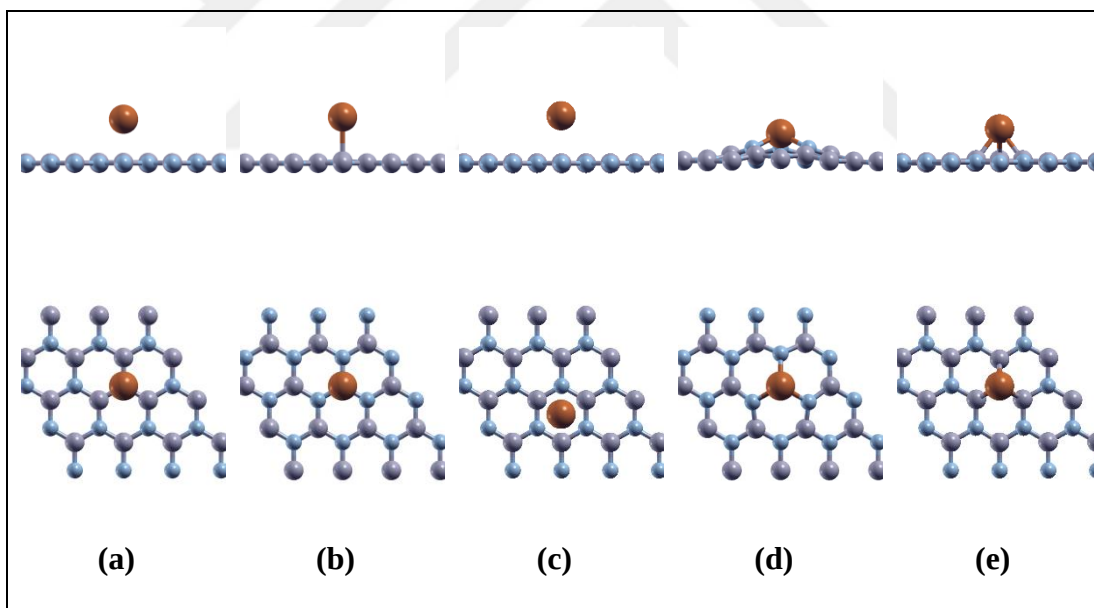


Figure 3.7: Various copper-doped BN surface configurations. **(a)** copper attached on top of a nitrogen atom, **(b)** copper attached on top of a boron atom, **(c)** copper at the center of hexagonal gap, **(d)** copper replacing a boron atom, **(e)** copper replacing a nitrogen atom.

Table 3.1: Relative energies obtained after doping BN surface with a single copper atom for several configurations including substitution and addition.

Configuration	ΔE (kJ/mol)
(a) Cu attached on N	0
(b) Cu attached on B	1
(c) Cu at the center of hex.	9
(d) Cu replacing B	261
(e) Cu replacing N	351

The configurations where copper was added on top of the surface instead of replacing a surface atom showed more stability in terms of relative energy comparison. However, it was not enough to select those surfaces because stability of copper at the surface, i.e. its resilience to mobilize or being ripped off from the surface was the main concern. Thus, the next trial was carried out.

Second, to test the stability of the Cu atom on the surface, a single methanol molecule was added on top of the copper atom to be adsorbed for one of the two layouts where Cu was attached to B or N. **Figure 3.8** shows the resulting mobile copper atom, binding to the surface only at a single point.

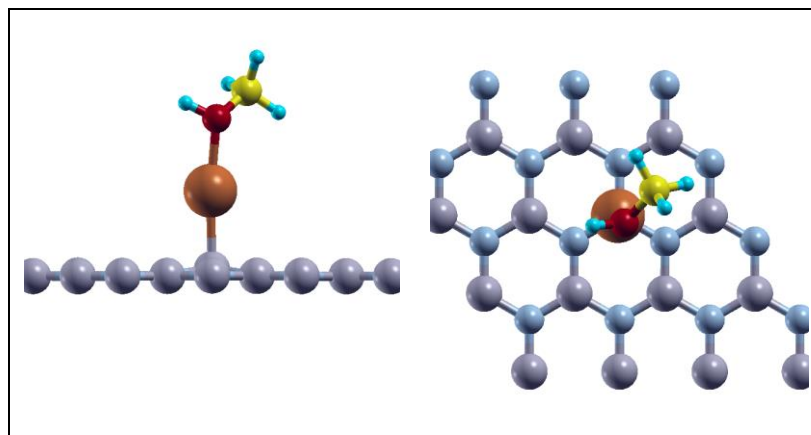


Figure 3.8: Methanol adsorption on the surface where copper atom was adsorbed on the central boron atom with a single bond.

As the methanol interaction showed, Cu addition on stoichiometric *h*BN surface (i.e. decoration) is in fact mobile and Cu is not expected to stay on the surface under reaction conditions. Thus, all calculations in this study were conducted using

configurations in which the copper atom replaces a surface atom, as this approach offers greater stability and aligns with previous literature.

3.10. Thermodynamic Corrections

Three additional operations were performed on converged GS and TS computations to reach the thermodynamic correction values and also for TSs to ensure that vibrational frequencies align with expected movement pattern of atoms between the two GSs.

3.10.1. Vibrational Enthalpy and Entropy Corrections

DFT calculations inherently assume absolute zero temperature (0 K) and often neglect nuclear vibrations when reporting total energies. In order to improve DFT results into more realistic and meaningful data, a series of additions and corrections were applied, ultimately obtaining a temperature specific Gibbs free energy data from the theoretical energy results from DFT. Gibbs free energy of each individual step was determined following the Equation (3.4).

$$\Delta G = \Delta H_{vib} - T * \Delta S_{vib} \quad (3.4)$$

In order to benchmark obtained Gibbs free energies, experimental values from literature were processed to tabulate Gibbs free energy of methanol decomposition following $\text{CH}_3\text{OH}(\text{g}) \rightarrow \text{CO}(\text{g}) + 2\text{H}_2(\text{g})$ reaction at 338.15K, which was the temperature selected to resemble normal DMFC operating conditions. Gibbs free energies at an elevated temperature were evaluated based on the ideal gas standard enthalpy of formation, ideal gas Gibbs free energy of formation, ideal gas entropies and specific heats of methanol, carbon monoxide and hydrogen, all of which were taken from Perry's Handbook [71]. Equation (3.5) shows the calculation of Gibbs free energy of reaction for methanol decomposition into CO and H₂.

$$\Delta G_{rxn} = \Delta G_{out} - \Delta G_{in} = (\Delta G_{CO} + 2 * \Delta G_{H_2}) - \Delta G_{CH_3OH} \quad (3.5)$$

In order to calculate the Gibbs free energy of reaction, Gibbs free energies of individual product and reactants were evaluated by starting from values corresponding to normal

conditions. Equation (3.6) shows the relation to obtain Gibbs free energies of individual molecules at 65°C (or 338.15K) to be used in Equation (3.5), to obtain Gibbs free energy of methanol decomposition at 338.15K ultimately.

$$\Delta G_{338.15K} = [\Delta H_f^\circ + C_{p,avg}\Delta T] - 338.15K * \left[\Delta S^\circ + C_{p,avg} * \ln \frac{338.15}{298.15} \right] \quad (3.6)$$

While specific heat capacity is a function of temperature, it varies only slightly with small temperature differences such as 40°C as is the case in this study, which allows the simplification to use the average C_p value of lowest and highest temperatures. Also, low dependence on temperature allowed neglecting the integration and simplifying the integral term into $C_{p,avg} * \Delta T$.

The zero-point energy (ZPE) correction accounts for the quantum mechanical vibrational energy that remains even at absolute zero temperature, and was calculated using the relation given in Equation (3.7) [72], [73] where ν_i are the positive vibrational frequencies of the system.

$$E_{ZPE} = \frac{1}{2} \sum_i h\nu_i \quad (3.7)$$

ZPE does provide results that are more realistic but even after this correction, DFT calculations assume no thermal contributions as they run on absolute zero temperature condition, which make them incomparable to real energies. To further improve ZPE-corrected results, thermal energies such as enthalpy and entropy need to be included. Additionally, vibrational enthalpy, that is the enthalpy of a molecule due to its vibrations at a certain temperature, can be calculated and implemented to the DFT results with the Equation (3.8) [72].

$$\Delta H_{vib} = E_{ZPE} + R \sum_i \frac{h\nu_i/k_B}{e^{h\nu_i/k_B T} - 1} \quad (3.8)$$

Similarly, temperature-dependent entropy contribution is required in order to compute Gibbs free energy, which is calculated from vibrational frequencies through the relationship given in Equation (3.9) [72].

$$\Delta S_{vib} = R \sum_i \frac{h\nu_i/k_B T}{e^{h\nu_i/k_B T} - 1} - \ln(1 - e^{-h\nu_i/k_B T}) \quad (3.9)$$

The raw final energies, whether obtained directly from DFT or after applying thermodynamic corrections, do not carry meaning on their own as they are referenced to an arbitrary baseline defined by the computational method. To extract meaningful information, energies of all computed results were compared relative to each other to obtain a relative energy profile along the reaction pathway, by assuming the initial state energies of clean surface and gaseous methanol molecule as the reference point that is chosen arbitrarily but allows interpretation of the results in a straightforward manner.

3.10.2. Reaction Rate Estimation

To estimate the kinetics of surface reactions, the rate constant was estimated based on the Gibbs free energy difference between the two ground states and the related transition state through the simplified version of the Eyring equation, following the formula shown below in Equation (3.10) [74]. The reaction was assumed as first order, resulting in unit of rate constant to be s⁻¹.

$$k = \frac{k_B T}{h} e^{-\Delta G^\ddagger/RT} \quad (3.10)$$

The activation energy for that specific transition state, denoted as $\Delta G^\ddagger$, corresponds to the energy difference between the transition state and initial ground state. While the reaction rate estimation like the DFT energies, can provide useful information, it is preferable to compare DFT results with each other to determine fast/slow/rate-determining steps instead of comparing the rates directly to experimental data as the estimation may deviate significantly due to inherent methodological approximations.

3.11. Reaction Pathway Construction

In order to construct a meaningful reaction pathway, this study focused on a single, literature-supported decomposition route, previously proposed by Greeley and

Mavrikakis for a Cu(111) surface [36] and used for methanol on copper-doped graphene research by Akça et al. [20]. This route was adapted for Cu–h-BN surface and assumed sequential dehydrogenation of the methanol molecule, ultimately forming CO as the final product. By narrowing the scope to one likely mechanism, computational efforts were concentrated on evaluating each elementary step in detail rather than exhaustively testing all theoretical possibilities. Adsorption energies and relative Gibbs free energies, which were determined by the procedure that was explained in Section 3.10, for each intermediate were later used to visualize the energy profile of the entire reaction sequence and to identify the rate-determining steps. The temperature for computing thermodynamic terms was selected as 338.15K.

Methanol decomposition is a stepwise reaction that can follow numerous possible pathways. There are at least four atoms to be removed until reaching the carbon dioxide as the final product, even when omitting the oxygenation of the carbon monoxide that is still adsorbed on the surface, which was not covered within the scope of this study. Even by varying only the sequence of hydrogen desorption, up to 24 different pathways can arise, not accounting for variations like simultaneous hydrogen removal or early C–O bond cleavage. Due to this combinatorial complexity, this study narrowed its focus to a single, literature-supported pathway previously proposed for methanol decomposition on copper-doped graphene [20]. This allowed detailed analysis of each elementary step on the catalytic surface while maintaining computational feasibility.

4. RESULTS

In this section, findings obtained during this research will be listed, starting from preliminary work including surface modelling and gas molecules in vacuum as mentioned in Section 4.1. The results obtained via computations of Cu/B and Cu/N surfaces with and without thermodynamic corrections will be given in sections 4.2, 4.3 and 4.4 while rate constant estimation will be explained in Section 4.5. Sections 4.6 and 4.7 shows the comparison of results to two similar research from literature on same topic but different catalyst materials.

4.1. Surface Doping and Gaseous Molecules

Substitution energies of both configurations as shown in **Table 4.1**. For clean surfaces listed below, no thermodynamically corrective operations were carried out as the surface vibrations were neglected.

Table 4.1: Calculated substitution energies of clean and doped surface configurations.

Layout	E _{sub} (kJ/mol)
B-center Cu/B	731
N-center Cu/N	826

Intermediates or adsorbates that were atoms or molecules in gas phase observed during the reaction were subjected to geometrical relaxation. **Table 4.2** shows thermodynamically corrected computational energies of intermediates.

Table 4.2: Corrected computational energies of gas phase reaction intermediates in vacuum.

Species	ΔG (Ry)
CH ₃ OH	-64.71
CO	-60.00
H ₂	-2.31
N ₂	-56.42

Adsorption of reaction intermediates on BN surface, before introducing the copper atom, was tested to observe the interaction without an active site.

First the adsorption of the intermediates were tested for their possible interactions with B-atom of the undoped surface. The adsorption energy of single H-atom on B-center configuration was determined as 225 kJ/mol by assuming energy of a single hydrogen atom as half of an H₂ molecule. When the energy of a single hydrogen atom was used by neglecting the energy of dissociation, however, the adsorption energy was evaluated as -87 kJ/mol. Other molecules shown in **Figure 4.1** only gave weak physisorption with adsorption energies of 5, 5 and 2 kJ/mol respectively for CH₃OH, CH₂O and CO.

On B-center configuration, none of the molecules were attached while a hydrogen initially placed directly on top of a boron atom, was adsorbed on the surface, as shown in. The binding energy of hydrogen atom on central boron atom was determined as 225 kJ/mol.

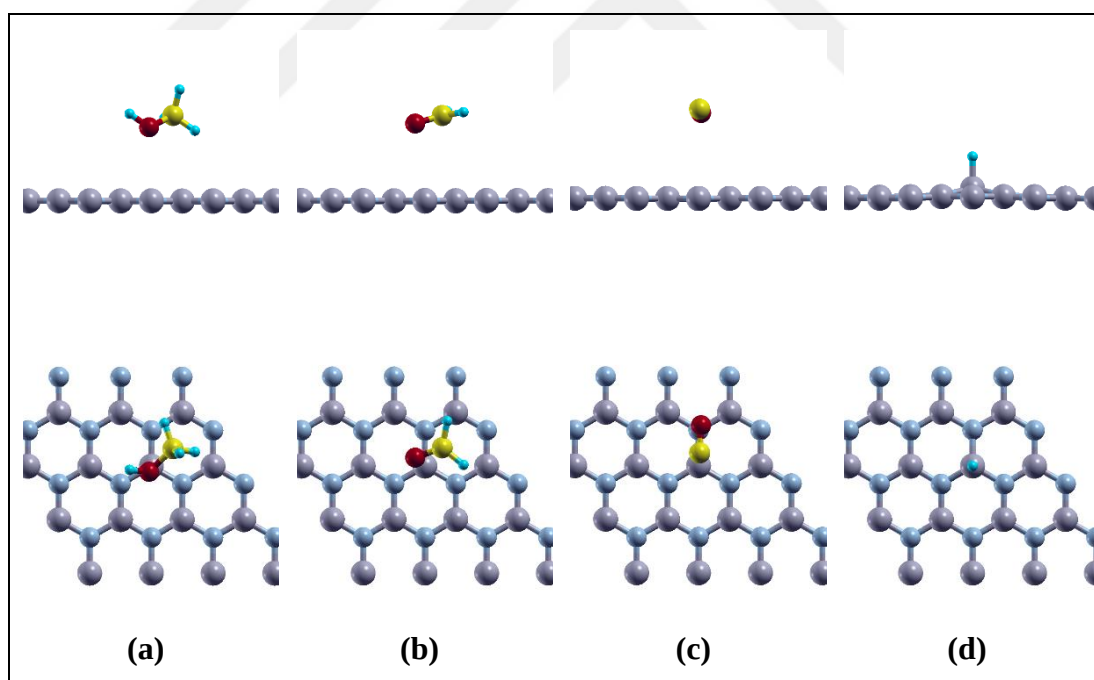


Figure 4.1: Obtained geometries after adsorption trials on B-center surface of (a) CH₃OH, (b) CH₂O, (c) CO, (d) H.

The interactions of these molecules with the N-atom of the undoped surface produced very similar results, but in this configuration, the hydrogen atom was placed on top of

a nitrogen atom, by which it was adsorbed. **Figure 4.2** shows the floating molecules and adsorbed hydrogen atom.

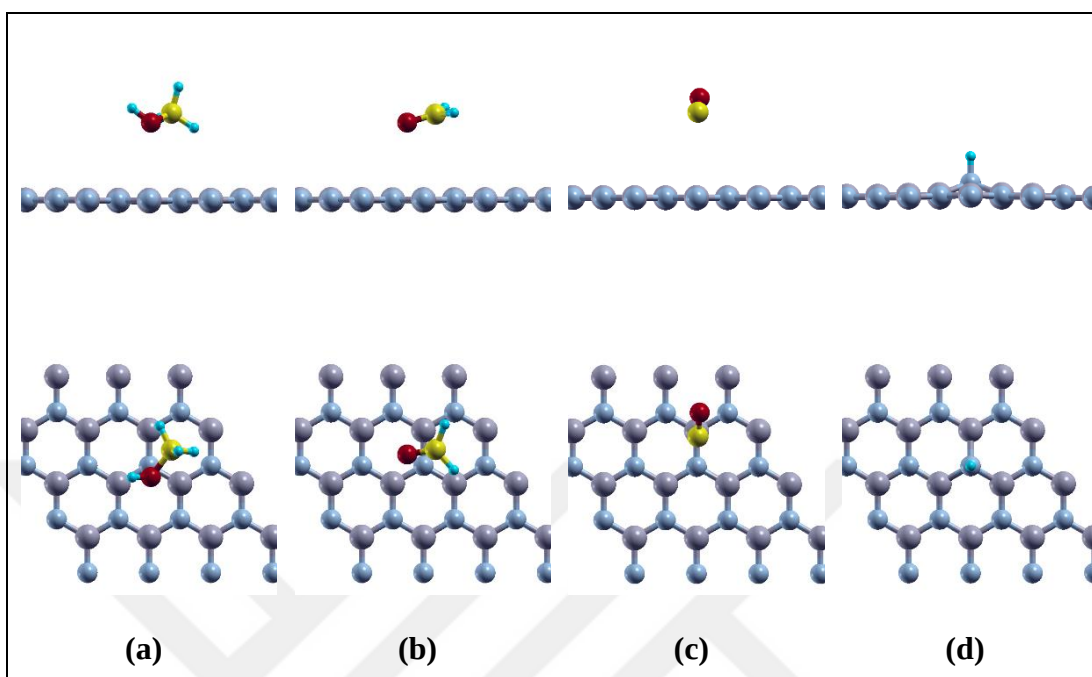


Figure 4.2: Obtained geometries after adsorption trials on N-center surface of (a) CH_3OH , (b) CH_2O , (c) CO , (d) H .

The binding energy of hydrogen atom on central nitrogen atom was determined as -13 and 299 kJ/mol for evaluating hydrogen energy as half of molecular H_2 or a single atom, respectively, meaning a significantly weaker bond between hydrogen and boron atom on clean surface configurations. Like B-center surface, other molecules shown in **Figure 4.2** only gave weak physisorption with adsorption energies of 7, 5 and 2 kJ/mol respectively for CH_3OH , CH_2O and CO .

Adsorption trials on both B-center and N-center configurations concluded an active site was necessary for adsorption of methanol while the clean surfaces were capable of attracting hydrogen atoms leaving the methanol molecule on either surface species.

4.2. Reaction Intermediates on Cu/B Surface

Methanol decomposition on Cu/B and Cu/N surfaces were investigated in terms of ground and transition steps in compliance with the proposed pathway. For each individual step, several conformations were tested and the one with the minimum energy (i.e. global minima) was chosen as the corresponding ground state. For

instance, a CH₃O adsorbed on copper and a hydrogen adsorbed on the surface defines a specific ground state, but the hydrogen can be adsorbed on Cu, B or N. Moreover, it can be adsorbed on a close or a far atom, too. To determine the layout with the least energy, several variants of each state were tested and compared in sections 4.2 and 4.3.

In order to keep the material balance consistent, total energies of each state were determined by adding energy of gas phase molecules to energy of surface/adsorbate assembly for comparability but in sections 4.2 and 4.3, only the relative energies of the surface/adsorbate were given under each conformation as they were computed through the relaxation. Total raw and corrected energies were tabulated to form a complete energy profile as shown in Section 4.4 (see APPENDIX-C.1: TABULATED RESULTS AND ENERGIES SPREADSHEET). For each geometry, selected state was assigned the letter *a* while the discarded alternative geometries were assigned the subsequent letters.

The total, activation and reaction energies of the ground and transition states in this and upcoming chapter, were presented in their uncorrected form as directly obtained from the DFT calculations, prior to applying ZPE and thermodynamic vibrational corrections, allowing both easier reproducibility and direct comparison with literature. Rest of the Section 4.2 shows the geometries and relative energies of both selected and neglected surfaces of GS's and the corresponding TSs detected between selected GSs.

4.2.1. GS0 (GS10): Clean Cu/B Surface

First and last ground state was the clean surface and the gaseous methanol molecule. Instead of modelling gas phase bodies around the surface, methanol was neglected in the computation. Its contribution was added later for comparability. **Figure 4.3** shows the optimized geometry of GS0 and GS10.

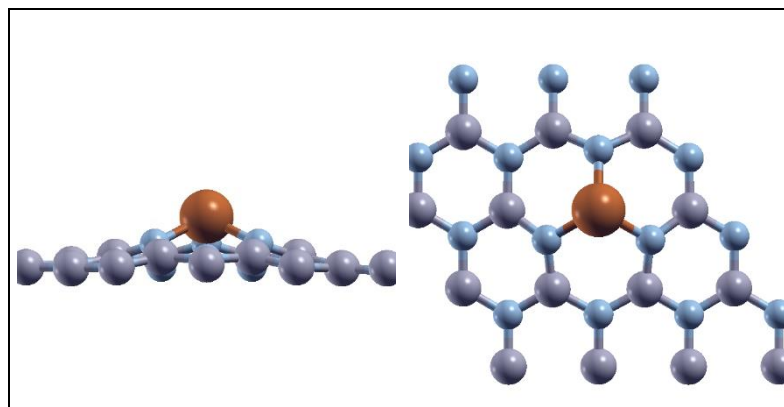


Figure 4.3: Visual representation of optimized geometry of GS0 (GS10) on Cu/B layout.

4.2.2. GS1: CH_3OH^*

The first step of methanol decomposition was the adsorption of methanol on the surface, denoted as GS1. Methanol was expected to bind on copper, so, several different inputs were prepared and simulated to screen possible geometries. All trials resulted in the same, stable geometry, where methanol binds from its oxygen side and has a tilted orientation. **Figure 4.4** shows the stable geometry of adsorbed methanol.

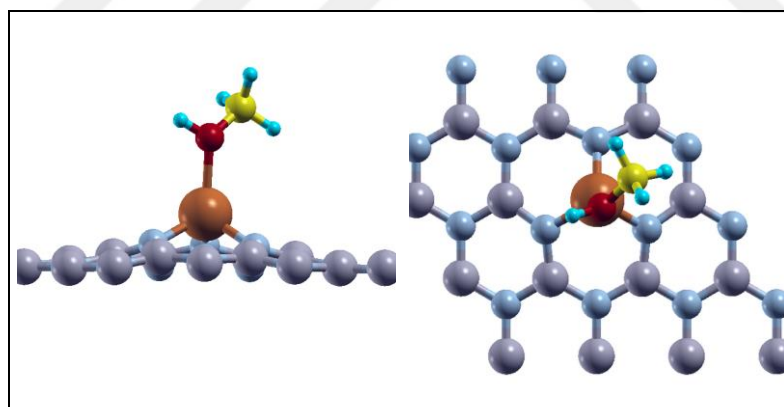


Figure 4.4: Visual representation of optimized geometry of GS1 on Cu/B layout.

4.2.3. GS2: $\text{CH}_3\text{O}^* + \text{H}^*\text{Cu}$

Second ground state was the structure with one hydrogen atom abstracted from methanol and was adsorbed on the surface, but strictly on the copper, denoted as GS2. It was observed that hydrogen eventually transfers to the main surface atoms B or N,

but since the direct path was rather long, a two-step hydrogen transfer was observed, adsorbing on copper first and on surface atoms next.

Based on both literature and trials, it was observed that the lowest energy was achieved when the O-H bond breaks and that hydrogen from the oxygen transfers to the surface. The trials were omitted due to having significantly higher energies. **Figure 4.5** shows the selected GS2 geometry. With the transfer of first hydrogen, the remaining methoxy part and the hydrogen were adsorbed on opposite sides of the copper atom.

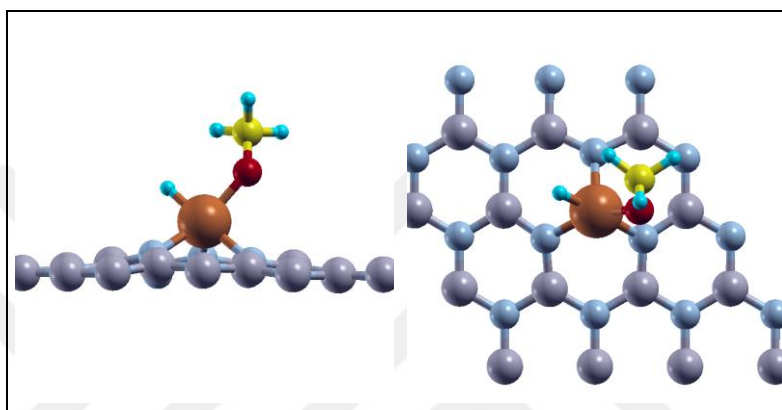


Figure 4.5: Visual representation of optimized geometry of GS2 on Cu/B layout.

4.2.4. GS3: $\text{CH}_3\text{O}^* + \text{H}^*$

Third ground state, denoted as GS3, was the step where hydrogen from copper had completely moved onto the boron or nitrogen atoms of surface while methoxy was still adsorbed on copper, by the oxygen side. With the hydrogen-surface interaction, several options had arisen because hydrogen could be adsorbed on a boron or a nitrogen atom. Also, it could be adsorbed on a surface atom that is neighboring copper or would be adsorbed on a further atom. Besides, the orientation of the methoxy had an impact on overall energy of the surface/adsorbate system, too.

To determine the most stable geometry for GS3, several trials were carried out. It was determined that in all trials, the hydrogen from copper tended to bind to one of the nitrogen atoms that were next to the copper. The position of methoxy structure varied between different trials.

Through exploration of several configurations, three final states were selected as GS3 candidates. All three alternatives had similar energies. So, instead of selecting solely

based on their energies, their synergy with the subsequent GS4 and the transition state between them was considered. **Figure 4.6** shows the geometries and relative energies of each conformation.

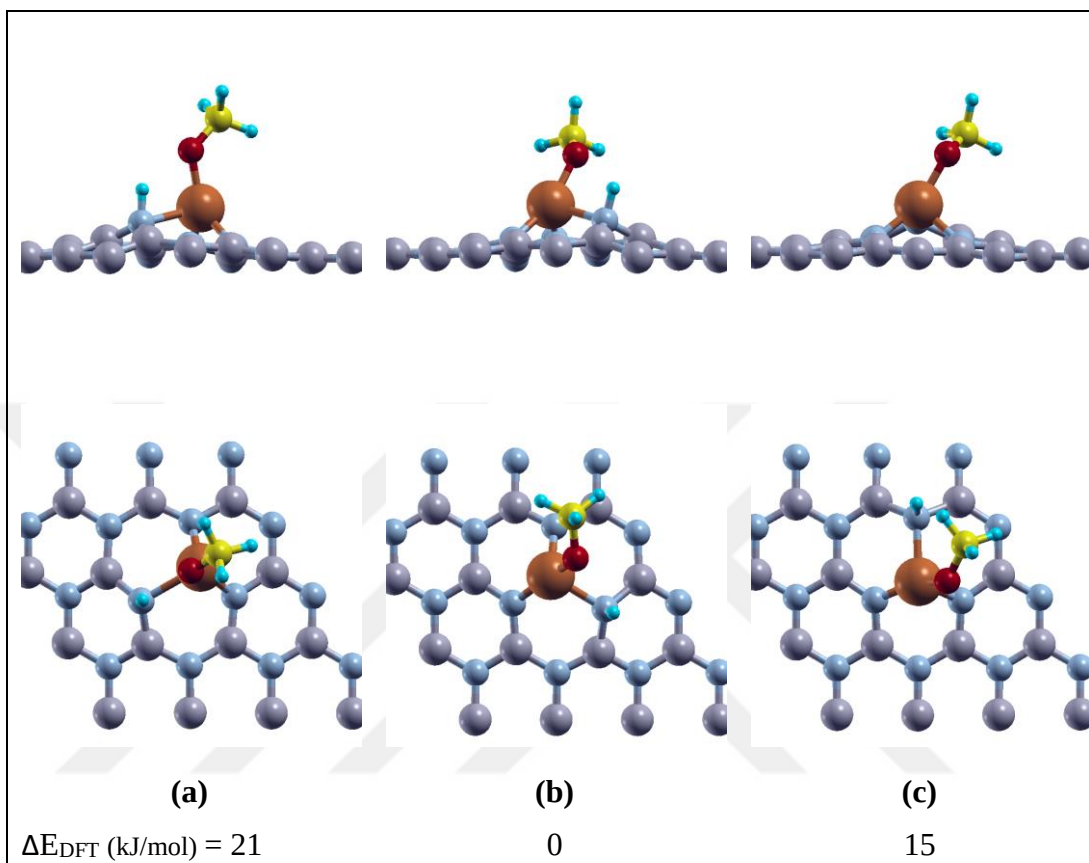


Figure 4.6: Visual representation of optimized geometries of GS3 on Cu/B layout. **(a)** The selected geometry, **(b, c)** neglected geometries with slightly lower energies but lacking a smooth transition to next state.

4.2.5. GS4: CH₂O* + H* + H*_{Cu}

Fourth ground state was observed after abstraction of second hydrogen from the methoxy group, leaving the adsorbate in a formaldehyde structure while the transferred hydrogen attached on the copper, mostly opposite to the hydrogen adsorbed on the surface in previous step. All alternative geometries showed that the formaldehyde binds to surface mainly from oxygen side while the position and orientation with respect to two hydrogens varied, as shown in **Figure 4.7**. Variant that showed a horizontal formaldehyde orientation and closer hydrogens showed the most stable form and was selected as GS4.

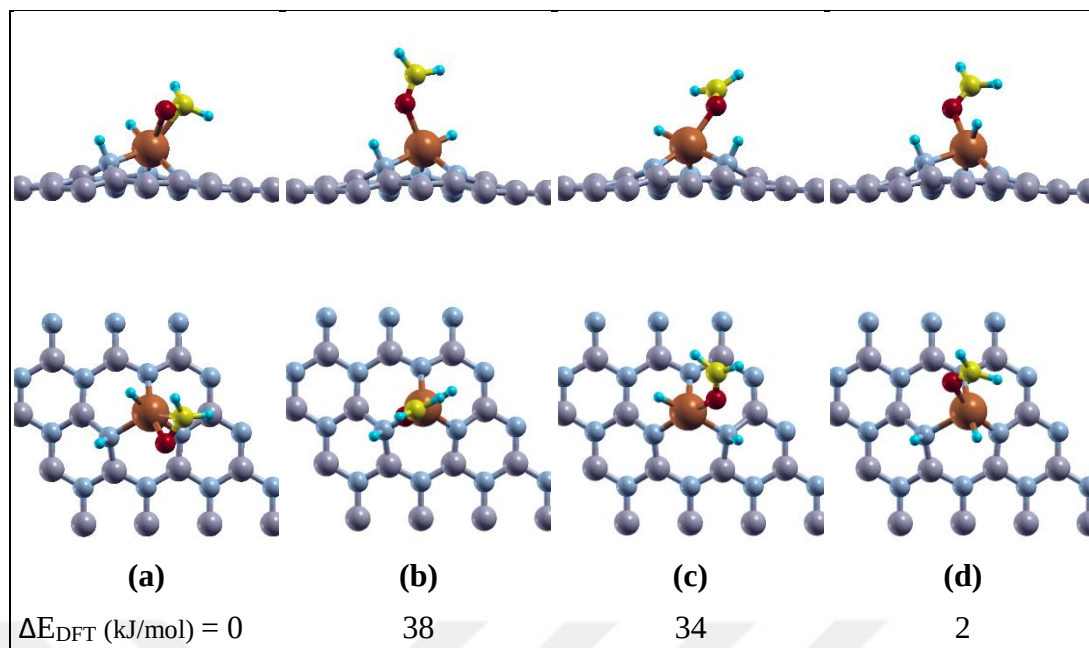


Figure 4.7: Visual representation of optimized geometries of GS4 on Cu/B layout. **(a)** The selected geometry, **(b, c, d)** neglected geometries with similar energies and structures.

4.2.6. GS5: $\text{CH}_2\text{O}^* + 2\text{H}^*$

Fifth ground state had two hydrogen atoms on surface and formaldehyde adsorbed on copper atom. In all alternative geometries, it was observed that one of the hydrogens that was absorbed on the nitrogen adjacent to the copper tends to move downward below the surface plane. This movement causes the bond between that specific nitrogen and the copper atom to break, resulting in a less stable catalytic site despite having a lower total energy. Structures with high energy and high stability were preferred over low stability and low energy alternatives whenever possible throughout this study because there were some geometries where copper was holding onto the surface from a single nitrogen, which results in a highly unstable and undesirable surface. In this step, however, breaking of a single copper bond was acceptable because in the next ground state, two surface hydrogens were removed, reinstating the broken bond.

The orientation of the formaldehyde molecule made a difference, neglecting the effects of hydrogen placement. The horizontally oriented version with both a Cu-O and a Cu-C bond showed the lowest total energy by a significant margin over 140 kJ/mol.

Figure 4.8 shows the alternatives and their relative energies.

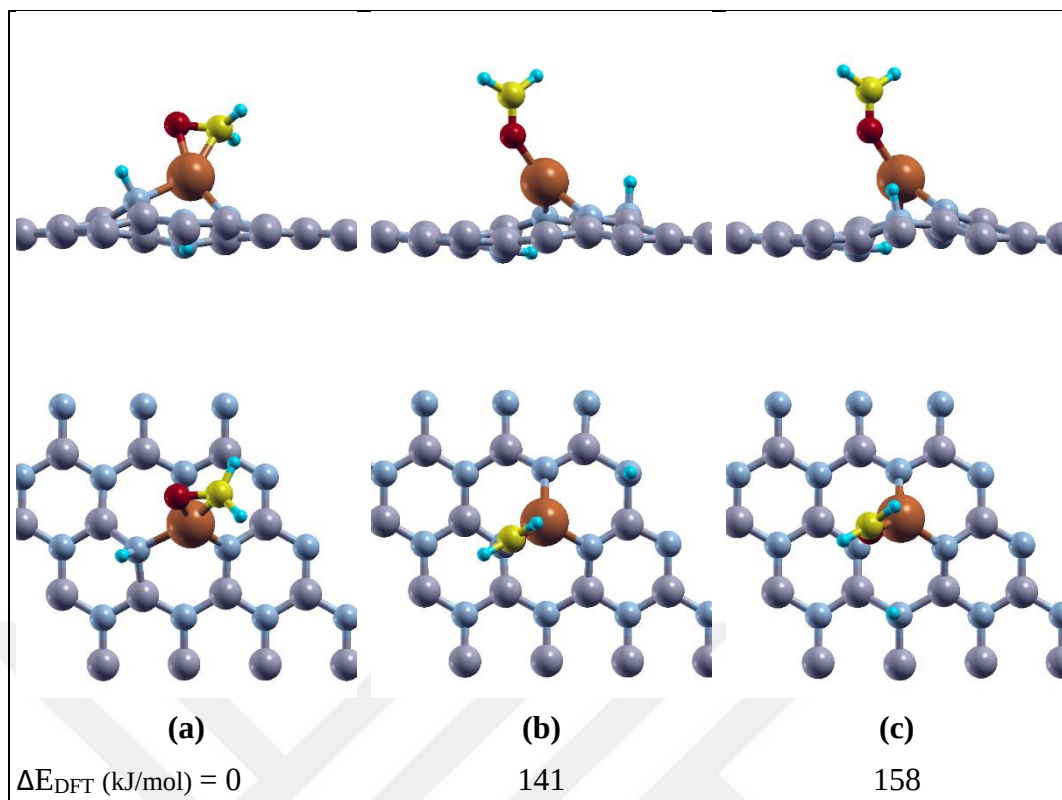


Figure 4.8: Visual representation of optimized geometries of GS5 on Cu/B layout. **(a)** The selected geometry, **(b, c)** neglected geometries with similar energies and structures.

4.2.7. GS6: Possible $\text{C}_1\text{O}_1\text{H}_2^*$ Intermediates

This ground state is essentially the same as the previous one in terms of reaction progress with respect to the methanol molecule, but it is an elementary step where two hydrogen atoms accumulated on the surface individually were assumed as removed, by recombining and forming a gaseous H_2 molecule. The hydrogen recombination steps were not computed.

With a couple of hydrogen atoms leaving the surface, computational results on surface energy drops accordingly. In order to have a comparable value, computed surface energy and the total energy of all gas phase particles were added when building an energy profile and determining critical energies such as activation and reaction. Within this and the upcoming Cu/N section, however; energies of only the surface and adsorbate were illustrated, directly as obtained from the relaxation. Gas phase energies were taken into account in upcoming chapters, namely the complete energy profile and literature comparison sections.

There were four alternative formaldehyde positions on top of copper. The horizontal layout with double bond showed one of the lowest energies and offered a smooth transition from the previous and to the next ground states. Also, at some point during the reaction, the remainder of the methanol changes the binding site from oxygen to carbon. The first two alternatives shown below is in accordance with this expectation, with one already has switched from oxygen to carbon while the other has a double bond, thus has the flexibility to keep one and break the other bond. **Figure 4.9** displays the four main alternatives for GS6.

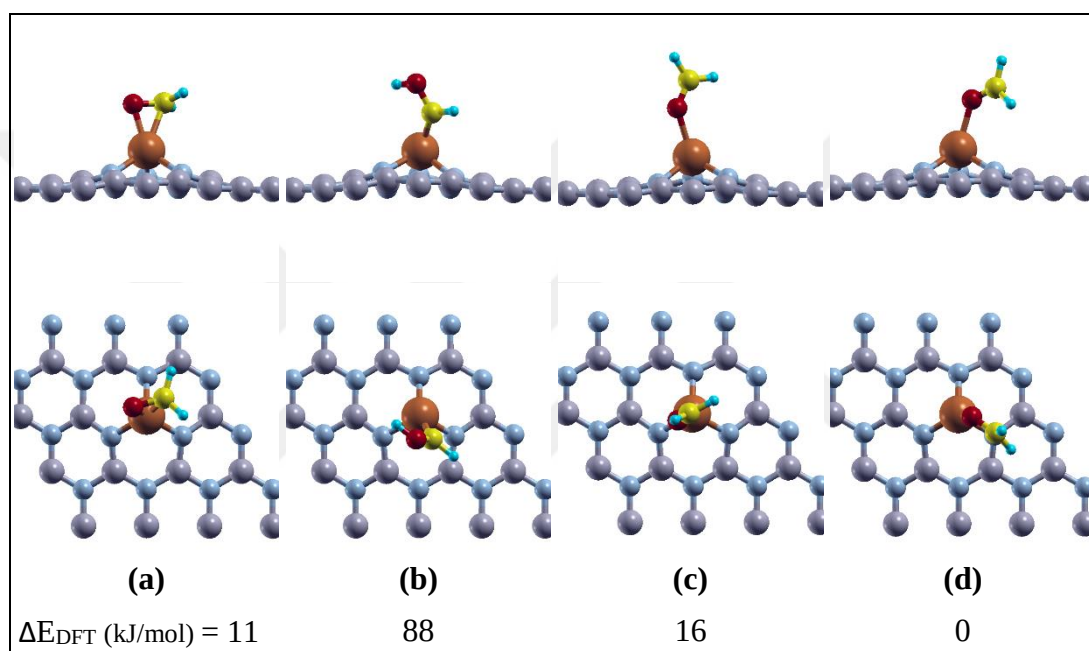


Figure 4.9: Visual representation of optimized geometries of GS6 on Cu/B layout (a) and (b) show the Cu-C bond while (c) and (d) are still adsorbed by the oxygen, which was less preferable.

4.2.8. GS7: Possible C₁H₁O₁* + H* Intermediates

This state had one hydrogen on the surface while the remaining formyl group was adsorbed on the copper. In all cases, the hydrogen was adsorbed on the nitrogen adjacent to the copper while form and shape of CHO group made a difference. Linear CHO or COH structures showed a significantly larger total energy, thus less stability. The structures where CHO followed the formyl form were preferred, one of them selected as the main GS7. **Figure 4.10** illustrates the selected and omitted alternatives.

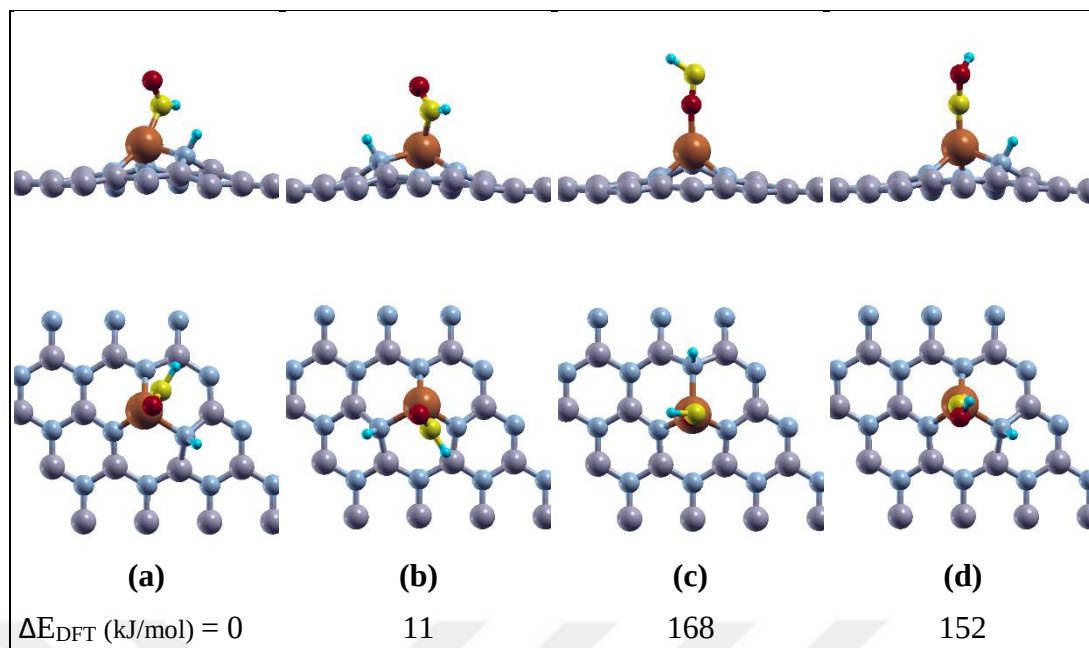


Figure 4.10: Visual representation of optimized geometries of GS7 on Cu/B layout. **(a)** The selected geometry, **(b)** similar geometry with mirrored hydrogen, **(c, d)** neglected linear, less stable structures.

4.2.9. GS8: CO* + 2H* Configurations

After complete transfer of fourth hydrogen to the surface, a CO molecule remained adsorbed on copper and a couple of hydrogen atoms were on the surface. A significantly lower energy was achieved when both hydrogens were adsorbed on surface nitrogen atoms. **Figure 4.11** shows covered alternative configurations. While the variant where both hydrogen atoms were adsorbed on nitrogen atoms next to copper (**Figure 4.11 (a)**) showed a symmetrical and stable behavior, the variant where one hydrogen was adsorbed on a further nitrogen (**Figure 4.11 (c)**) had a lower energy as well as one hydrogen showing the sinking behavior. The variant with slightly more energy was selected as it was more in line with GS7, allowing a smoother transition state.

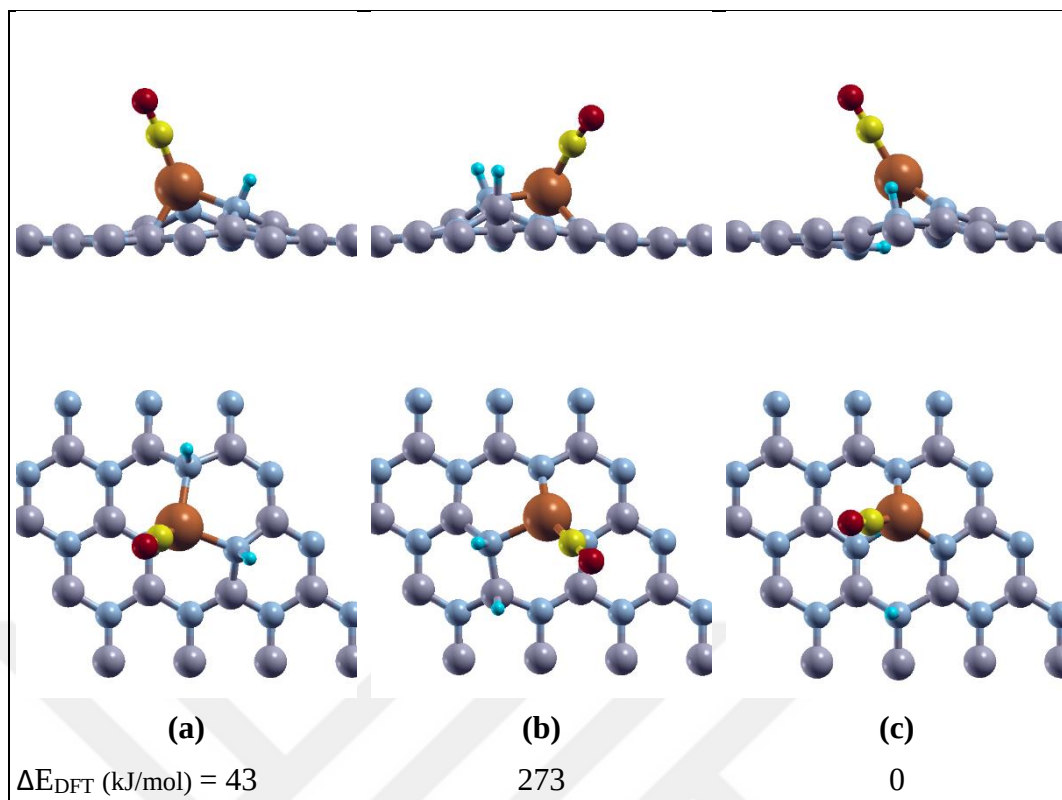


Figure 4.11: Visual representation of optimized geometries of GS8 on Cu/B layout. **(a)** The selected geometry, **(b)** neglected geometry with significantly larger energy, and **(c)** slightly more stable geometry neglected due to sinking hydrogen.

4.2.10. GS9: CO*

After the second couple of hydrogen atoms on surface were assumed to recombine and leave the surface by forming gaseous H_2 , only CO remained adsorbed on the surface.

Figure 4.12 shows the optimum geometry.

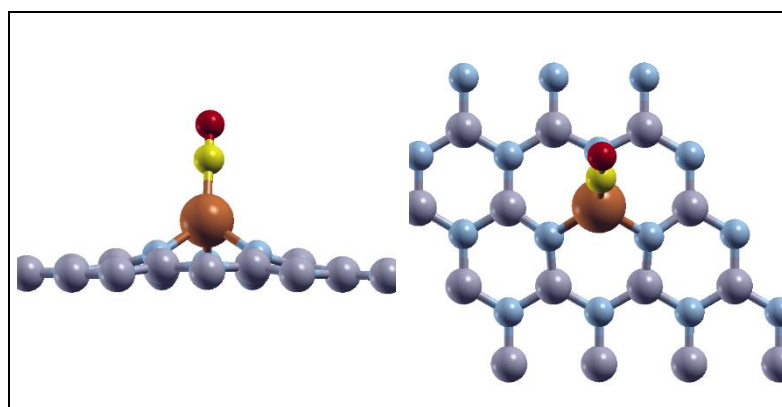


Figure 4.12: Visual representation of optimized geometry of GS9 on Cu/B layout.

4.2.11. TS12: $\text{CH}_3\text{OH}^* \rightarrow \text{CH}_3\text{O}^* + \text{H}^*_{\text{Cu}}$

As the transition states were determined only between the selected ground states due to significantly demanding computational efforts compared to ground states, there were no alternatives systematically tried. So, the only TSs determined via CI-NEB methods were listed here.

First transition state was between GS1 and GS2, so it was called TS12. This naming pattern was used for the rest of the transition states as well. The geometry obtained for first hydrogen abstraction through CI-NEB method resembles GS2, that also consisted of a single hydrogen and the methoxy adsorbed on copper simultaneously. **Figure 4.13** illustrates the geometry, activation and reaction energies.

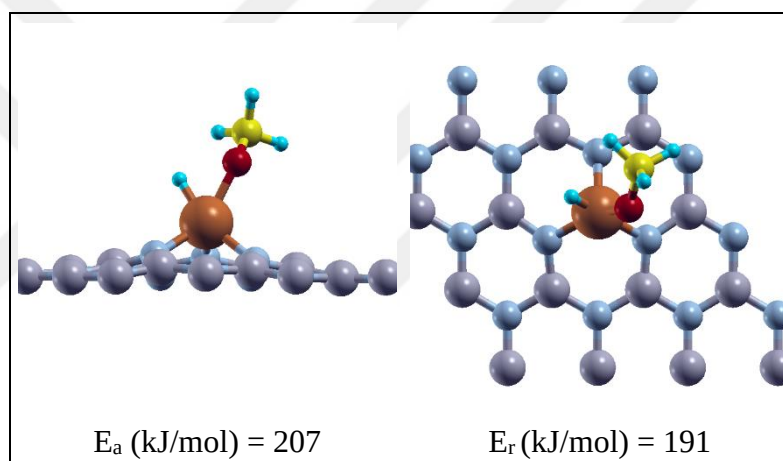


Figure 4.13: Optimized TS12 geometry obtained using CI-NEB method on the Cu/B layout.

4.2.12. TS34: $\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_2\text{O}^* + \text{H}^* + \text{H}^*_{\text{Cu}}$

Second transition state was observed during second hydrogen abstraction. The hydrogen atom leaving the methoxy was transferred onto the copper atom, resulting in one hydrogen atom that was previously adsorbed on surface along with another hydrogen and the formaldehyde structure bound to the copper atom simultaneously, on opposite sides. The transition state shows the rotation of formaldehyde to bond to the surface horizontally. **Figure 4.14** shows the TS geometry and related energies.

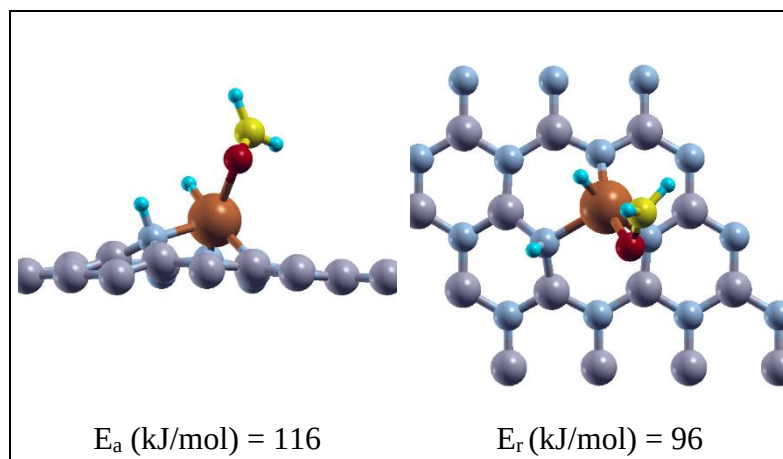


Figure 4.14: Optimized TS34 geometry obtained using CI-NEB method on the Cu/B layout.

4.2.13. TS45: $\text{CH}_2\text{O}^* + \text{H}^* + \text{H}^*_{\text{Cu}} \rightarrow \text{CH}_2\text{O}^* + 2\text{H}^*$

By comparing energies and geometries between GS4 and GS5, the requirement for an additional TS was noticed despite this step covering only the movement of second hydrogen from copper onto the surface. Two key findings for TS45 are as follows: the hydrogen atom that was initially adsorbed on copper migrates onto the surface and is repulsed below the surface level; and the formaldehyde molecule rotates around the copper, coming closer to the sinking hydrogen and the broken Cu-N bond. **Figure 4.15** shows the geometry of TS45. While the activation energy is considerably low, significant reaction energy suggests a dominant irreversible reaction mechanism for this step.

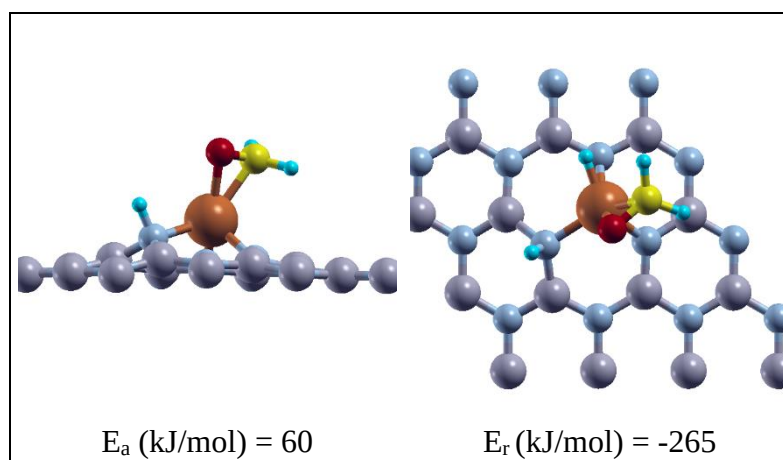


Figure 4.15: Optimized TS45 geometry obtained using CI-NEB method on the Cu/B layout.

4.2.14. TS67: $\text{CH}_2\text{O}^* \rightarrow \text{CHO}^* + \text{H}^*$

Third hydrogen abstraction took place directly from formaldehyde to the surface, bypassing the copper because the formaldehyde molecule was aligned horizontally, making the distance between the surface and hydrogen atom significantly short, and allowing it to migrate without requiring an intermediate ground or transition state. This intermediate image was captured during the transition state, showing a very similar behavior to previous transitions: the hydrogen from formaldehyde passes by the copper and appears to be momentarily adsorbed while moving towards the surface. **Figure 4.16** presents this geometry and the related energies.

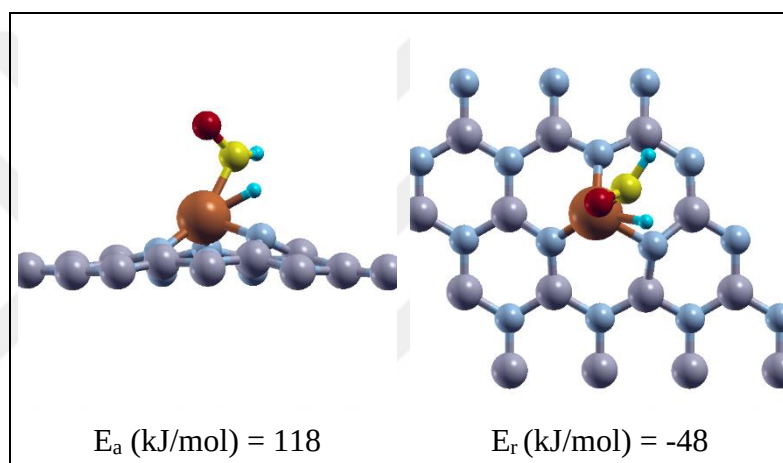


Figure 4.16: Optimized TS67 geometry obtained using CI-NEB method on the Cu/B layout.

4.2.15. TS78: $\text{CHO}^* + \text{H}^* \rightarrow \text{CO}^* + 2\text{H}^*$

Final hydrogen transfer, from formyl towards the surface, did also not need an additional ground state where the hydrogen momentarily adsorbs onto copper. Instead, it migrates directly onto the surface, to another nitrogen atom adjacent to the copper atom. The transition state captured between the initial and final states show that the hydrogen had already moved to the surface but the orientation of CO is far from its final form as seen in GS8, where it is pointing straight away from the two hydrogens on the surface, on the opposite side of the copper. **Figure 4.17** displays this transition state.

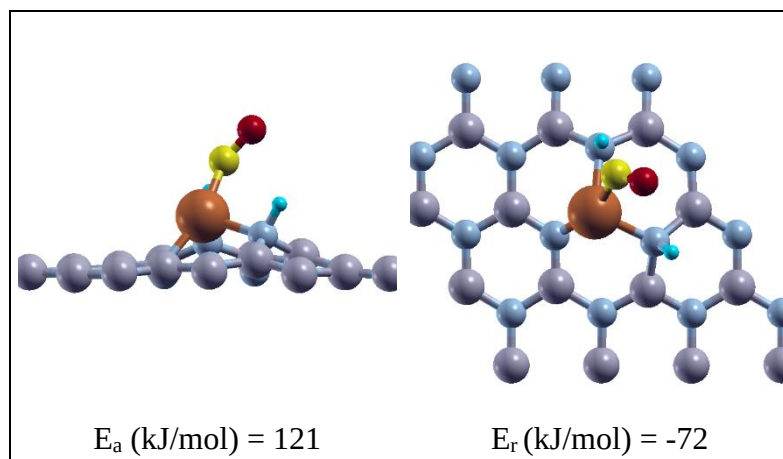


Figure 4.17: Optimized TS78 geometry obtained using CI-NEB method on the Cu/B layout.

4.3. Reaction Intermediates on Cu/N Surface

This section shows the geometries and relative energies of both selected and neglected surfaces of GS's and the corresponding TSs detected between selected GSs.

4.3.1. GS0 (GS10): Clean Cu/N Surface

The clean surface for Cu/N layout was created by replacing the central nitrogen atom. Compared to its Cu/B counterpart, **Figure 4.18** reveals that the surface showed rather less bending and retained a more planar structure.

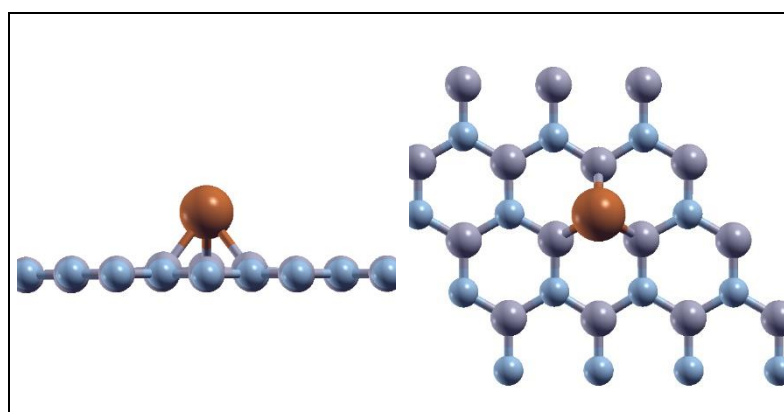


Figure 4.18: Visual representation of optimized geometry of GS0 (GS10) on Cu/N layout.

4.3.2. GS1: CH₃OH*

Three alternative ground states for methanol adsorption with almost identical energies were investigated. **Figure 4.19** depicts that methanol was adsorbed by the oxygen and adopted a diagonal orientation, while the positions of hydrogen atoms and the carbon atom varied slightly, as shown in. The layout that offered the smoothest transition to next ground state was selected as the main geometry.

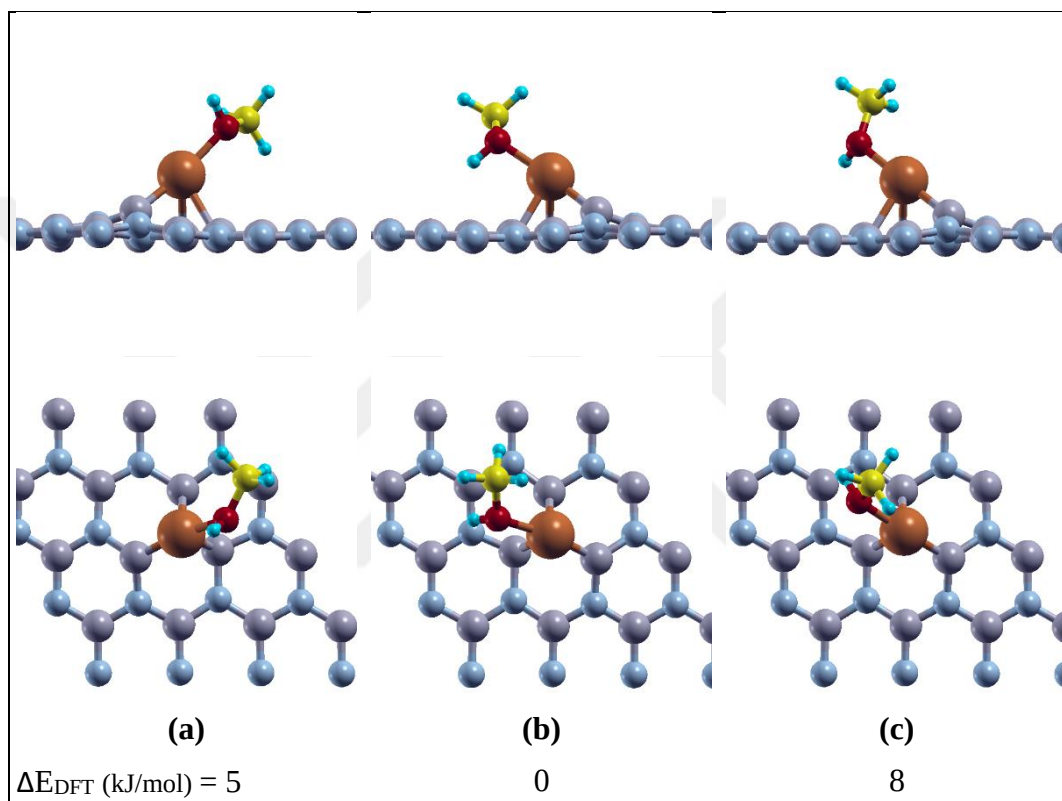


Figure 4.19: Visual representation of optimized geometries of GS1 on Cu/N layout. (a) The selected geometry, (b, c) geometries with similar energies.

4.3.3. GS2: CH₃O* + H*_{Cu}

The first hydrogen abstraction step showed that in Cu/N layout, the copper and the adjacent boron atoms attract the loose hydrogen particle and this affinity results in the hydrogen particle to be captured between the copper and the boron atoms, while in GS2 of Cu/B layout, the hydrogen was clearly adsorbed only on the copper. Adsorption of hydrogen at one side of the copper pushed the methoxy group onto the

other side of the copper. **Figure 4.20** shows two alternative geometries with identical energies.

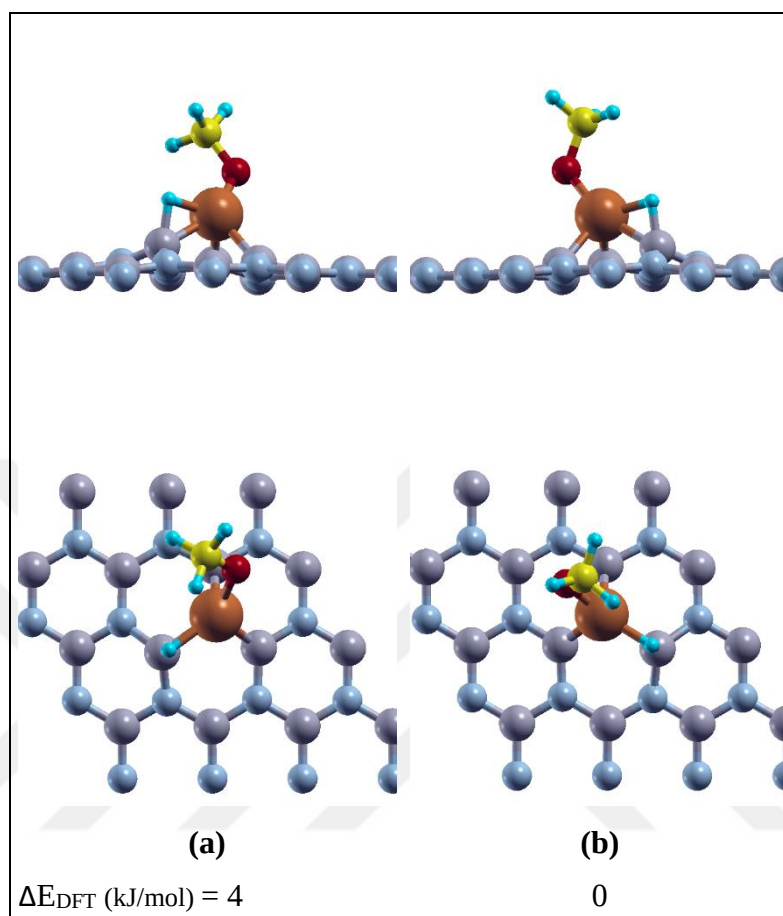


Figure 4.20: Visual representation of optimized geometries of GS2 on Cu/N layout. **(a)** The selected geometry, **(b)** neglected geometry with identical energy.

4.3.4. GS3: $\text{CH}_3\text{O}^* + \text{H}^*$

This step, in which methoxy group is bound to the copper and hydrogen atom to the surface, was introduced to ensure comparable atomic distribution between Cu/B and Cu/N layouts. In GS2, the hydrogen atom exhibited affinity towards both the boron and the copper atoms, resulting in a structure that could also reasonably be considered as GS3, which by the definition is the structure where methoxy is adsorbed on the copper and the hydrogen adsorbed on the surface. In order to achieve a structure where the hydrogen atom migrates unambiguously onto the surface, the boron and nitrogen atoms that were distant to the copper atom were selected as the adsorption sites. Two

candidate geometries were distinguished by the distance between the surface hydrogen and the CH₃ group as shown in **Figure 4.21**. The structure that showed a repulsive relation between those two groups (**Figure 4.21 (b)**) had a considerably larger energy. The layout with closer hydrogen and CH₃ group showed a smoother transition to next ground state as well as offering a lower total energy.

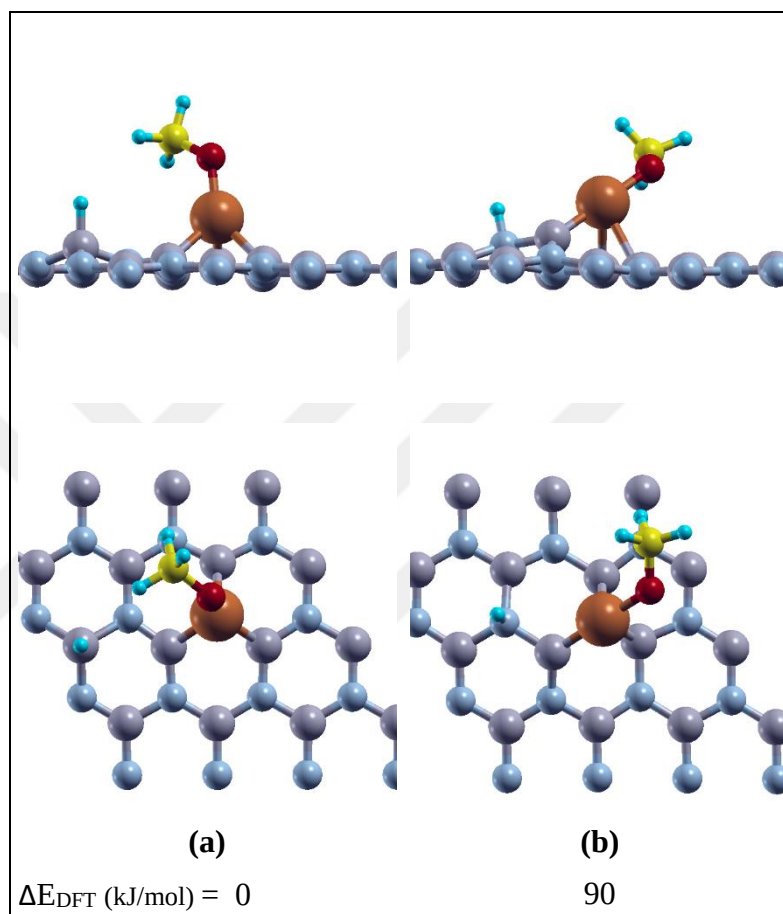


Figure 4.21: Visual representation of optimized geometries of GS3 on Cu/N layout. **(a)** The selected geometry, **(b)** neglected geometry with slightly more energy.

4.3.5. GS5: CH₂O* + 2H*

This ground state was made up of formaldehyde adsorbed on copper with two hydrogen atoms also adsorbed on surface. It was the last step before surface hydrogen recombination and was one of the most complex structures to decide on due to the number of adsorbed bodies. Because of this complexity, the ground state that allowed the smoothest transition in previous step, TS35, was the strongest candidate.

Comparing with other alternatives, there was a noticeable energy difference between the selected geometry and the other variants but selecting this geometry did not cause an undesirable difficulty. Besides, in the next ground state, two surface hydrogens were removed. Therefore, a transition state between the selected, relatively high-energy surface of GS5 and the GS6 was not sought. **Figure 4.22** illustrates the alternative geometries and their relative energies.

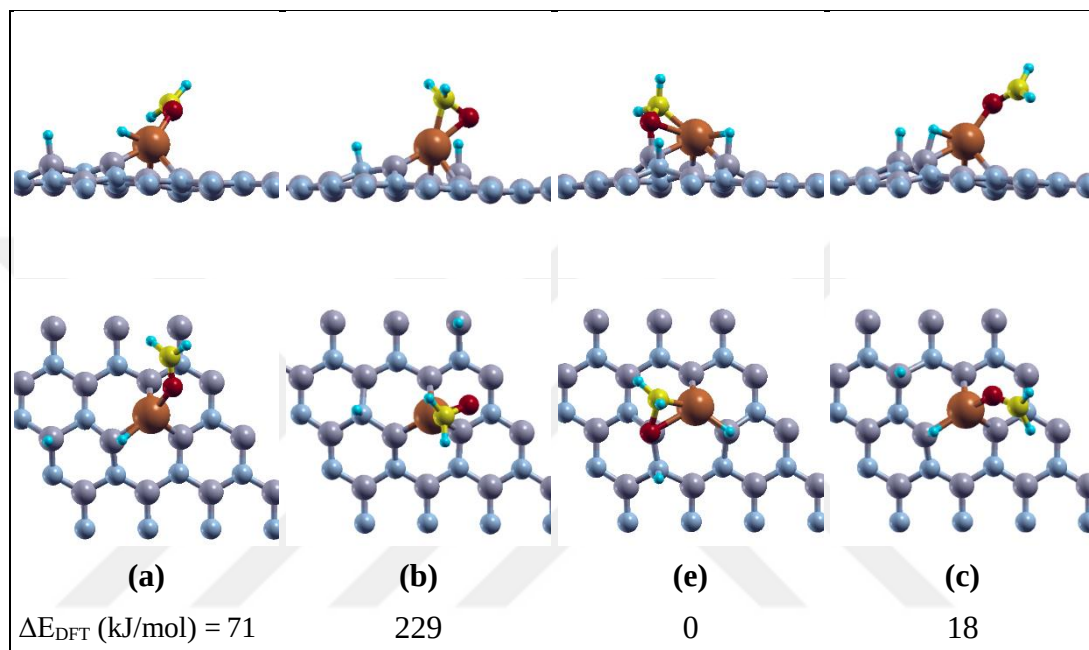


Figure 4.22: Visual representation of optimized geometries of GS5 on Cu/N layout. **(a)** The selected geometry, **(b)** neglected geometry with more energy, **(c, d)** neglected geometries with slightly lower energies but offering difficult transitions.

4.3.6. GS6: CH₂O*

After recombination of two hydrogen atoms, formaldehyde was the remainder from methanol, adsorbed on copper. As observed in Cu/B counterpart, the horizontal formaldehyde in contact with the copper from both the carbon and the oxygen sides as **Figure 4.23** shows had the most stable structure and was selected as GS6.

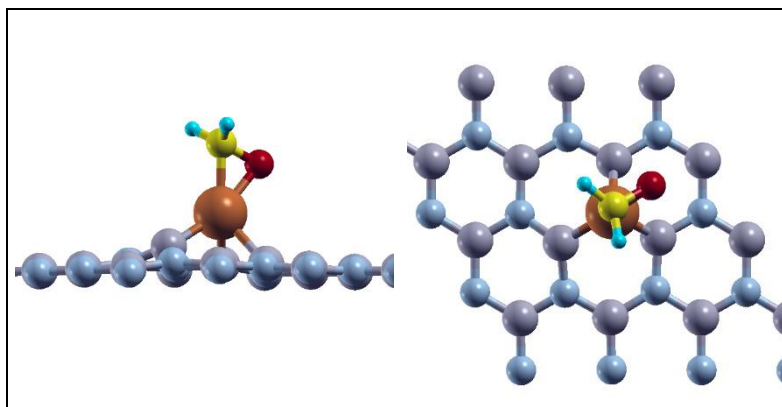


Figure 4.23: Visual representation of optimized geometry of GS6 on Cu/N layout.

4.3.7. GS7: $\text{CHO}^* + \text{H}^*$

Third hydrogen transfer resulted in the hydrogen being captured between the copper atom and the adjacent boron atom while the formyl structure was repulsed to the opposite side of the copper. The resulting placement of hydrogen and the shape of formyl group were consistent with those observed, most stable geometries in other states for both Cu/B and Cu/N. Therefore, no further structural alternatives were explored. **Figure 4.24** displays the selected geometry and its energy.

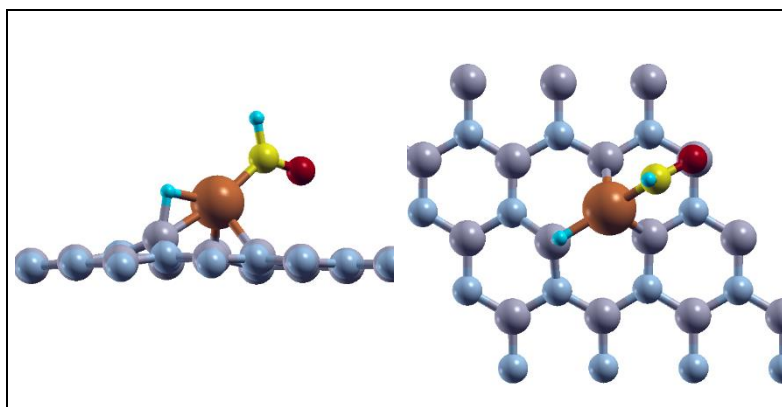


Figure 4.24: Visual representation of optimized geometry of GS7 on Cu/N layout.

4.3.8. GS8: $\text{CO}^* + 2\text{H}^*$ Configurations

After the final hydrogen migration, only CO remained adsorbed on copper while two boron atoms adjacent to the copper captured both hydrogen atoms. **Figure 4.25**

illustrates that the adsorbed hydrogens and the CO were positioned on opposite sides of the copper atom as shown in, consistent with the structure observed in Cu/B GS8.

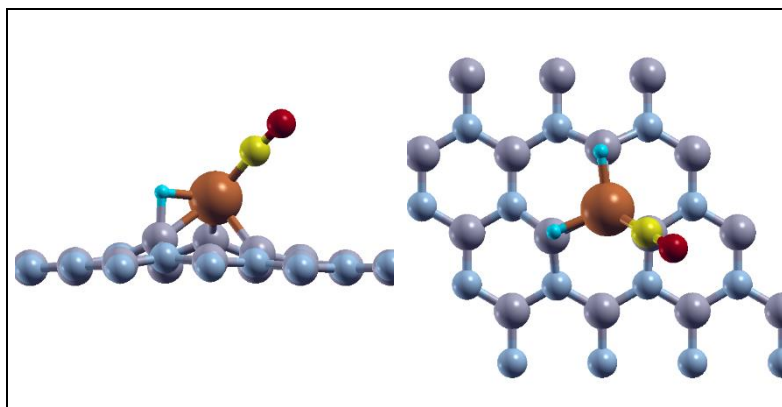


Figure 4.25: Visual representation of optimized geometry of GS8 on Cu/N layout.

4.3.9. GS9: CO*

The CO molecule adsorbed on copper through the carbon atom showed a vertical alignment after the two hydrogen atoms recombined and left the surface. **Figure 4.26** shows this geometry.

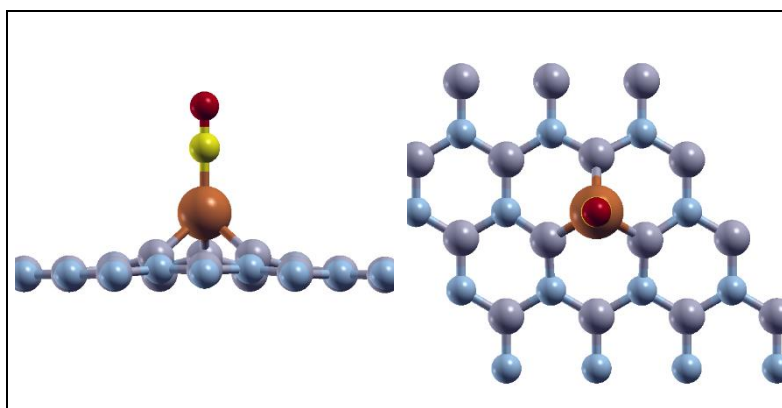


Figure 4.26: Visual representation of optimized geometry of GS9 on Cu/N layout.

4.3.10. TS12: $\text{CH}_3\text{OH}^* \rightarrow \text{CH}_3\text{O}^* + \text{H}^*_{\text{Cu}}$

First transition state was captured during the first hydrogen abstraction step. During transition phase, hydrogen atom leaving the oxygen atom appears to be momentarily

bound on top of the copper, as shown in **Figure 4.27**. This TS showed significantly lower activation and reaction energies compared to the TS12 of Cu/B.

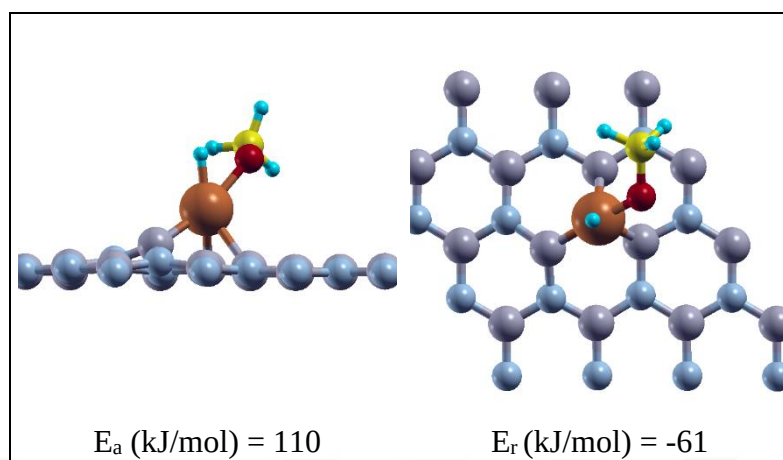


Figure 4.27: Optimized TS12 geometry obtained using CI-NEB method on the Cu/N layout.

4.3.11. TS35: $\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_2\text{O}^* + 2\text{H}^*$

The second transition phase for Cu/N surface was observed during the hydrogen abstraction from methoxy structure. The hydrogen was adsorbed on one side of copper that is close to the other hydrogen already adsorbed on surface in previous step, while the remainder formaldehyde molecule was observed to momentarily float around the copper before binding on the oxygen atom and orienting itself horizontally at the opposite site to the adsorbed hydrogen. Since there was almost no distinction between the two states where the second hydrogen was adsorbed on copper or the surface, the second hydrogen abstraction step was carried out in a single transition state, TS35, in Cu/N layout. In contrast, it was observed to take place in two transition states, TS34 and TS45 in Cu/B layout because there were two distinguishable geometries for the two aforementioned ground states. **Figure 4.28** depicts the details of TS35.

This step offered the most various combination of initial, transition and final states with completely different energies and structures. While one alternative that was structurally and energetically acceptable was selected, studying this surface further could yield further results.

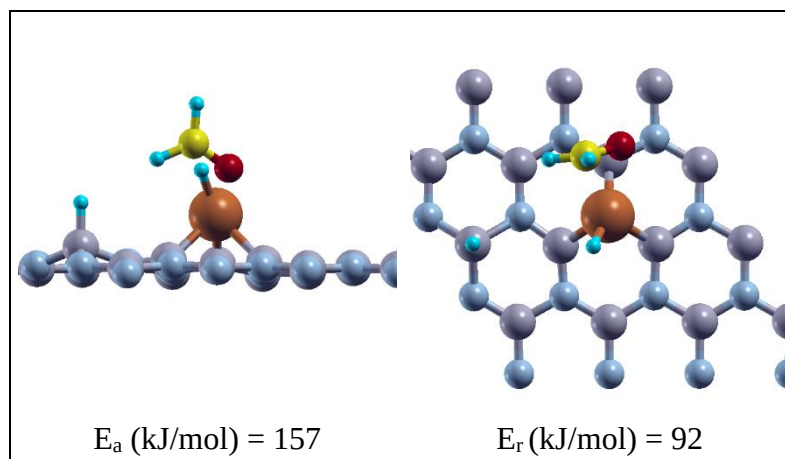


Figure 4.28: Optimized TS35 geometry obtained using CI-NEB method on the Cu/N layout.

4.3.12. TS67: $\text{CH}_2\text{O}^* \rightarrow \text{CHO}^* + \text{H}^*$

Transition state corresponding to the conversion of formaldehyde into formyl and hydrogen was designated as TS67. **Figure 4.29** indicates that the overall structure retained its horizontal orientation but shifted away from top of the copper site, leaving one hydrogen atom adsorbed on the copper.

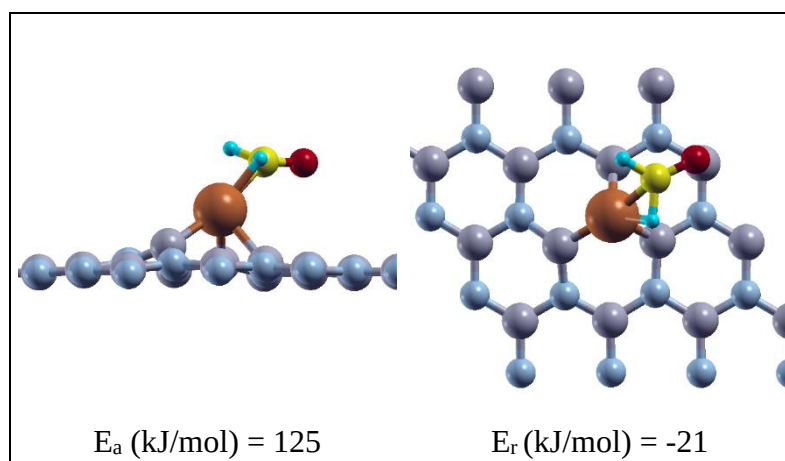


Figure 4.29: Optimized TS67 geometry obtained using CI-NEB method on the Cu/N layout.

4.3.13. TS78: $\text{CHO}^* + \text{H}^* \rightarrow \text{CO}^* + 2\text{H}^*$

The final transition state depicted the movement of hydrogen leaving the formyl group to bind the surface at the spot between boron and copper atoms. While the hydrogen

was moving towards that site, the carbon and oxygen atoms were repulsed to the opposite side. **Figure 4.30** shows the geometries and related energies of the TS78.

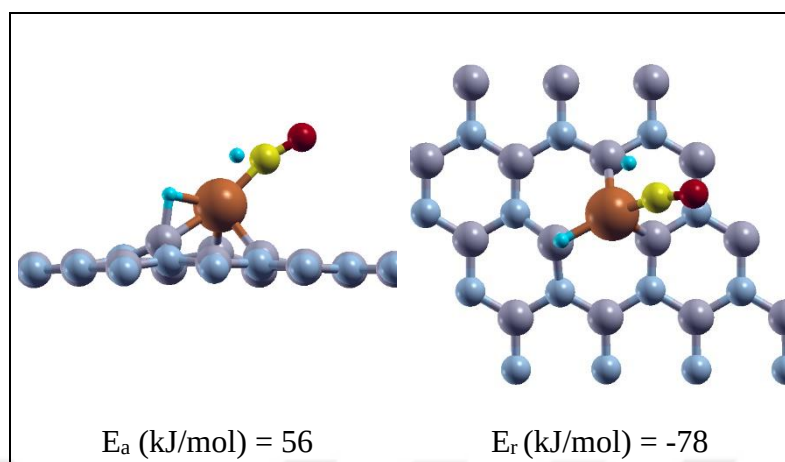


Figure 4.30: Optimized TS78 geometry obtained using CI-NEB method on the Cu/N layout.

4.4. Methanol Decomposition Pathway

The reaction pathway for methanol decomposition, starting with methanol adsorption and ending with CO desorption, adopted from previous study [20] was replicated in this study, in accordance with given intermediate steps. In some cases, hydrogen abstracted from methanol was observed to adsorb first on the copper and then move to BN surface, so, hydrogen abstraction reactions were analyzed in two steps, where applicable, against the single step results presented in literature. **Table 4.5** lists the complete reaction pathway in this study, with the names and descriptions of each intermediate state and reaction.

Computed relative energies were used for forming an energy profile of the reaction, visual representation of individual geometries were also generated to analyze the mechanism and behavior of substances further. **Figure 4.31** and **Figure 4.32** illustrate the top and side views of individual ground and transition states of both Cu/B and Cu/N followed during complete methanol decomposition reaction.

The energies obtained from the relaxation of geometries and subsequent SCF calculations were treated as raw DFT results and were compared against available literature in their respective subsections. **Figure 4.33** shows the forward and **Figure 4.34** shows the backward (methanol synthesis) energy profiles drawn from raw results.

By applying ZPE correction, vibrational enthalpy and entropy corrections, final results were obtained in terms of Gibbs free energy. Energy profiles of complete reaction along the proposed pathway based on corrected Gibbs free energies were displayed in Figure 4.35 (and reverse reaction in **Figure 4.36**) to analyze the activation barriers, reaction energies and to compare Cu/B and Cu/N variants.

Based on raw DFT results, there was a 181 kJ/mol difference between initial and final states of the reaction, pointing to an endothermic decomposition reaction. Cu/B showed greater fluctuations and a more irregular energy profile, along with higher energy levels overall. The apparent barrier was observed between GS5 and TS67 for Cu/B layout, with a gap reaching 405 kJ/mol. The highest activation energy of an individual transition state (i.e. rate determining step) was calculated as 207 kJ/mol for Cu/B layout during TS12, which is significantly high.

Cu/N, on the other hand, exhibited a smoother and consistent energy profile with results comparable to the literature. The apparent barrier for Cu/N was observed between GS2 and TS35 as 289 kJ/mol, which was arguably lower than Cu/B's apparent barrier. Lastly, Cu/N showed a lower methanol capture energy, -99 kJ/mol which was also lower than the literature, pointing to an easier methanol adsorption step.

Starting from GS0 (0 kJ/mol), we observe that the highest energy requirement for the Cu/B surface occurs at TS67, with a barrier of 198 kJ/mol, while for the Cu/N surface, the highest point is GS10, at 181 kJ/mol. According to the definitions in [75], [76] and **Table 4.3** that shows the classification of reaction speeds; these barriers correspond to moderate-to-slow reaction rates, with estimated rate constants on the order of $k \approx 10^{-18}$ and $k \approx 10^{-16}$. To shift these reactions into the fast regime, temperatures exceeding 1200 K would be required.

Table 4.3: Classification of reaction speeds as a function of activation energy and temperature [75], [76].

Ea/RT	Reaction Speed
>30	Negligible
25–30	Slow
20–25	Moderate
15–20	Fast
<15	Very fast

The thermodynamic corrections affected each state differently, by contributing some states' energies positively while decreasing others'. After applying corrections based on ZPC, vibrational enthalpy and entropy calculated at 338.15K, the difference between total energies of initial and final states that was calculated as 181 kJ/mol previously in this section for uncorrected energies, was determined as 113 kJ/mol. Based on tabulated data listed in Perry's Handbook [71], the Gibbs free energy of methanol decomposition into CO and 2H₂ was calculated as 25 kJ/mol at 298.15K and 16 kJ/mol at 338.15K while the enthalpy of reaction was found as 90 kJ/mol for the same temperatures.

Increasing the temperature by several hundreds of degrees Celsius was observed to affect the energies of intermediate steps only by a few kJ/mol while it offers a kinetic advantage. In addition, considering how BN surfaces have very low electron conductivity in contrast to graphene surface's significant conductivity, employment of Cu-BN surfaces as a catalyst in a reformer setup becomes more viable. Thus, the catalytic activity of Cu-BN at elevated temperatures can be effectively utilized in reformers, where electron conductivity is not a limiting factor for performance.

Cu/N's superiority over Cu/B in terms of milder fluctuations, lower barriers, methanol adsorption energy and smaller apparent barrier persisted in corrected results. The peak relative energy for Cu/B was observed during TS67 as 156 kJ/mol whereas for Cu/N layout, it was found as 114 kJ/mol during TS35. The apparent barriers for both layouts remained between the same states as the uncorrected results. The energy gap changed from 405 kJ/mol to 355 kJ/mol for Cu/B. Likewise, it fell from 289 kJ/mol to 277 kJ/mol for Cu/N. Methanol adsorption energies were observed as -50 kJ/mol for Cu/B and -92 kJ/mol for Cu/N. The individual transition state activation energies were observed during the same states as the uncorrected results, but the new gaps were determined as 194 kJ/mol and 141 kJ/mol for Cu/B and Cu/N, respectively, which are slightly lower than the barriers observed in uncorrected results.

While only the complete decomposition reaction was investigated thoroughly, a side reaction where methanol decomposes into gaseous formaldehyde and a hydrogen molecule was also computed and shown in the energy profiles in **Figure 4.33** and Figure 4.35 as a green line. The formaldehyde route had a smaller energy gap between the final and initial states, 126 and 89 kJ/mol in contrast to 181 and 113 kJ/mol of carbon monoxide route for raw and corrected relative energies, respectively. The

smaller energy gap for formaldehyde suggests that, under conditions where the energy input is insufficient for the CO route, the reaction may preferentially proceed via the formaldehyde side pathway. **Figure 4.33** and Figure 4.35 further support that the Cu/N surface offers a more favorable pathway for methanol decomposition. However, the relatively lower energy of the (CH₂O(g) + H₂(g)) product state—compared to the full decomposition route yielding CO(g) + 2H₂(g)—suggests that the dominant products may be formaldehyde and hydrogen, rather than complete decomposition.

At this point, rather than ruling out the investigated systems for methanol decomposition, alternatives should be considered (though not directly explored in this study). First one is the methanol formation instead of decomposition. Reversing the energy profile (see **Figure 4.34** for uncorrected and **Figure 4.36** for corrected energies, redrawn left-to-right for CO + 2H₂ → CH₃OH) reveals that the system may function effectively as a catalyst for methanol synthesis, a possibility to be evaluated in future work. Second is the oxidative methanol reforming in the presence of water. If complete methanol oxidation is considered (e.g. CH₃OH + H₂O → CO₂ + 3H₂), the additional exothermicity from water splitting could lower the overall energy landscape. In this context, with the added exothermicity of the water reactions high-energy states such as TS67 (198 kJ/mol) would reduce to moderate values, rendering the overall reaction more feasible.

Also, adsorption energies of reaction intermediates were calculated by discarding the gas phase molecules or hydrogens adsorbed on the surface. The adsorption energy was evaluated following the same procedure as before, by subtracting the energy of gas phase intermediate and clean surface from the energy of surface-intermediate complex. **Table 4.4** shows the adsorption energies for both surfaces.

Cu/N offers a promising energy profile coupled with other key aspects while results of Cu/B suggested slow kinetics and high barriers to be overcome, which prevents it from being a strong candidate catalyst for DMFC.

Table 4.4: Adsorption energies of reaction intermediates, given in kJ/mol.

Intermediate Layout	CH ₃ OH	CH ₃ O	CH ₂ O	CHO	CO
Cu/B	-54	-227	-46	-196	-71
Cu/N	-99	-331	-138	-233	-87

Table 4.5: Methanol decomposition pathway with individually labelled intermediate states.

Initial State		Final State	Description
Surf. + CH ₃ OH(g) GS0 (ref)	→	CH ₃ OH* GS1	Methanol adsorption
CH ₃ OH* GS1	→ TS12	CH ₃ O* + H _{Cu} * GS2	O-H bond cleavage of methanol with hydrogen transfer to Cu
CH ₃ O* + H _{Cu} * GS2	→	CH ₃ O* + H* GS3	Transfer of hydrogen from Cu to BN surface
CH ₃ O* + H* GS3	→ TS34	CH ₂ O* + H* + H _{Cu} * GS4	First C-H bond cleavage with H transfer to Cu
CH ₂ O* + H* + H _{Cu} * GS4	→ TS45	CH ₂ O* + 2H* GS5	Transfer of second hydrogen from Cu to BN surface
CH ₂ O* + 2H* GS5	→	CH ₂ O* + H ₂ (g) GS6	Recombination and desorption of two surface H atoms as H _{2(g)}
CH ₂ O* + H ₂ (g) GS6	→ TS67	CHO* + H* + H ₂ (g) GS7	Second C-H bond cleavage with H transfer to surface
CHO* + H* + H ₂ (g) GS7	→ TS78	CO* + 2H* + H ₂ (g) GS8	Third C-H bond cleavage with H transfer to surface
CO* + 2H* + H ₂ (g) GS8	→	CO* + 2H ₂ (g) GS9	Recombination and desorption of two surface H atoms as H _{2(g)}
CO* + 2H ₂ (g) GS9	→	Surf. + CO(g) + 2H ₂ (g) GS10	Desorption of CO from copper side of the surface

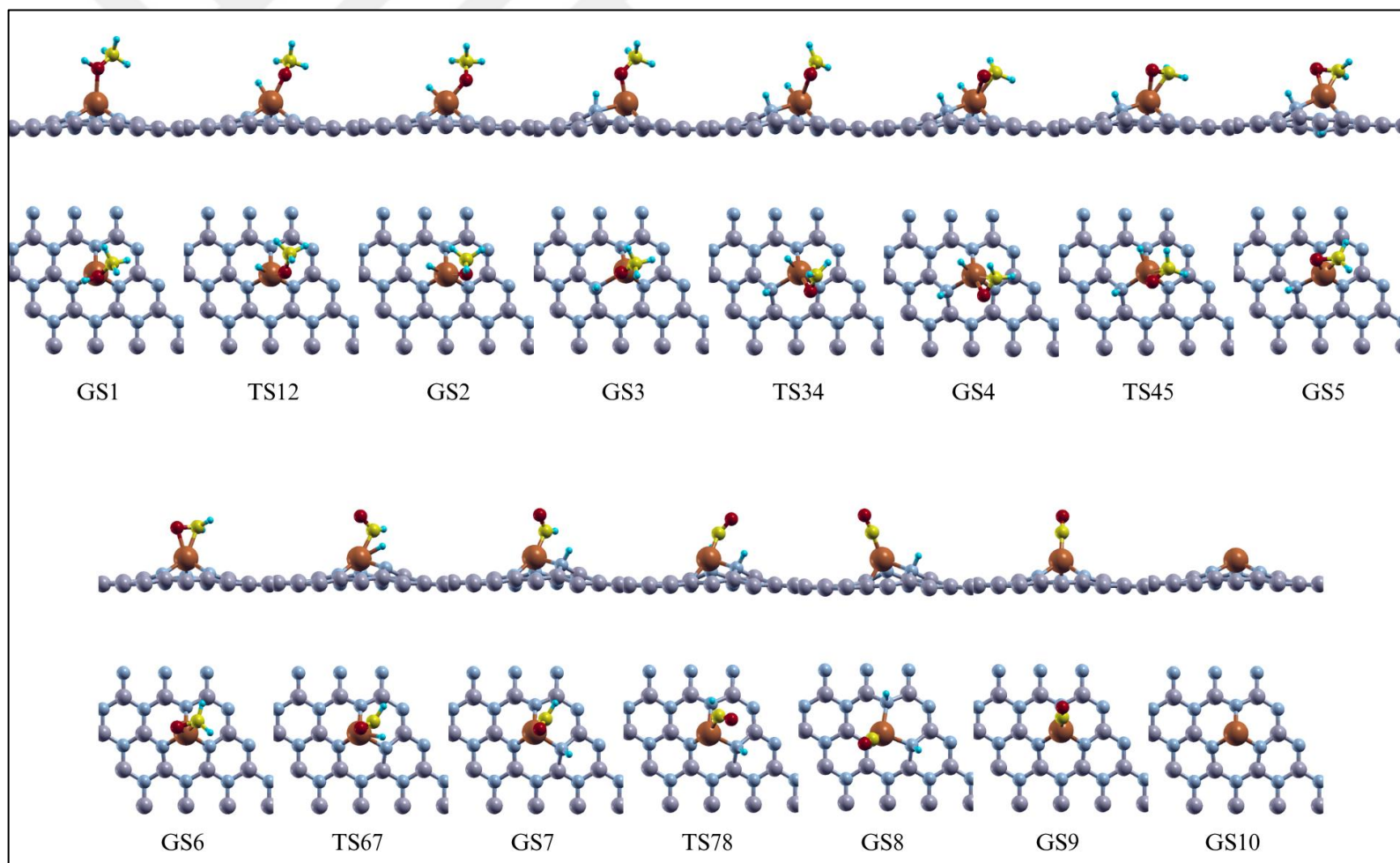


Figure 4.31: Optimized geometries along the complete methanol decomposition pathway on the Cu/B surface configuration, including all intermediate ground states (GS) and transition states (TS).

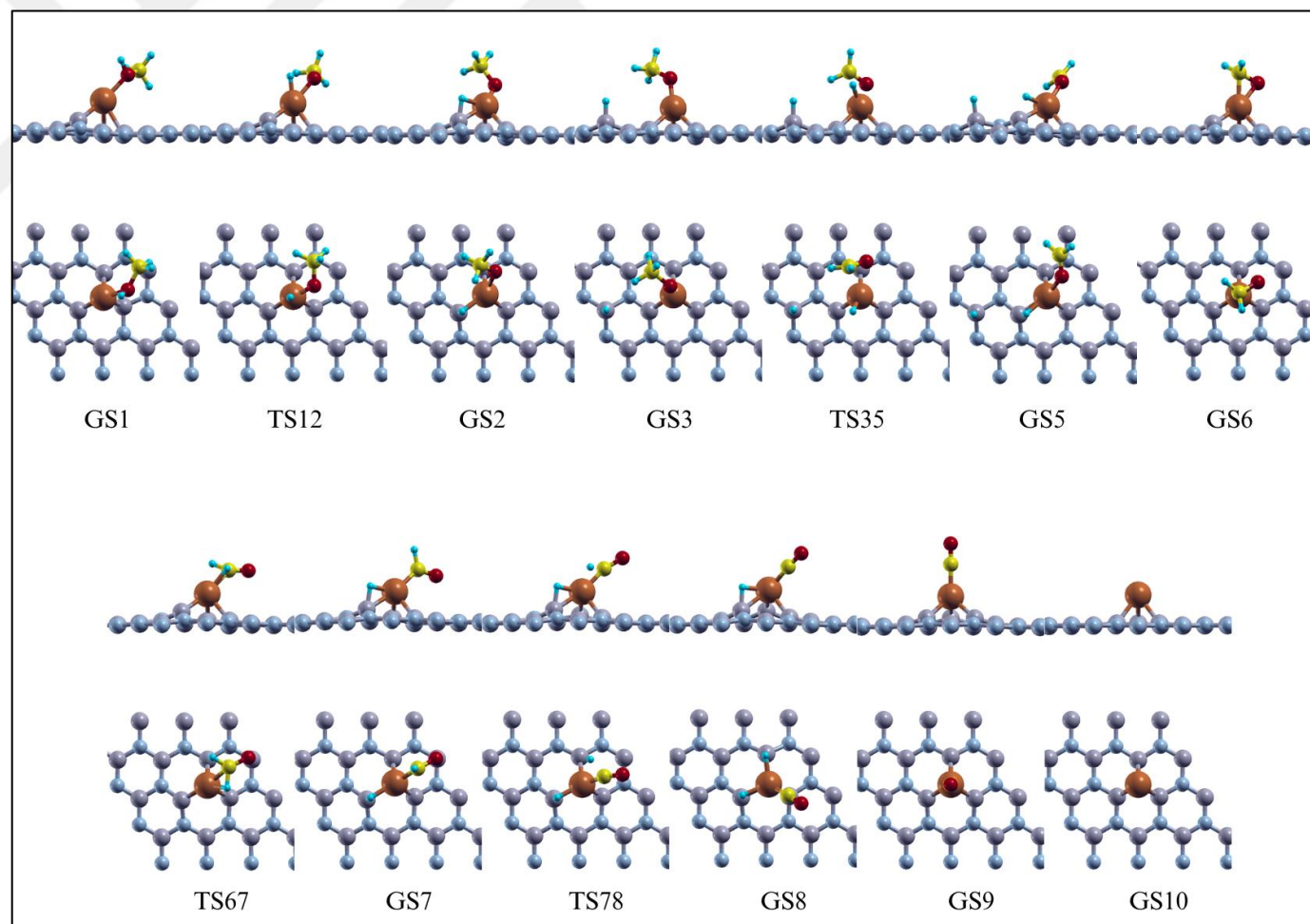


Figure 4.32: Optimized geometries along the complete methanol decomposition pathway on the Cu/N surface configuration, including all intermediate ground states (GS) and transition states (TS).

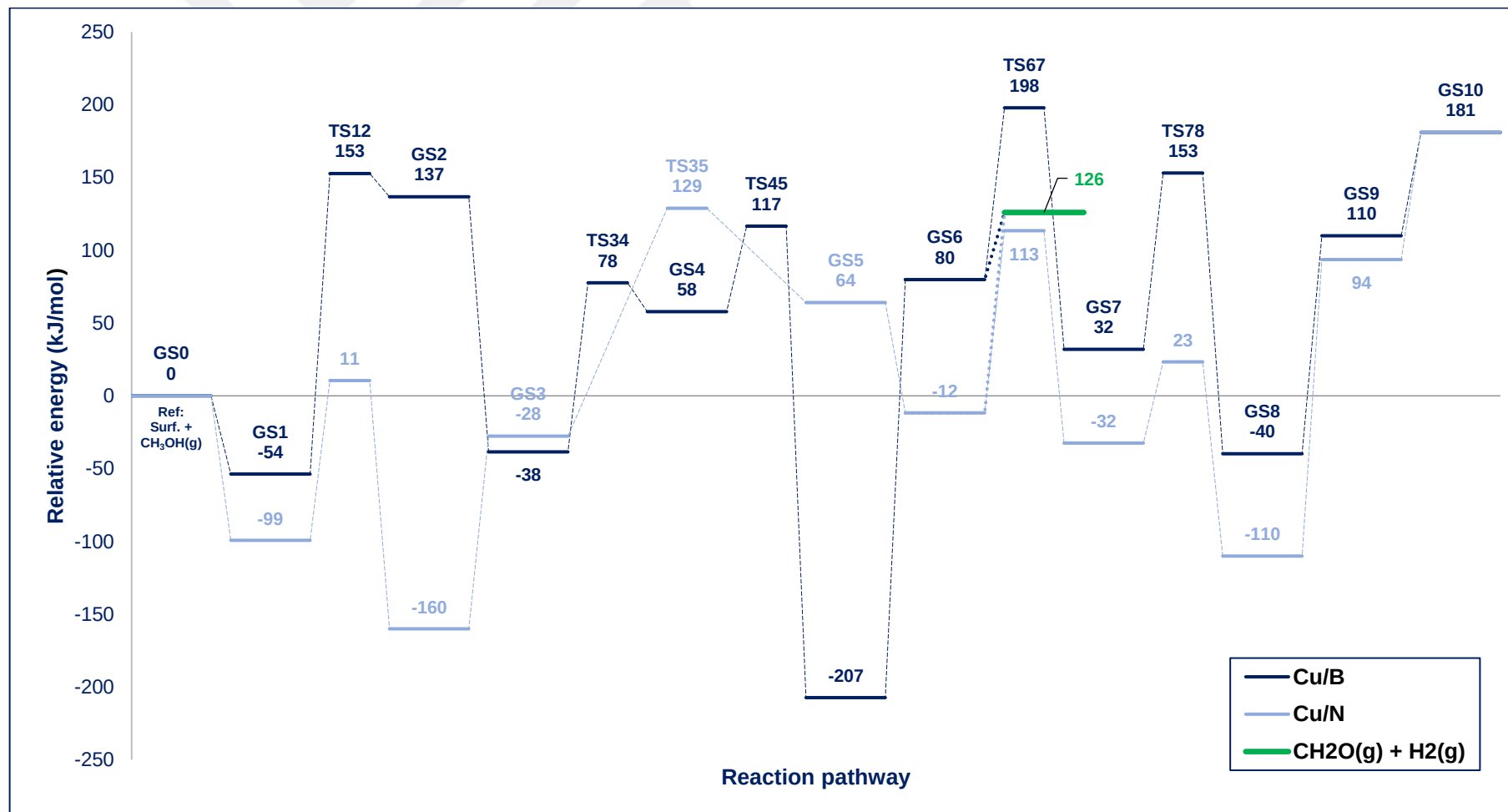


Figure 4.33: Energy profiles of complete methanol decomposition on Cu/B and Cu/N surfaces from raw DFT results, illustrating the relative energies of GSs and TSs for each elementary step along the proposed reaction pathway.

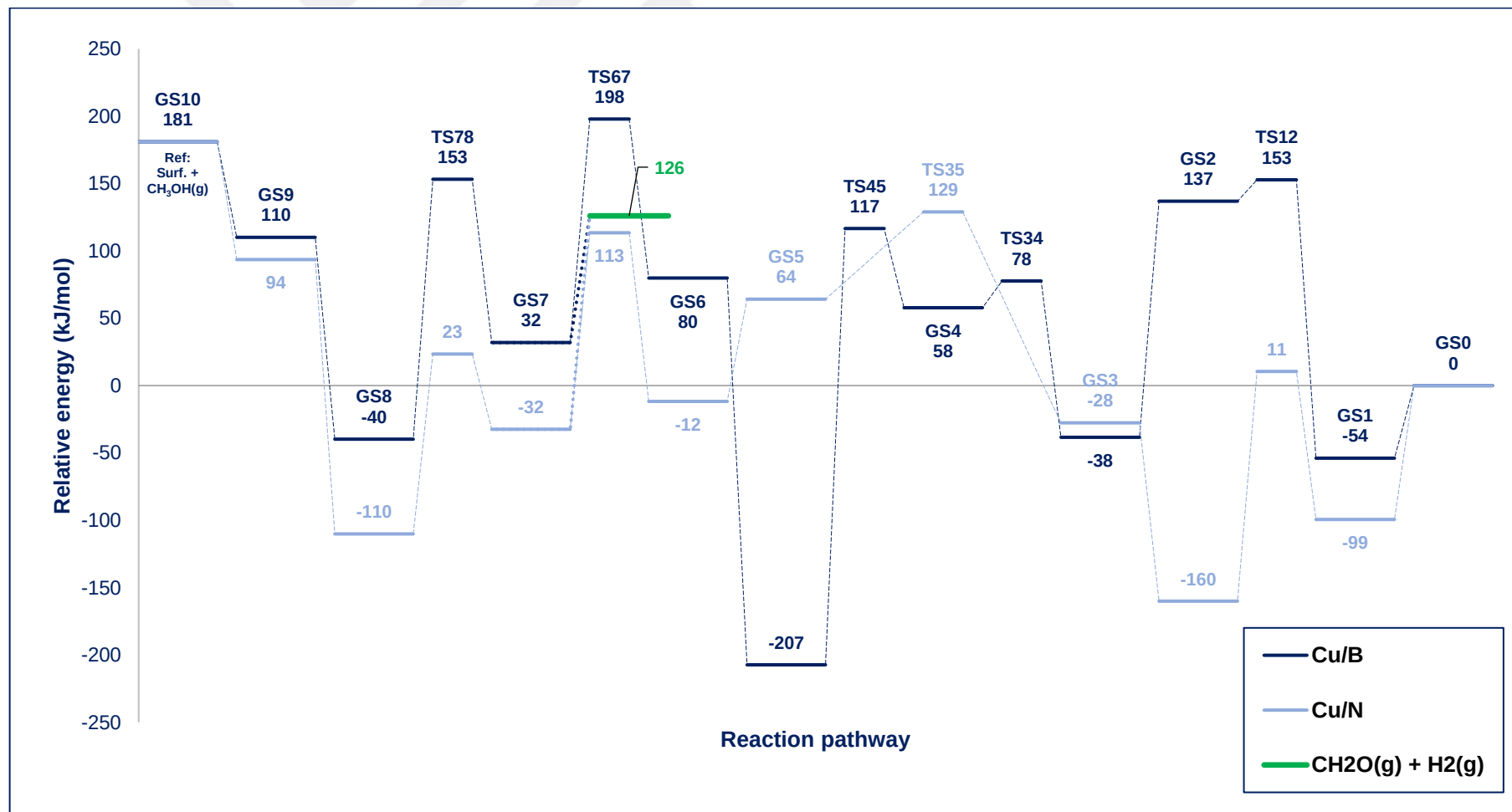


Figure 4.34: Energy profiles of reverse reaction (i.e. methanol synthesis) on Cu/B and Cu/N surfaces from raw DFT results, illustrating the relative energies of GSs and TSs for each elementary step along the proposed reaction pathway.

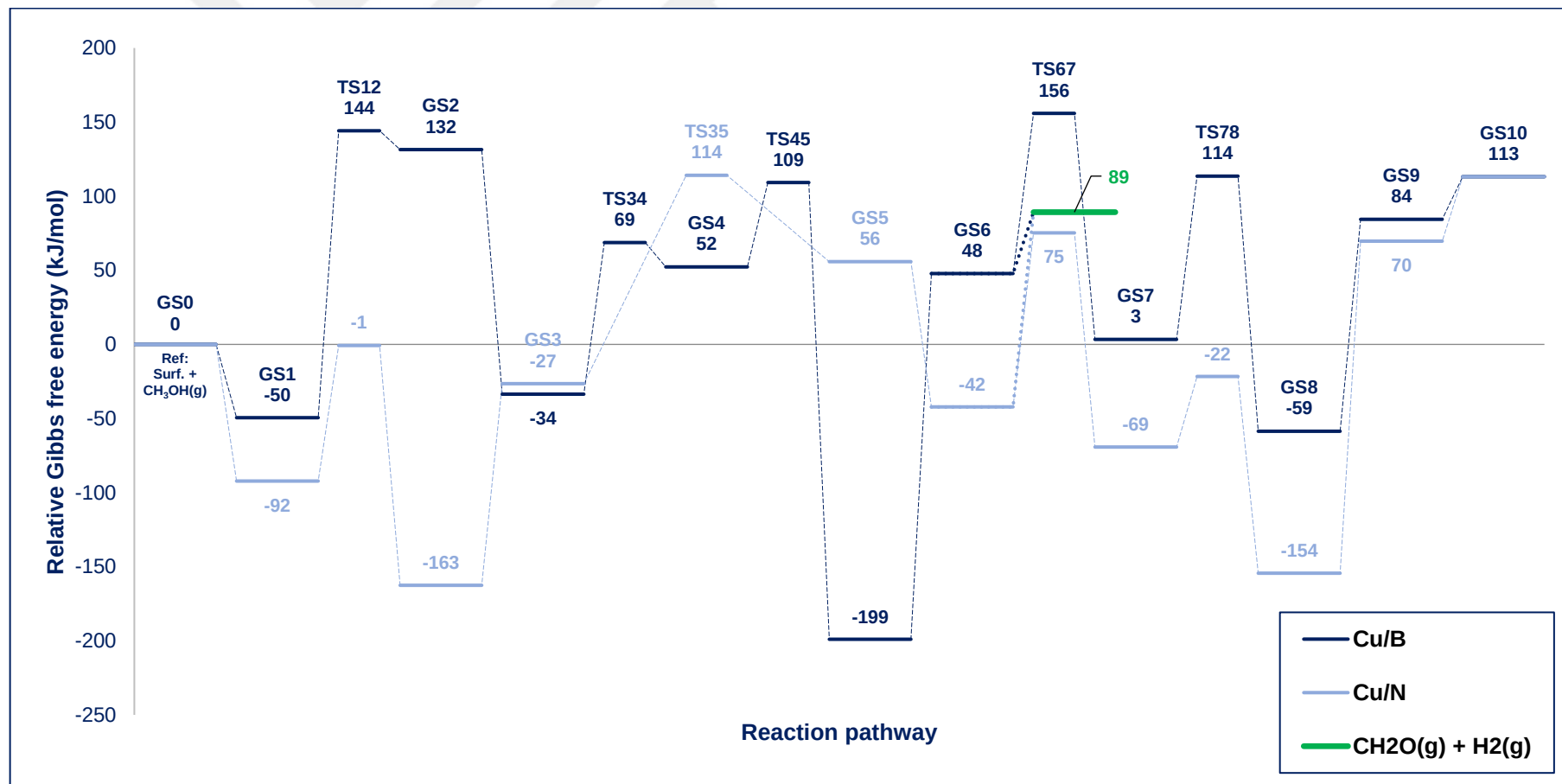


Figure 4.35: Thermodynamically corrected relative energy profiles of complete methanol decomposition on Cu/B and Cu/N surfaces, illustrating the relative Gibbs free energies of GSs and TSs for each elementary step along the proposed reaction pathway. T = 338.15K.

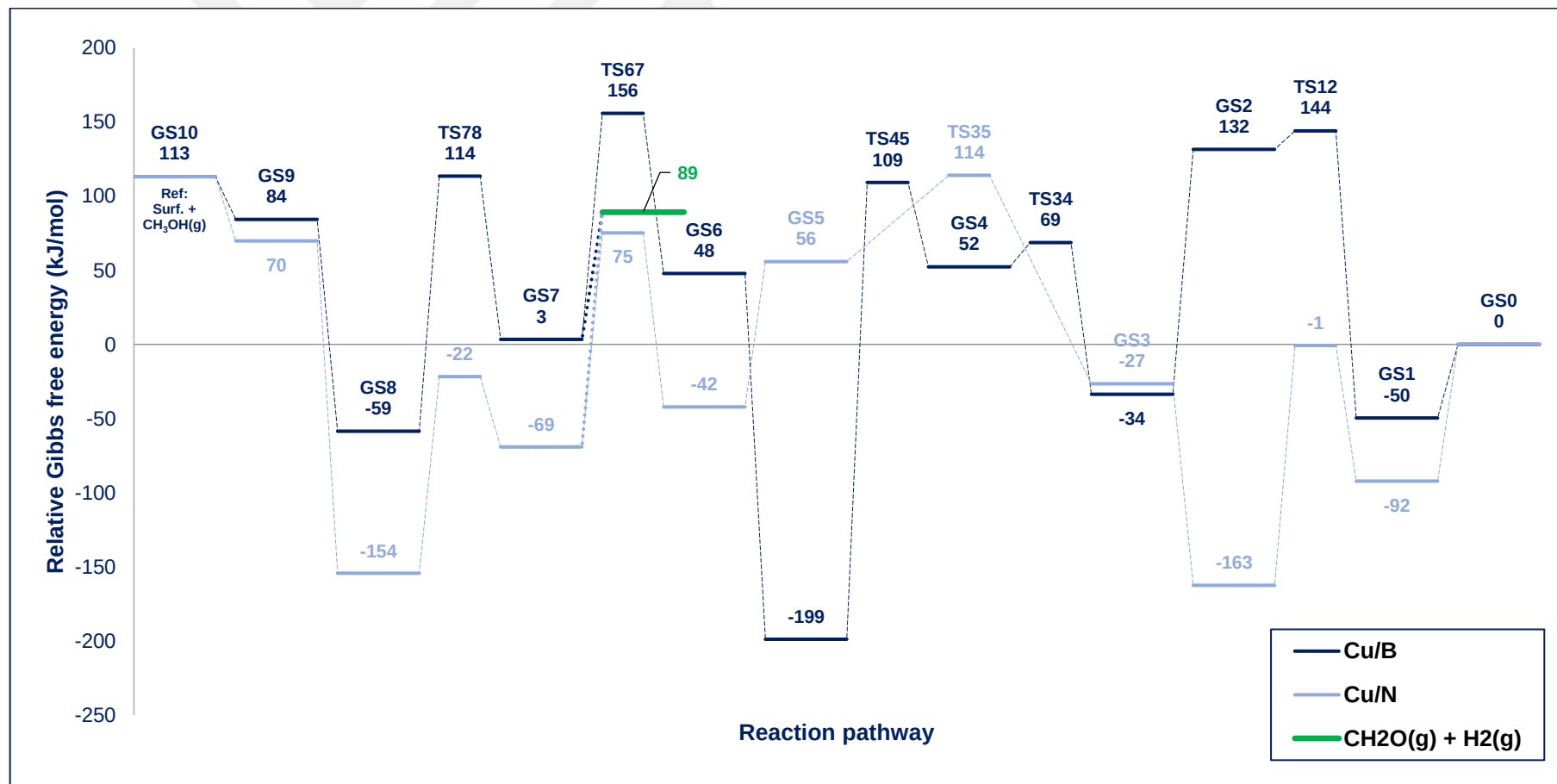


Figure 4.36: Thermodynamically corrected relative energy profile of reverse reaction (i.e. methanol synthesis) on Cu/B and Cu/N surfaces, illustrating the relative Gibbs free energies of GSs and TSs for each elementary step along the proposed reaction pathway. $T = 338.15\text{K}$.

4.5. Reaction Rate Estimation

The reaction rates of TSs were compared by approximating the rate constant k via the Eyring equation that is based on the Gibbs free energy of activation of that specific transition step. Gibbs free energy of activation, denoted as $\Delta G^\ddagger$, was found by subtracting the corrected energies of initial GS from the energy of TS, including the contributions of raw DFT energy, ZPC, ΔH_{vib} and ΔS_{vib} . For thermodynamic corrections, the operating temperature was selected as 65°C (338.15K) to achieve comparable results to normal operating conditions of DMFCs. **Table 4.6** lists the details of estimated reaction rate constants with respect to different layouts and transition states.

Table 4.6: Estimated reaction rate constants and related Gibbs free energies of activation for different layouts, evaluated at 338.15K.

Layout	Transition State		$\Delta G^\ddagger$ (kJ/mol)	k (1/s)
Cu/B	CH ₃ OH* GS1	→ TS12	194	8.5*10 ⁻¹⁸
	CH ₃ O* + H* GS3	→ TS34	102	1.1*10 ⁻³
	CH ₂ O* + H* + H _{Cu} * GS4	→ TS45	57	1.2*10 ⁴
	CH ₂ O* GS6	→ TS67	108	1.4*10 ⁻⁴
	CHO* + H* GS7	→ TS78	110	6.6*10 ⁻⁵
Cu/N	CH ₃ OH* GS1	→ TS12	92	4.9*10 ⁻²
	CH ₃ O* + H* GS3	→ TS35	141	1.3*10 ⁻⁹
	CH ₂ O* GS6	→ TS67	118	5.0*10 ⁻⁶
	CHO* + H* GS7	→ TS78	47	3.3*10 ⁵

Rate constants varied greatly depending on the activation energies. While some states such as TS45 of Cu/B and TS78 of Cu/N were expected to proceed instantaneously at normal operating temperature due to large rate constants, other transitions pointed to

mostly moderate rates with only a couple of very slow reactions, such as TS12 of Cu/B and TS35 Cu/N layout. While moderate and slow steps are undesirable for the overall reaction, the magnitude of rate constants resemble a typical reaction with moderate speed, apart from the two very slow steps. Given the exponential relation between operating temperature and Gibbs free energy of activation, rate constants are expected to increase significantly with increasing temperature.

Based on the relation between activation energy and reaction speed given in **Table 4.3**, comparing individual transition states' speed based on their activation energies became possible. Based on the reaction temperature selected as 65°C to resemble methanol fuel cell operating conditions, any activation energy greater than 85 kJ/mol points to negligibly slow reaction rates. This value drops to 74 kJ/mol for room temperature. So, the comparison of activation energies of each TS on different layouts were meaningful only below 85 kJ/mol because above this threshold, the reaction becomes negligibly slow regardless of the magnitude. In the upcoming sections 4.6 and 4.7 where the results found for Cu/B and Cu/N will be compared to Cu-doped graphene and pure Cu(111) surface, this threshold will be taken into account for a meaningful comparison.

4.6. Comparison to Cu-doped Graphene

Results obtained for Cu/B and Cu/N surfaces were also compared to methanol decomposition on a copper doped graphene surface [20]. The same reaction pathway proposed by Akça et al. [20] was replicated in this study owing to the missing intermediates and unmatching material balances. One major difference is the continuing presence of H-atoms on the surface while they were excluded from energy calculations in subsequent steps in contrast to our work. Thus, a reaction energy profile could not be extracted from the reference work. Nevertheless, activation and reaction energies were compared for each reaction individually, so, the difference in assumed hydrogen behavior was not a concern for error. Since Akça et al. did not apply ZPE or vibrational corrections to their step-wise energy values; here, raw DFT results were used for comparison to ensure consistency. In the reference, several alternative reaction pathways were considered, some including excess oxygen on the surface but in this study, only the proposed pathway was studied while preserving the total atom

number between the surface/adsorbate complex and the gas phase molecules at 38, not allowing excess or missing atoms to influence the total energy.

First step was the adsorption of gas phase methanol on the surface. In both Cu/B-Cu/N and CuG, this step occurs without a transition state and methanol was observed to bind the surface on the oxygen atom.

Table 4.7 illustrates the related adsorption energies for this reaction. Results were close although Cu/B layout exhibited a smaller affinity to adsorb methanol.

Table 4.7: CH₃OH adsorption energies for different layouts.

Layout	Reaction			Adsorption Energy (kJ/mol)
Cu/B	Surf. + CH ₃ OH(g) GS0 (ref.)	→	CH ₃ OH* GS1	-54
Cu/N	Surf. + CH ₃ OH(g) GS0 (ref.)	→	CH ₃ OH* GS1	-99
Reference [20]	Surf. + CH ₃ OH(g)	→	CH ₃ OH*	-83

Adsorbed methanol undergoes dehydrogenation until reaching carbon monoxide as the final molecule. First hydrogen atom leaving methanol and binding on the surface is the one bound to the oxygen atom, while the three hydrogens bound to the carbon atom transfer afterwards. Hydrogen adsorbed on the surface on the copper atom, denoted as H_{Cu}*, was investigated as an intermediate step between the transfer of hydrogen from methanol to the boron or nitrogen atoms on the surface but in the reference study, it was assumed that hydrogen would be adsorbed on the surface whether it is on the copper or graphene surface. **Table 4.8** shows the activation and reaction energies related to the first transition state where the hydrogen transfers from oxygen to the surface.

Table 4.8: Activation and reaction energies for the first hydrogen transfer step from methanol to the surface.

Layout	Reaction			Ea (kJ/mol)	Er (kJ/mol)
Cu/B	CH ₃ OH* GS1	→ TS12	CH ₃ O* + H _{Cu} * GS2	207	191
Cu/N	CH ₃ OH* GS1	→ TS12	CH ₃ O* + H _{Cu} * GS2	110	-61
Reference [20]	CH ₃ OH*	→ TS3	CH ₃ O* + H*	115	105

While Cu/N is in agreement with the reference activation energy, it has a remarkably lower reaction energy. Cu/B has significantly larger activation and reaction energies compared to other layouts.

During the second hydrogen transfer from the initial methanol to the surface, the intermediate step where hydrogen first binds to copper and then transfers to the surface atoms was observed in Cu/B layout whereas in Cu/N layout, this step did not occur. **Table 4.9** presents activation and reaction energies related to the second transition state.

Table 4.9: Activation and reaction energies for the second hydrogen transfer step from methanol to the surface.

Layout	Reaction			Ea (kJ/mol)	Er (kJ/mol)
Cu/B	CH ₃ O* + H* GS3	→ TS34	CH ₂ O* + H* + H _{Cu} * GS4	116	96
Cu/N	CH ₃ O* + H* GS3	→ TS35	CH ₂ O* + 2H* GS5	157	92
Reference [20]	CH ₃ O*	→ TS5	CH ₂ O* + H*	142	140

The activation energies are close but Cu/B shows the lowest barrier. BN variants have lower reaction energies compared to graphene alternative.

Third dehydrogenation step took place from the formaldehyde intermediate towards the surface, forming a formyl structure as the final state. **Table 4.10** shows activation and reaction energies related to the third transition state.

Table 4.10: Activation and reaction energies for the third hydrogen transfer step from methanol to the surface.

Layout	Reaction			Ea (kJ/mol)	Er (kJ/mol)
Cu/B	CH ₂ O* GS6	→ TS67	CHO* + H* GS7	118	-48
Cu/N	CH ₂ O* GS6	→ TS67	CHO* + H* GS7	125	-21
Reference [20]	CH ₂ O*	→ TS6	CHO* + H*	75	69

Cu/B and Cu/N exhibits similar results whereas the reference reaction has a slightly lower activation barrier but a higher reaction energy.

Last dehydrogenation step starts from the formyl structure with the hydrogen transferring to the surface to form carbon monoxide, the final product. **Table 4.11** shows related energies of the reactions.

Table 4.11: Activation and reaction energies for the fourth hydrogen transfer step from methanol to the surface.

Layout	Reaction			Ea (kJ/mol)	Er (kJ/mol)
Cu/B	CHO* + H* GS7	→ TS78	CO* + 2H* GS8	121	-72
Cu/N	CHO* + H* GS7	→ TS78	CO* + 2H* GS8	56	-78
Reference [20]	CHO*	→ TS9	CO* + H*	24	13

The desorption of surface hydrogens or CO from the surface were covered in this study but they were not within the scope of the reference study. Nevertheless, two adsorption energies from the reference study, one for a single H atom (-2.17 eV) and the other for

the CO and H together (-3.09 eV), were compared to estimate the adsorption energy of the CO alone as 89 kJ/mol. **Table 4.12** shows all desorption energies.

Table 4.12: Desorption energies of CO from the surface.

Layout	Reaction			Desorption Energy (kJ/mol)
Cu/B	CO* GS9	→	CO(g) GS10	71
Cu/N	CO* GS9	→	CO(g) GS10	87
Reference [20]	CO* + H* and H* difference			89

In the reference study [20], the conclusion was that CuG surface was a feasible catalyst according to DFT results. CuG exhibited manageable activation barriers, with the highest activation barrier of the complete reaction observed during hydrogenation of CH₃O as 142 kJ/mol. In contrast, Cu/B surface had higher Ea requirements than both alternatives for different steps, with the highest barrier being 207 kJ/mol (TS67). Cu/N had the best CH₃OH adsorption energy, -99 kJ/mol, and showed moderate activation barriers in further steps, with the highest barrier observed during TS35 as 157 kJ/mol, which is comparable to highest activation barrier of CuG. The higher activation energies in Cu/B surface point to reduced catalytic efficiency, indicating that methanol decomposition on these surfaces would require higher thermal input or occur more slowly. On the other hand, Cu/N showed a smoother energy profile than Cu/B and activation barrier comparable to CuG. It had similar results and a slightly higher activation barrier than the CuG surface, which had been previously suggested as a catalyst alternative. These characteristics support Cu/N as a strong catalyst candidate.

The CuG surface favored C-H bond activation over C-O, enhancing hydrogen adsorption and supports the desorption of final CO. Similarly, both Cu/B and Cu/N surfaces promoted hydrogen adsorption on B or N atoms but showed negligible affinity toward other intermediates, including CH₃OH and CO. This behavior not only favors methanol dehydrogenation but also minimizes poisoning of non-active sides, which primarily adsorb hydrogen released during methanol decomposition.

Lastly, one of the advantages of CuG over the conventional PGM catalysts was the reduced cost as both carbon and copper are readily available. Likewise, boron and nitrogen molecules are also cheap and easy to access, resulting in a much cheaper catalyst than the conventional PGM catalysts.

In conclusion, CuG was proposed as a feasible DMFC catalyst for moderate activation barriers and favorable C-H selectivity, making it a promising low-cost alternative to PtRu catalysts. While Cu/B and Cu/N showed similar C-H selectivity that favors the methanol decomposition, they exhibited different energy barriers at different steps which hinders or favors the reaction kinetics. Cu/N showed promising results and can directly be proposed as a material for further investigation like CuG due to comparable performance. Cu/B layout had to overcome higher activation barriers in multiple steps, peaking at 207 kJ/mol, which may still allow catalytic activity, but a considerably slower conversion should be expected over Cu/N or CuG surfaces. BN and graphene variants had low costs and low methanol adsorption energies in common while BN surfaces also showed desirable catalytic activity in terms of selectivity towards adsorbates.

4.7. Methanol Decomposition on Clean Cu(111) vs. Cu/B and Cu/N Surfaces

Obtained results were also compared to literature data for methanol decomposition on a pure Cu(111) surface, computed by periodic, self-consistent DFT-GGA calculations by Greeley and Mavrikakis in 2002 [36]. The proposed reaction pathway, $\text{CH}_3\text{OH}^* \rightarrow \text{CH}_3\text{O}^* \rightarrow \text{CH}_2\text{O}^* \rightarrow \text{CHO}^* \rightarrow \text{CO}^*$, aligns with this study although there is a minor deviation: in the reference study, hydrogen atoms dissociated from methanol were assumed to remain adsorbed on the surface throughout the reaction. In contrast, this study assumes that adsorbed hydrogen atoms combine into H_2 molecules and desorb into the gas phase as soon as two are available.

This approach reduces computational effort and simplifies the surface model. To maintain consistency, DFT energies of desorbed, relaxed gaseous hydrogen molecules were added to the calculated DFT total energies of the surface. Additionally, ZPE and vibrational corrections were discussed but not directly applied to the results in the reference study. Likewise, only raw DFT energies from this study, for both surface and gaseous molecules, were compared for consistency.

In this study, transfer of hydrogen from methanol to surface was assumed in two steps: first, adsorption on copper, when applicable, and second, adsorption on surface. Because of that, more intermediate states were identified in this study than in the reference but for a meaningful comparison, results from matching states were compared. **Figure 4.37** shows the comparison between energy profiles from Cu/B, Cu/N and reference Cu(111) surfaces are shown in.

Similar to graphene and BN comparison, Cu/N variant shows comparable performance to Cu(111) while Cu/B underperforms relative to both alternatives. Cu/B and Cu/N are superior to Cu(111) in methanol adsorption step, offering an easier methanol binding on the copper site. The highest activation barrier that should be overcome along the pathway on Cu(111) was reported as approximately 139 kJ/mol, during second hydrogen abstraction, which is slightly lower than the barrier of Cu/N observed as 157 kJ/mol during second hydrogen abstraction step as well. Cu/B has a considerably higher rate-determining barrier than both, determined as 207 kJ/mol during first hydrogen abstraction. This difference suggests significantly slower methanol decomposition kinetics on Cu/B surface despite the easier adsorption of methanol.

Overall, Cu/N shows lower energies in all steps, despite having a slightly higher rate-determining barrier compared to pure Cu(111) while Cu/B suffers from high activation barriers. Thanks to the selective affinity towards reaction intermediates and the lower methanol adsorption energies of both BN surfaces, it can be concluded that Cu/N could perform better than Cu(111) based on computational results while Cu/B suffers from slow reaction kinetics.

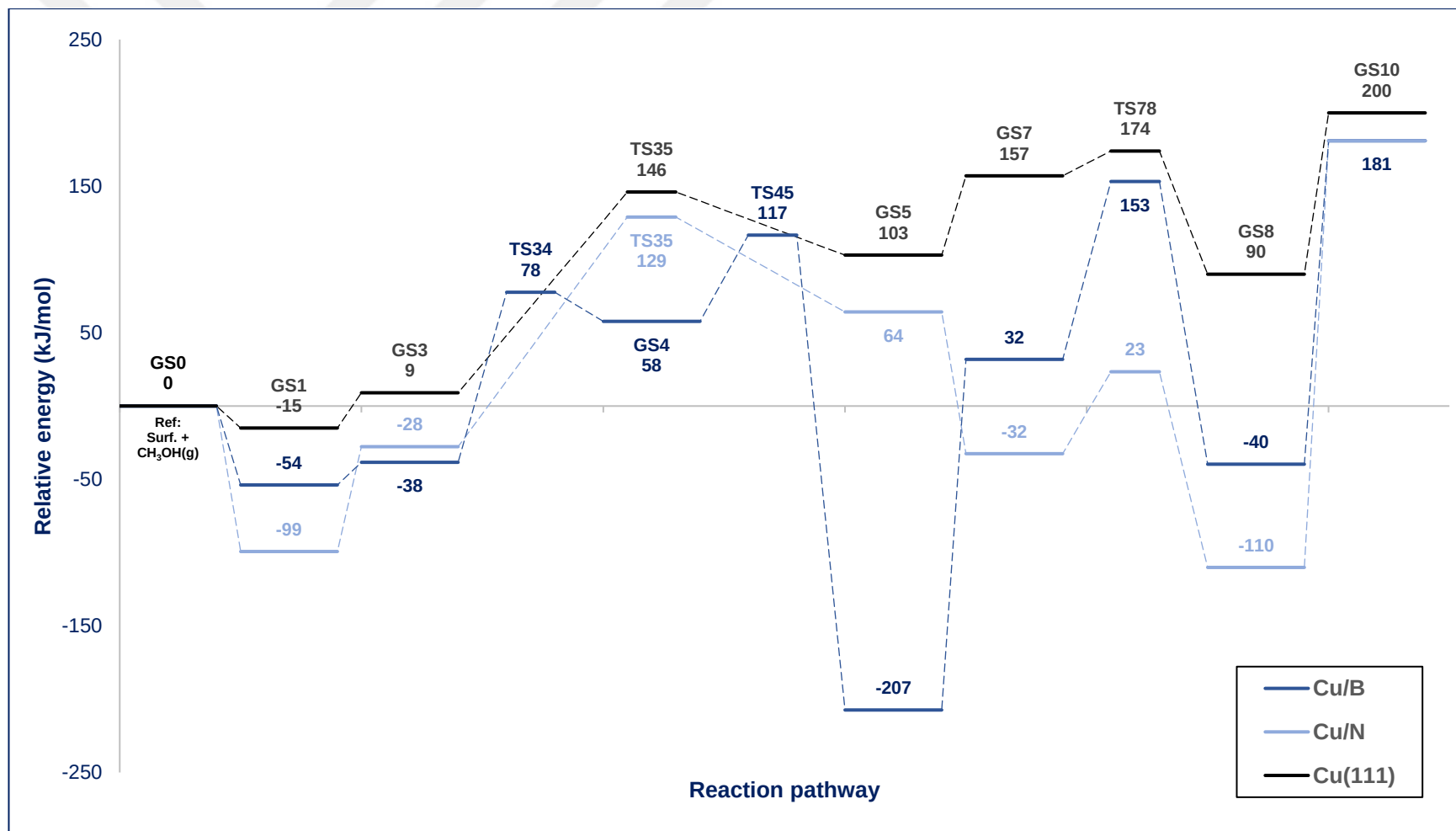


Figure 4.37: Relative energy profiles based on non-ZPE corrected DFT results for methanol decomposition on Cu/B, Cu/N and Cu(111) [36] surfaces. Results and identical states from the reference study were renamed to match Cu/B and Cu/N counterparts for simplicity.

4.8. Comparison to Pt(111)

Comparison with copper-based catalysts allowed an assessment on the performance of copper-doped boron nitride surface. But the catalysts that are currently used in DMFCs are platinum based catalysts, so a comparison between Cu-*h*BN and Pt-based catalysts was also done. One study [77] was DFT-based investigation of methanol decomposition on Pt(111) and Pd(111) surfaces, following two pathways, one of them being the same pathway as in this study while the other followed hydroxymethyl route. Their results showed that hydroxymethyl route was more preferable, hence, the related energy barriers for methoxide pathway was not given explicitly. Another study [78], also the reference study for comparison, studied different reaction pathways and listed the activation energies for intermediate steps.

Table 4.13 shows first, **Table 4.14** shows second, **Table 4.15** shows third and **Table 4.16** shows fourth dehydrogenation step energies of Pt(111) surface. The Pt(111) surface is clearly the superior surface for methanol dehydrogenation based on activation energies of intermediate steps as it offers significantly lower activation energies. On the other hand, **Table 4.17** shows the comparison of desorption energies of CO from surface, where Pt(111) exhibits a significantly higher energy, which is also in agreement with the known CO poisoning problem while Cu/B and Cu/N show relatively smaller desorption energies.

Table 4.13: Activation and reaction energies for the first hydrogen transfer step from methanol to the surface.

Layout	Reaction			Ea (kJ/mol)
Cu/B	CH_3OH^* GS1	$\rightarrow$ TS12	$\text{CH}_3\text{O}^* + \text{H}_{\text{Cu}}^*$ GS2	207
Cu/N	CH_3OH^* GS1	$\rightarrow$ TS12	$\text{CH}_3\text{O}^* + \text{H}_{\text{Cu}}^*$ GS2	110
Pt(111) [78]	CH_3OH^*	$\rightarrow$ s ₂	$\text{CH}_3\text{O}^* + \text{H}^*$	61

Table 4.14: Activation and reaction energies for the second hydrogen transfer step from methanol to the surface.

Layout	Reaction			Ea (kJ/mol)
Cu/B	$\text{CH}_3\text{O}^* + \text{H}^*$ GS3	$\rightarrow$ TS34	$\text{CH}_2\text{O}^* + \text{H}^* + \text{H}_{\text{Cu}}^*$ GS4	116
Cu/N	$\text{CH}_3\text{O}^* + \text{H}^*$ GS3	$\rightarrow$ TS35	$\text{CH}_2\text{O}^* + 2\text{H}^*$ GS5	157
Pt(111) [78]	CH_3O^*	$\rightarrow$ S ₃	$\text{CH}_2\text{O}^* + \text{H}^*$	11

Table 4.15: Activation and reaction energies for the third hydrogen transfer step from methanol to the surface.

Layout	Reaction			Ea (kJ/mol)
Cu/B	CH_2O^* GS6	$\rightarrow$ TS67	$\text{CHO}^* + \text{H}^*$ GS7	118
Cu/N	CH_2O^* GS6	$\rightarrow$ TS67	$\text{CHO}^* + \text{H}^*$ GS7	125
Pt(111) [78]	CH_2O^*	$\rightarrow$ S ₄	$\text{CHO}^* + \text{H}^*$	5

Table 4.16: Activation and reaction energies for the fourth hydrogen transfer step from methanol to the surface.

Layout	Reaction			Ea (kJ/mol)
Cu/B	$\text{CHO}^* + \text{H}^*$ GS7	$\rightarrow$ TS78	$\text{CO}^* + 2\text{H}^*$ GS8	121
Cu/N	$\text{CHO}^* + \text{H}^*$ GS7	$\rightarrow$ TS78	$\text{CO}^* + 2\text{H}^*$ GS8	56
Pt(111) [78]	CHO^*	$\rightarrow$ S ₅	$\text{CO}^* + \text{H}^*$	12

Table 4.17: Desorption energies of CO from the surface.

Layout	Reaction			Desorption Energy (kJ/mol)
Cu/B	CO* GS9	→	CO(g) GS10	71
Cu/N	CO* GS9	→	CO(g) GS10	87
Pt(111) [78]	CO*	→ S12	CO(g)	134

While the CO desorption energy is relatively favorable with Cu-BN surfaces, the Pt(111) surface shows extremely better activation energies. So, if the Cu-BN surfaces were to replace platinum based catalysts, related activation energies should be much lower despite the advantage against CO poisoning.

4.9. Summary of Activation and Reaction Energies across Surfaces

The results obtained in this work were compared to those from different alternative surfaces on which methanol decomposition was modelled using similar methods but the comparison was done only against Cu-BN surfaces and a single, other alternative. To enable a comprehensive evaluation, data from both this work and the references were consolidated into a single table, namely **Table 4.18**. While the main purpose was not to conduct an extensive review of all surfaces, this comparative overview allows for direct benchmarking of Cu-BN surfaces and highlight their strengths and weaknesses against selected alternatives at a glance. As the reference studies did not incorporate additional corrections such as ZPE or vibrational energies, only the raw DFT results were included in the comparison.

Table 4.18: Consolidated comparison of activation (Ea) and reaction (Er) energies of selected surfaces. For CH₃OH and CO steps, adsorption and desorption energies were given. All energies are given in kJ/mol. N/A: Not available in reference work.

Step	Reaction	Cu/B		Cu/N		CuG [20]		Cu(111) [36]		Pt(111) [78]	
		Ea	Er	Ea	Er	Ea	Er	Ea	Er	Ea	Er
CH₃OH ads.	CH ₃ OH(g) → CH ₃ OH*	-54		-99		-83		-15		-32	
TS12	CH ₃ OH* → CH ₃ O* + H*	207	191	110	-61	115	105	N/A	24	61	N/A
TS34	CH ₃ O* + H* → CH ₂ O* + H* + H _{Cu} *	116	96	N/A	N/A						
TS35	CH ₃ O* + H* → CH ₂ O* + 2H*	N/A	N/A	157	92	142	140	137	94	11	N/A
TS45	CH ₂ O* + H* + H _{Cu} * → CH ₂ O* + 2H*	59	-265	N/A	N/A						
TS67	CH ₂ O* → CHO* + H*	118	-48	125	-21	75	69	N/A	54	5	N/A
TS78	CHO* + H* → CO* + 2H*	121	-72	56	-78	24	13	17	-67	12	N/A
CO des.	CO* → CO(g)	71		87		89		110		134	

5. CONCLUSIONS

In this study, the catalytic activity and comprehensive energy profile of decomposition of methanol on a copper-doped 2D-*h*BN were investigated using periodic DFT methods. The aim was to explore efficient, cheap and sustainable catalysts to promote methanol decomposition in DMFCs, in response to rising environmental awareness and the importance of sustainability. Based on the copper's applications on methanol involving reactions and BN's similarity to graphene, copper-doped boron nitride surfaces were investigated. Following the methanol dehydrogenation route suggested in Akça et al. [20], reaction intermediates and TS's were optimized, obtaining a complete energy profile for whole reaction. Additional thermodynamic corrections; namely ZPC, vibrational enthalpy and entropy corrections evaluated at DMFC working temperatures were applied to raw results to resemble real operating conditions.

Comparing the results with the literature showed that clean BN surface showed an affinity towards hydrogen atoms but did not attract methanol. Copper addition to surface enabled methanol adsorption. Both Cu/B and Cu/N showed desirable results in terms of catalytic behavior such as **(i)** attracting hydrogen while showing no affinity towards other intermediates at non-active sites of surface and **(ii)** low methanol adsorption energy. Between Cu/B and Cu/N, the latter showed a better performance with significantly lower activation barrier at its rate-determining step, lower and more stable energy profile throughout the reaction as well as exhibiting a slightly easier methanol adsorption at the first step. Cu/B, showed a more fluctuating energy profile, with more activation and reaction energies in most steps and having the highest activation barrier peaking at 207 kJ/mol during the first hydrogen abstraction step, which significantly slows down the reaction kinetics compared to both Cu/N variant and the literature. Based on results of this study, it is safe to conclude that for the given reaction pathway and the selected computational settings, Cu/B surface lacks the catalytic performance to be an alternative to either CuG or Cu(111) surfaces in methanol decomposition reaction. Cu/N, on the other hand, showed comparable performance to the reference materials, exhibiting only mild fluctuations in energy profile and reasonable energy barriers to overcome, pointing that it can be considered

an alternative material. While Cu/N offered the desired performance surpassing Cu/B by a margin, it should be noted that computational results may not necessarily reflect the reality due to several reasons such as the error margin from approximations and simplifications, computational parameters and method selection. Moreover, the possibility of the same ground or transition states having an alternative, more stable geometry is always a point to consider. In this study, several geometrical variants of each ground state were tested and the states that were either more stable or that offered a smoother transition were selected over other alternatives, but this does not necessarily mean that the most stable state that could be experimentally achieved is the variant that was scanned and selected. Additionally, the reaction pathway in this study was proposed specifically for copper-doped graphene and pure copper surfaces, which poses the possibility that the methanol decomposition on Cu-doped BN surfaces might follow a different pathway with different, potentially lower activation barriers. Exploration of different pathways may yield completely different results.

Considering all these factors, it can be concluded that methanol decomposition on Cu/B surface following the proposed pathway has slow reaction kinetics and therefore Cu/B may not be proposed as future DMFC catalysts, based solely on the results of this specific study and the specific reaction pathway.

Cu/N, on the other hand, showed desirable catalytic behavior under the selected conditions and parameters, and is a candidate for experimental validation. Cu/B, against Cu/N and literature, fell short due to high activation energies within the scope of this study under current setup. However, it may still hold potential when approached with tweaked settings, different computational methods/approximations different reaction mechanisms. The alternative geometrical variants to the current ground and transition states are also another topic that could be investigated further.

A side reaction forming formaldehyde and hydrogen was also identified but not thoroughly inspected. It showed a smaller energy gap than the full decomposition route. This suggests that under limited energy input, methanol may preferentially decompose into CH_2O and H_2 rather than CO and H_2 .

Alternative approaches, though not explored in this study, should be considered rather than ruling out the surfaces for methanol decomposition. Based on reversed energy profiles, Cu/B and Cu/N surfaces hold potential as effective catalysts for methanol

synthesis, which could be explored in future works. Also, full methanol oxidation by reforming with water ($\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$) exhibits additional exothermicity from water splitting that could lower the energy profile and high barriers, making the reaction more feasible.

Boron nitride and copper remain promising materials due to thermal stability, chemical inertness, readily availability, especially against the PGM based conventional catalysts, and the observed catalytic behavior on both active site and the surface. With appropriate modifications such as co-doping, surface functionalization or investigating alternative reaction pathways, BN-based surfaces may evolve into more viable methanol decomposition catalysts. Therefore, the study of Cu/B and Cu/N variants may be a good starting point for future studies aimed at optimizing non-PGM catalysts for fuel cell applications.

REFERENCES

- [1] P. A. Owusu and S. Asumadu-Sarkodie, “A review of renewable energy sources, sustainability issues and climate change mitigation,” *Cogent Engineering*, vol. 3, no. 1, p. 1167990, Dec. 2016, doi: 10.1080/23311916.2016.1167990.
- [2] A. G. Olabi and M. A. Abdelkareem, “Renewable energy and climate change,” *Renewable and Sustainable Energy Reviews*, vol. 158, p. 112111, Apr. 2022, doi: 10.1016/j.rser.2022.112111.
- [3] D. J. Wuebbles and A. K. Jain, “Concerns about climate change and the role of fossil fuel use,” *Fuel Processing Technology*, vol. 71, no. 1–3, pp. 99–119, Jun. 2001, doi: 10.1016/s0378-3820(01)00139-4.
- [4] A. Pramuanjaroenkij and S. Kakaç, “The fuel cell electric vehicles: The highlight review,” *International Journal of Hydrogen Energy*, vol. 48, no. 25, pp. 9401–9425, Mar. 2023, doi: 10.1016/j.ijhydene.2022.11.103.
- [5] A. Kaur, G. Kaur, P. P. Singh, and S. Kaushal, “Supported bimetallic nanoparticles as anode catalysts for direct methanol fuel cells: A review,” *International Journal of Hydrogen Energy*, vol. 46, no. 29, pp. 15820–15849, Apr. 2021, doi: 10.1016/j.ijhydene.2021.02.037.
- [6] E. H. Ehite, “Study of two-phase flow pressure drop characteristics in Proton Exchange Membrane (PEM) fuel cell flow channels of different geometries,” Master of Science in Mechanical Engineering, Michigan Technological University, Houghton, Michigan, 2016. doi: 10.37099/mtu.dc.etrdr/81.
- [7] S. M. Haile, “Fuel cell materials and components☆☆☆The Golden Jubilee Issue—Selected topics in Materials Science and Engineering: Past, Present and Future, edited by S. Suresh,” *Acta Materialia*, vol. 51, no. 19, pp. 5981–6000, Nov. 2003, doi: 10.1016/j.actamat.2003.08.004.
- [8] “Types of Fuel Cells | Department of Energy.” Accessed: Apr. 15, 2025. Available: <https://www.energy.gov/eere/fuelcells/types-fuel-cells>
- [9] D. Hwan Jung, C. Hyeong Lee, C. Soo Kim, and D. Ryul Shin, “Performance of a direct methanol polymer electrolyte fuel cell,” *Journal of Power Sources*, vol. 71, no. 1–2, pp. 169–173, Mar. 1998, doi: 10.1016/s0378-7753(97)02793-6.
- [10] S. Surampudi *et al.*, “Advances in direct oxidation methanol fuel cells,” *Journal of Power Sources*, vol. 47, no. 3, pp. 377–385, Jan. 1994, doi: 10.1016/0378-7753(94)87016-0.
- [11] J. -Y. Park, J. -H. Kim, Y. Seo, D. -J. Yu, H. Cho, and S. J. Bae, “Operating Temperature Dependency on Performance Degradation of Direct Methanol Fuel Cells,” *Fuel Cells*, vol. 12, no. 3, pp. 426–438, Jun. 2012, doi: 10.1002/fuce.201100184.

- [12] P. Breeze, "Fuel Cells," in *Power Generation Technologies*, Elsevier, 2014, pp. 129–152. doi: 10.1016/B978-0-08-098330-1.00007-7.
- [13] N. Wan, "High performance direct methanol fuel cell with thin electrolyte membrane," *Journal of Power Sources*, vol. 354, pp. 167–171, Jun. 2017, doi: 10.1016/j.jpowsour.2017.04.037.
- [14] P. Kumar, K. Dutta, S. Das, and P. P. Kundu, "An overview of unsolved deficiencies of direct methanol fuel cell technology: factors and parameters affecting its widespread use: Unsolved deficiencies of direct methanol fuel cells," *International Journal of Energy Research*, vol. 38, no. 11, pp. 1367–1390, Sep. 2014, doi: 10.1002/er.3163.
- [15] W. Qian *et al.*, "Exfoliated graphene-supported Pt and Pt-based alloys as electrocatalysts for direct methanol fuel cells," *Carbon*, vol. 52, pp. 595–604, Feb. 2013, doi: 10.1016/j.carbon.2012.10.031.
- [16] R. Spragg, "Direct Methanol Fuel Cells Using Pure Methanol," Master's Thesis, Washington University, 2024. Accessed: Apr. 19, 2025. Available: https://openscholarship.wustl.edu/eng_etds/1113/
- [17] D.-H. Lim, W.-D. Lee, D.-H. Choi, D.-R. Park, and H.-I. Lee, "Preparation of platinum nanoparticles on carbon black with mixed binary surfactants: Characterization and evaluation as anode catalyst for low-temperature fuel cell," *Journal of Power Sources*, vol. 185, no. 1, pp. 159–165, Oct. 2008, doi: 10.1016/j.jpowsour.2008.05.092.
- [18] A. de Klerk, "Transport Fuel," in *Future Energy*, Elsevier, 2020, pp. 199–226. doi: 10.1016/B978-0-08-102886-5.00010-4.
- [19] K. Zhang, W. Guo, Z. Liang, and R. Zou, "Metal-organic framework based nanomaterials for electrocatalytic oxygen redox reaction," *Science China Chemistry*, vol. 62, no. 4, pp. 417–429, Apr. 2019, doi: 10.1007/s11426-018-9441-4.
- [20] A. Akça *et al.*, "Mechanism of methanol decomposition on the Cu-Embedded graphene: A DFT study," *International Journal of Hydrogen Energy*, vol. 48, no. 17, pp. 6624–6637, Feb. 2023, doi: 10.1016/j.ijhydene.2021.09.028.
- [21] S. Dhali *et al.*, "Graphene oxide supported Pd-Fe nanohybrid as an efficient electrocatalyst for proton exchange membrane fuel cells," *International Journal of Hydrogen Energy*, vol. 45, no. 37, pp. 18704–18715, Jul. 2020, doi: 10.1016/j.ijhydene.2019.09.131.
- [22] M. D. Esrafil and L. Dinparast, "The selective adsorption of formaldehyde and methanol over Al- or Si-decorated graphene oxide: A DFT study," *Journal of Molecular Graphics and Modelling*, vol. 80, pp. 25–31, Mar. 2018, doi: 10.1016/j.jmgm.2017.12.025.

- [23] W. Li *et al.*, “Preparation and Characterization of Multiwalled Carbon Nanotube-Supported Platinum for Cathode Catalysts of Direct Methanol Fuel Cells,” *The Journal of Physical Chemistry B*, vol. 107, no. 26, pp. 6292–6299, Jul. 2003, doi: 10.1021/jp022505c.
- [24] R. M. Nauman Javed, A. Al-Othman, M. Tawalbeh, and A. G. Olabi, “Recent developments in graphene and graphene oxide materials for polymer electrolyte membrane fuel cells applications,” *Renewable and Sustainable Energy Reviews*, vol. 168, p. 112836, Oct. 2022, doi: 10.1016/j.rser.2022.112836.
- [25] M. F. Jamil, E. Biçer, B. Yarar Kaplan, and S. Alkan Gürsel, “One-step fabrication of new generation graphene-based electrodes for polymer electrolyte membrane fuel cells by a novel electrophoretic deposition,” *International Journal of Hydrogen Energy*, vol. 46, no. 7, pp. 5653–5663, Jan. 2021, doi: 10.1016/j.ijhydene.2020.11.039.
- [26] M. D. Esrafil and R. Nurazar, “Potential of C-doped boron nitride fullerene as a catalyst for methanol dehydrogenation,” *Computational Materials Science*, vol. 92, pp. 172–177, Sep. 2014, doi: 10.1016/j.commatsci.2014.05.043.
- [27] J. Zhao and Z. Chen, “Carbon-Doped Boron Nitride Nanosheet: An Efficient Metal-Free Electrocatalyst for the Oxygen Reduction Reaction,” *The Journal of Physical Chemistry C*, vol. 119, no. 47, pp. 26348–26354, Nov. 2015, doi: 10.1021/acs.jpcc.5b09037.
- [28] M. D. Esrafil and P. Nematollahi, “Potential of Si-doped boron nitride nanotubes as a highly active and metal-free electrocatalyst for oxygen reduction reaction: A DFT study,” *Synthetic Metals*, vol. 226, pp. 129–138, Apr. 2017, doi: 10.1016/j.synthmet.2017.02.011.
- [29] B. Chettri, P. K. Patra, N. N. Hieu, and D. P. Rai, “Hexagonal boron nitride (h - BN) nanosheet as a potential hydrogen adsorption material: A density functional theory (DFT) study,” *Surfaces and Interfaces*, vol. 24, p. 101043, Jun. 2021, doi: 10.1016/j.surfin.2021.101043.
- [30] P. S. Krstic, L. Han, S. Irle, and H. Nakai, “Simulations of the synthesis of boron-nitride nanostructures in a hot, high pressure gas volume,” *Chemical Science*, vol. 9, no. 15, pp. 3803–3819, 2018, doi: 10.1039/c8sc00667a.
- [31] S. Ogawa, S. Fukushima, and M. Shimatani, “Hexagonal Boron Nitride for Photonic Device Applications: A Review,” *Materials*, vol. 16, no. 5, p. 2005, Feb. 2023, doi: 10.3390/ma16052005.
- [32] P. M. Revabhai, R. K. Singhal, H. Basu, and S. K. Kailasa, “Progress on boron nitride nanostructure materials: properties, synthesis and applications in hydrogen storage and analytical chemistry,” *Journal of Nanostructure in Chemistry*, vol. 13, no. 1, pp. 1–41, Feb. 2023, doi: 10.1007/s40097-022-00490-5.

- [33] L. Li *et al.*, “Framework Cu-doped boron nitride nanobelts with enhanced internal electric field for effective Fenton-like removal of organic pollutants,” *Journal of Materials Chemistry A*, vol. 7, no. 12, pp. 6946–6956, 2019, doi: 10.1039/c9ta00255c.
- [34] F. Liu, Q. Zhou, Y. Li, and J. Pang, “Cu-Doped Boron Nitride Nanosheets for Solid-Phase Extraction and Determination of Rhodamine B in Foods Matrix,” *Nanomaterials*, vol. 12, no. 3, p. 318, Jan. 2022, doi: 10.3390/nano12030318.
- [35] M. Ikram *et al.*, “Evaluation of antibacterial and catalytic potential of copper-doped chemically exfoliated boron nitride nanosheets,” *Ceramics International*, vol. 46, no. 13, pp. 21073–21083, Sep. 2020, doi: 10.1016/j.ceramint.2020.05.180.
- [36] J. Greeley and M. Mavrikakis, “Methanol Decomposition on Cu(111): A DFT Study,” *Journal of Catalysis*, vol. 208, no. 2, pp. 291–300, Jun. 2002, doi: 10.1006/jcat.2002.3586.
- [37] M. O. Özbek, “Computational study of ethylene epoxidation,” 2011, PhD Thesis, *Technische Universiteit Eindhoven*. doi: 10.6100/IR716445.
- [38] E. Schrödinger, “Quantisierung als Eigenwertproblem,” *Annalen der Physik*, vol. 384, no. 4, pp. 361–376, Jan. 1926, doi: 10.1002/andp.19263840404.
- [39] L. D. Landau and E. M. Lifshitz, “THE ATOM,” in *Quantum Mechanics*, Elsevier, 1977, pp. 249–297. doi: 10.1016/B978-0-08-020940-1.50017-7.
- [40] J. P. Perdew, “Jacob’s ladder of density functional approximations for the exchange-correlation energy,” in *AIP Conference Proceedings*, Antwerp (Belgium): AIP, 2001, pp. 1–20. doi: 10.1063/1.1390175.
- [41] I. Ciofini *et al.*, “Theoretical studies of linear and non-linear optical properties of biomolecules,” PhD Thesis, Université de Rouen Normandie, 2019. Accessed: Apr. 21, 2025. Available: https://www.researchgate.net/publication/337074587_Theoretical_studies_of_linear_and_non-linear_optical_properties_of_biomolecules
- [42] P. Giannozzi *et al.*, “Advanced capabilities for materials modelling with QUANTUM ESPRESSO,” *Journal of Physics: Condensed Matter*, vol. 29, no. 46, p. 465901, 2017.
- [43] P. Giannozzi *et al.*, “QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials,” *Journal of Physics: Condensed Matter*, vol. 21, no. 39, p. 395502 (19pp), 2009.
- [44] P. Giannozzi *et al.*, “Quantum ESPRESSO toward the exascale,” *The Journal of Chemical Physics*, vol. 152, no. 15, p. 154105, 2020, doi: 10.1063/5.0005082.
- [45] A. Kokalj, “XCrySDen—a new program for displaying crystalline structures and electron densities,” *Journal of Molecular Graphics and Modelling*, vol. 17, no. 3–4, pp. 176–179, Jun. 1999, doi: 10.1016/S1093-3263(99)00028-5.

- [46] M. J. van Setten *et al.*, “The PseudoDojo: Training and grading a 85 element optimized norm-conserving pseudopotential table,” *Computer Physics Communications*, vol. 226, pp. 39–54, 2018, doi: <https://doi.org/10.1016/j.cpc.2018.01.012>.
- [47] K. Lejaeghere *et al.*, “Reproducibility in density functional theory calculations of solids,” *Science*, vol. 351, p. 1415, 2016.
- [48] K. F. Garrity, J. W. Bennett, K. M. Rabe, and D. Vanderbilt, “Pseudopotentials for high-throughput DFT calculations,” *Computer Physics Communications*, vol. 81, p. 446, 2014.
- [49] D. R. Hamann, “Optimized norm-conserving Vanderbilt pseudopotentials,” *Physical Review B*, vol. 88, p. 085117, 2013.
- [50] F. Jollet, M. Torrent, and N. Holzwarth, “Generation of Projector Augmented-Wave atomic data: A 71 element validated table in the XML format,” *Computer Physics Communications*, vol. 185, p. 1246, 2014.
- [51] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, “A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu,” *The Journal of Chemical Physics*, vol. 132, no. 15, p. 154104, Apr. 2010, doi: 10.1063/1.3382344.
- [52] H. J. Monkhorst and J. D. Pack, “Special points for Brillouin-zone integrations,” *Physical Review B*, vol. 13, no. 12, pp. 5188–5192, Jun. 1976, doi: 10.1103/PhysRevB.13.5188.
- [53] G. Henkelman, B. P. Uberuaga, and H. Jónsson, “A climbing image nudged elastic band method for finding saddle points and minimum energy paths,” *The Journal of Chemical Physics*, vol. 113, no. 22, pp. 9901–9904, Dec. 2000, doi: 10.1063/1.1329672.
- [54] Q. An, K. M. Reddy, K. Y. Xie, K. J. Hemker, and W. A. Goddard, “New Ground-State Crystal Structure of Elemental Boron,” *Physical Review Letters*, vol. 117, no. 8, p. 085501, Aug. 2016, doi: 10.1103/PhysRevLett.117.085501.
- [55] M. Aykol, S. S. Dwaraknath, W. Sun, and K. A. Persson, “Thermodynamic limit for synthesis of metastable inorganic materials,” *Science Advances*, vol. 4, no. 4, p. eaaq0148, Apr. 2018, doi: 10.1126/sciadv.aaq0148.
- [56] M. De Jong *et al.*, “Charting the complete elastic properties of inorganic crystalline compounds,” *Scientific Data*, vol. 2, no. 1, p. 150009, Mar. 2015, doi: 10.1038/sdata.2015.9.
- [57] M. De Jong, W. Chen, H. Geerlings, M. Asta, and K. A. Persson, “A database to enable discovery and design of piezoelectric materials,” *Scientific Data*, vol. 2, no. 1, p. 150053, Sep. 2015, doi: 10.1038/sdata.2015.53.

- [58] H. Ding, S. S. Dwaraknath, L. Garten, P. Ndione, D. Ginley, and K. A. Persson, "Computational Approach for Epitaxial Polymorph Stabilization through Substrate Selection," *ACS Applied Materials & Interfaces*, vol. 8, no. 20, pp. 13086–13093, May 2016, doi: 10.1021/acsami.6b01630.
- [59] M. K. Horton, J. H. Montoya, M. Liu, and K. A. Persson, "High-throughput prediction of the ground-state collinear magnetic order of inorganic materials using Density Functional Theory," *npj Computational Materials*, vol. 5, no. 1, p. 64, Jun. 2019, doi: 10.1038/s41524-019-0199-7.
- [60] A. Jain *et al.*, "Formation enthalpies by mixing GGA and GGA + U calculations," *Physical Review B*, vol. 84, no. 4, p. 045115, Jul. 2011, doi: 10.1103/PhysRevB.84.045115.
- [61] A. Jain *et al.*, "Commentary: The Materials Project: A materials genome approach to accelerating materials innovation," *APL Materials*, vol. 1, no. 1, p. 011002, Jul. 2013, doi: 10.1063/1.4812323.
- [62] K. Latimer, S. Dwaraknath, K. Mathew, D. Winston, and K. A. Persson, "Evaluation of thermodynamic equations of state across chemistry and structure in the materials project," *npj Computational Materials*, vol. 4, no. 1, p. 40, Jul. 2018, doi: 10.1038/s41524-018-0091-x.
- [63] J. M. Munro, K. Latimer, M. K. Horton, S. Dwaraknath, and K. A. Persson, "An improved symmetry-based approach to reciprocal space path selection in band structure calculations," *npj Computational Materials*, vol. 6, no. 1, p. 112, Jul. 2020, doi: 10.1038/s41524-020-00383-7.
- [64] A. M. Patel, J. K. Nørskov, K. A. Persson, and J. H. Montoya, "Efficient Pourbaix diagrams of many-element compounds," *Physical Chemistry Chemical Physics*, vol. 21, no. 45, pp. 25323–25327, 2019, doi: 10.1039/C9CP04799A.
- [65] K. A. Persson, B. Walckiewicz, P. Lazic, and G. Ceder, "Prediction of solid-aqueous equilibria: Scheme to combine first-principles calculations of solids with experimental aqueous states," *Physical Review B*, vol. 85, no. 23, p. 235438, Jun. 2012, doi: 10.1103/PhysRevB.85.235438.
- [66] I. Petousis *et al.*, "High-throughput screening of inorganic compounds for the discovery of novel dielectric and optical materials," *Scientific Data*, vol. 4, no. 1, p. 160134, Jan. 2017, doi: 10.1038/sdata.2016.134.
- [67] A. K. Singh *et al.*, "Electrochemical Stability of Metastable Materials," *Chemistry of Materials*, vol. 29, no. 23, pp. 10159–10167, Dec. 2017, doi: 10.1021/acs.chemmater.7b03980.
- [68] R. Tran *et al.*, "Surface energies of elemental crystals," *Scientific Data*, vol. 3, no. 1, p. 160080, Sep. 2016, doi: 10.1038/sdata.2016.80.

- [69] A. Wang *et al.*, “A framework for quantifying uncertainty in DFT energy corrections,” *Scientific Reports*, vol. 11, no. 1, p. 15496, Jul. 2021, doi: 10.1038/s41598-021-94550-5.
- [70] H. Zheng *et al.*, “Grain boundary properties of elemental metals,” *Acta Materialia*, vol. 186, pp. 40–49, Mar. 2020, doi: 10.1016/j.actamat.2019.12.030.
- [71] R. H. Perry and D. W. Green, Eds., *Perry’s chemical engineers’ handbook*, 7. ed., [3. Nachdr.]. in Perry’s chemical engineers’ platinum edition. New York, NY: McGraw-Hill, 1999.
- [72] C. E. Buelna-Garcia *et al.*, “Exploration of Free Energy Surface and Thermal Effects on Relative Population and Infrared Spectrum of the Be₆B₁₁– Fluxional Cluster,” *Materials*, vol. 14, no. 1, p. 112, Dec. 2020, doi: 10.3390/ma14010112.
- [73] D. S. Sholl and J. A. Steckel, *Density Functional Theory: A Practical Introduction*, 1st ed. Wiley, 2009. doi: 10.1002/9780470447710.
- [74] Henry. Eyring, “The Activated Complex and the Absolute Rate of Chemical Reactions.,” *Chemical Reviews*, vol. 17, no. 1, pp. 65–77, Aug. 1935, doi: 10.1021/cr60056a006.
- [75] I. Chorkendorff and J. W. Niemantsverdriet, *Concepts of Modern Catalysis and Kinetics*, 1st ed. Wiley, 2003. doi: 10.1002/3527602658.
- [76] R. A. van Santen, *Theoretical heterogeneous catalysis*. in World scientific lecture and course notes in chemistry, no. 5. Singapore London Hong Kong: World scientific, 1991.
- [77] S. K. Desai, M. Neurock, and K. Kourtakis, “A Periodic Density Functional Theory Study of the Dehydrogenation of Methanol over Pt(111),” *The Journal of Physical Chemistry B*, vol. 106, no. 10, pp. 2559–2568, Mar. 2002, doi: 10.1021/jp0132984.
- [78] S. Vilekar, I. Fishtik, and R. Datta, “Topological analysis of catalytic reaction networks: Methanol decomposition on Pt(111),” *Journal of Catalysis*, vol. 252, no. 2, pp. 258–270, Dec. 2007, doi: 10.1016/j.jcat.2007.09.020.

BIOGRAPHY

Gökberk Çelikel graduated from İstanbul (Males) High School in 2012 and obtained his B.Sc. degree from Chemical Engineering department of Middle East Technical University in 2021. In 2022, he began his M.Sc. studies in Gebze Technical University while simultaneously working full time in the private sector.

As part of his academic career, he participated in 17th Quantum Reactive Scattering Workshop and 7th Anatolian School of Catalysis as a poster presenter, which were held in İstanbul, June 2024 and in İzmir, September 2024, respectively. He also attended 10th National Catalysis Conference as a poster presenter at Sivas, in June 2025.



PUBLICATIONS AND PRESENTATIONS FROM THE THESIS

[1] G. Çelikel and M. O. Özbek, “Quantum Chemical Investigation of Methanol Decomposition on Copper Embedded Boron Nitride Surface to be Used in a Fuel Cell,” presented at the 17th Quantum Reactive Scattering (QRS) Workshop, Yıldız Technical University, Türkiye, Jun. 26, 2024.

[2] G. Çelikel and M. O. Özbek, “Quantum Chemical Investigation of Methanol Decomposition on Copper Embedded Boron Nitride Surface to be Used in a Fuel Cell,” presented at the 7th Anatolian School of Catalysis, İzmir Institute of Technology, Türkiye, Sep. 04, 2024.

[3] G. Çelikel and M. O. Özbek, “DFT-based Comparison of Cu-doped BN vs. Graphene as MFC Catalysts,” presented at the 10th National Catalysis Conference, Sivas Cumhuriyet University, Jun. 27, 2025.

APPENDICES

APPENDIX-A: EXAMPLE INPUT FILES

APPENDIX-A.1: DFT GROUND STATE INPUT

&CONTROL

```
calculation      = 'relax' ,  
!restart_mode    = 'restart' ,  
outdir           = './temp' ,  
pseudo_dir       = '/okyanus/users/gcelikel/work/pseudopotentials',  
prefix           = 'BN' ,  
tefield          = .true.,  
dipfield         = .true.,  
/  

```

&SYSTEM

```
edir            = 3,  
emaxpos         = 0.8,  
  
ibrav           = 0,  
nat             = 38,  
ntyp            = 6,  
ecutwfc         = 50 ,  
ecutrho         = 350 ,  
occupations     = 'smearing' ,  
smearing        = 'gaussian' ,
```

degauss = 0.02 ,

/

&ELECTRONS

/

&IONS

/

CELL_PARAMETERS (angstrom)

10.0569477081	0.0000000000	0.0000000000
-5.0284738541	8.7095721998	0.0000000000
0.0000000000	0.0000000000	15.0000000000

ATOMIC_SPECIES

B 10.8100 B.pbe-n-kjpaw_psl.1.0.0.UPF

N 14.0070 N.pbe-n-kjpaw_psl.1.0.0.UPF

Cu 63.5460 Cu.pbe-dn-kjpaw_psl.1.0.0.UPF

C 12.0110 C.pbe-n-kjpaw_psl.1.0.0.UPF

H 1.0080 H.pbe-kjpaw_psl.1.0.0.UPF

O 15.9990 O.pbe-n-kjpaw_psl.1.0.0.UPF

K_POINTS automatic

4 4 1 0 0 0

ATOMIC_POSITIONS (angstrom)

B	-0.054261077	0.093953124	-0.084360200
B	-1.318789733	2.271213142	-0.103062494
B	3.722241028	6.655859320	0.155056856
B	2.457439272	0.100763735	0.008596413
B	7.484529557	0.098143398	-0.110943420
B	1.172724397	2.253719176	0.198970120
B	-3.827427580	6.629676072	-0.010531998
B	-2.570154870	4.455352749	-0.079190899
B	4.968703821	0.093501084	-0.065794018
B	-0.084643786	4.436860958	0.203124595
B	1.196668446	6.651020043	0.184742024
B	-1.308681376	6.626251555	0.013196061
B	3.729785443	2.257529128	0.158938442
B	6.229074360	2.272753913	-0.114422685
B	4.997275882	4.447367565	0.134709118
N	-0.067577634	1.536710632	-0.067193917
N	3.718126528	8.091102356	-0.089980777
N	-3.826115164	8.080886373	-0.036610480
N	-1.327259695	3.722335892	-0.061812276
N	2.465761011	6.080921847	0.497427964
N	-1.314876261	8.079047067	-0.022905193
N	1.196045437	8.088571242	-0.062883713
N	1.031162433	3.625451668	0.555716990
N	-2.568771778	5.905150137	-0.035115111
N	2.453575496	1.546628729	0.134800694

N	7.483651114	1.547040253	-0.168765062
N	4.976319247	5.907596159	0.098531663
N	-0.057180506	5.900396374	0.148297305
N	4.977809446	1.538118168	-0.071908514
N	6.241678982	3.724392052	-0.091035276
N	3.865520967	3.645978993	0.438702257
Cu	2.484341187	4.451565287	1.388341075
O	2.604671151	4.243426755	3.521819088
C	3.467158188	5.054239350	4.355184667
H	1.791289888	4.014515945	4.002334562
H	2.992296803	6.013972625	4.602833284
H	3.731223057	4.513197011	5.273119413
H	4.372457551	5.239576662	3.767472546

APPENDIX-A.2: DFT TRANSITION STATE INPUT

BEGIN

BEGIN_PATH_INPUT

&PATH

!restart_mode = 'restart',

string_method = 'neb',

!CI_scheme = "auto",

nstep_path = 100,

!ds = 2,

opt_scheme = "broyden",

num_of_images = 10,

```
!k_max          = 0.3D0,  
!k_min          = 0.2D0,  
!path_thr       = 0.2D0,  
use_masses      = .true.,
```

```
/
```

```
END_PATH_INPUT
```

```
BEGIN_ENGINE_INPUT
```

```
&CONTROL
```

```
prefix          = "neb"  
outdir          = "./temp",  
pseudo_dir      = '/okyanus/users/oozbek/work/pseudopotentials',
```

```
/
```

```
&SYSTEM
```

```
ibrav           = 0,  
nat             = 38,  
ntyp            = 6,  
ecutwfc         = 50,  
ecutrho         = 350,  
occupations     = 'smearing',  
smearing        = 'gaussian' ,  
degauss         = 0.02,  
  
vdw_corr        = 'DFT-D3',
```

/

&ELECTRONS

electron_maxstep = 200,

mixing_beta = 0.1,

conv_thr = 1.D-5,

/

&IONS

/

CELL_PARAMETERS (angstrom)

10.0569477081	0.0000000000	0.0000000000
-5.0284738541	8.7095721998	0.0000000000
0.0000000000	0.0000000000	15.0000000000

ATOMIC_SPECIES

B 10.8100 B.pbe-n-kjpaw_psl.1.0.0.UPF

N 14.0070 N.pbe-n-kjpaw_psl.1.0.0.UPF

Cu 63.5460 Cu.pbe-dn-kjpaw_psl.1.0.0.UPF

C 2.0107 C.pbe-n-kjpaw_psl.1.0.0.UPF

O 15.9991 O.pbe-n-kjpaw_psl.1.0.0.UPF

H 1.0080 H.pbe-kjpaw_psl.1.0.0.UPF

K_POINTS automatic

4 4 1 0 0 0

BEGIN_POSITIONS

FIRST_IMAGE

ATOMIC_POSITIONS (angstrom)

B	-0.054261077	0.093953124	-0.0843602	0	0	0
B	-1.318789733	2.271213142	-0.103062494	0	0	0
B	3.722241028	6.65585932	0.155056856	0	0	0
B	2.457439272	0.100763735	0.008596413	0	0	0
B	7.484529557	0.098143398	-0.11094342	0	0	0
B	1.172724397	2.253719176	0.19897012	0	0	0
B	-3.82742758	6.629676072	-0.010531998	0	0	0
B	-2.57015487	4.455352749	-0.079190899	0	0	0
B	4.968703821	0.093501084	-0.065794018	0	0	0
B	-0.084643786	4.436860958	0.203124595	0	0	0
B	1.196668446	6.651020043	0.184742024	0	0	0
B	-1.308681376	6.626251555	0.013196061	0	0	0
B	3.729785443	2.257529128	0.158938442	0	0	0
B	6.22907436	2.272753913	-0.114422685	0	0	0
B	4.997275882	4.447367565	0.134709118	0	0	0
N	-0.067577634	1.536710632	-0.067193917	0	0	0
N	3.718126528	8.091102356	-0.089980777	0	0	0
N	-3.826115164	8.080886373	-0.03661048	0	0	0
N	-1.327259695	3.722335892	-0.061812276	0	0	0
N	2.465761011	6.080921847	0.497427964	0	0	0

N	-1.314876261	8.079047067	-0.022905193	0	0	0
N	1.196045437	8.088571242	-0.062883713	0	0	0
N	1.031162433	3.625451668	0.55571699	0	0	0
N	-2.568771778	5.905150137	-0.035115111	0	0	0
N	2.453575496	1.546628729	0.134800694	0	0	0
N	7.483651114	1.547040253	-0.168765062	0	0	0
N	4.976319247	5.907596159	0.098531663	0	0	0
N	-0.057180506	5.900396374	0.148297305	0	0	0
N	4.977809446	1.538118168	-0.071908514	0	0	0
N	6.241678982	3.724392052	-0.091035276	0	0	0
N	3.865520967	3.645978993	0.438702257	0	0	0
Cu	2.484341187	4.451565287	1.388341075	0	0	0
O	2.604671151	4.243426755	3.521819088			
C	3.467158188	5.05423935	4.355184667			
H	2.992296803	6.013972625	4.602833284			
H	3.731223057	4.513197011	5.273119413			
H	4.372457551	5.239576662	3.767472546			
H	1.791289888	4.014515945	4.002334562			

LAST_IMAGE

ATOMIC_POSITIONS (angstrom)

B	-0.046846700	0.064271011	-0.004264624
B	-1.310513466	2.241010735	-0.019153415
B	3.735617061	6.603379171	0.177892748
B	2.461540957	0.067713698	0.061459546
B	7.491110031	0.064158517	-0.030206843
B	1.201344331	2.229912058	0.220726219

B	-3.824968590	6.595275000	0.054241250
B	-2.564447163	4.421083844	-0.014542652
B	4.974185307	0.062827368	-0.016181466
B	-0.077934969	4.414992968	0.259541575
B	1.187586056	6.612656903	0.221499640
B	-1.312997313	6.597720384	0.085763006
B	3.735960984	2.235194272	0.114840287
B	6.235690817	2.240450334	-0.075033456
B	4.994349401	4.403389930	0.130081150
N	-0.054596074	1.514677008	0.006802978
N	3.722188455	8.054634389	-0.009423658
N	-3.822420615	8.048729532	0.035149485
N	-1.315573830	3.691597402	0.017110903
N	2.458170424	6.017212489	0.429105653
N	-1.310746331	8.048374232	0.034370867
N	1.202619076	8.055396934	0.007743848
N	1.078711855	3.626776384	0.540985801
N	-2.566427029	5.871937022	0.032986712
N	2.463438533	1.513141961	0.151718038
N	7.493057002	1.514366274	-0.084662724
N	4.983964023	5.868860493	0.128656443
N	-0.063628154	5.872836450	0.215810129
N	4.984691091	1.504656147	-0.068965459
N	6.249388948	3.691231107	-0.061131829
N	3.815203979	3.635040517	0.305808460
Cu	2.516397292	4.400661975	1.456602312

```

O      3.722794430  4.424014904  2.837597357
C      3.736911136  5.240407922  3.981187809
H      2.872558606  5.915293283  4.065344209
H      3.746744288  4.584629007  4.872415191
H      4.671692480  5.829292223  4.000701894
H      1.520974906  4.916982693  2.402821716

END_POSITIONS

END_ENGINE_INPUT

END

```

APPENDIX-A.3: SCF INPUT

```
&CONTROL
```

```
calculation      = 'scf' ,
```

```
!restart_mode    = 'restart' ,
```

```
outdir           = './temp' ,
```

```
pseudo_dir      = '/okyanus/users/oozbek/work/pseudopotentials',
```

```
prefix          = 'BN' ,
```

```
teffield        = .true.,
```

```
dipfield        = .true.,
```

```
/
```

```
&SYSTEM
```

```
edir            = 3,
```

```
emaxpos        = 0.8,
```

```

ibrav      = 0,
nat        = 38,
ntyp       = 6,
ecutwfc    = 50 ,
ecutrho    = 350 ,
occupations = 'smearing' ,
smearing   = 'gaussian' ,
degauss    = 0.02 ,

```

```
/
```

```
&ELECTRONS
```

```

conv_thr   = 1.D-10,
!mixing_beta = 0.3

```

```
/
```

```
&IONS
```

```
/
```

```
CELL_PARAMETERS (angstrom)
```

10.0569477081	0.0000000000	0.0000000000
-5.0284738541	8.7095721998	0.0000000000
0.0000000000	0.0000000000	15.0000000000

```
ATOMIC_SPECIES
```

```
B 10.8100 B.pbe-n-kjpaw_psl.1.0.0.UPF
```

N 14.0070 N.pbe-n-kjpaw_psl.1.0.0.UPF
Cu 63.5460 Cu.pbe-dn-kjpaw_psl.1.0.0.UPF
C 12.0110 C.pbe-n-kjpaw_psl.1.0.0.UPF
H 1.0080 H.pbe-kjpaw_psl.1.0.0.UPF
O 15.9990 O.pbe-n-kjpaw_psl.1.0.0.UPF

K_POINTS automatic

4 4 1 0 0 0

ATOMIC_POSITIONS (angstrom)

B	-0.054261077	0.093953124	-0.084360200
B	-1.318789733	2.271213142	-0.103062494
B	3.722241028	6.655859320	0.155056856
B	2.457439272	0.100763735	0.008596413
B	7.484529557	0.098143398	-0.110943420
B	1.172724397	2.253719176	0.198970120
B	-3.827427580	6.629676072	-0.010531998
B	-2.570154870	4.455352749	-0.079190899
B	4.968703821	0.093501084	-0.065794018
B	-0.084643786	4.436860958	0.203124595
B	1.196668446	6.651020043	0.184742024
B	-1.308681376	6.626251555	0.013196061
B	3.729785443	2.257529128	0.158938442
B	6.229074360	2.272753913	-0.114422685
B	4.997275882	4.447367565	0.134709118
N	-0.067577634	1.536710632	-0.067193917

N	3.718126528	8.091102356	-0.089980777
N	-3.826115164	8.080886373	-0.036610480
N	-1.327259695	3.722335892	-0.061812276
N	2.465761011	6.080921847	0.497427964
N	-1.314876261	8.079047067	-0.022905193
N	1.196045437	8.088571242	-0.062883713
N	1.031162433	3.625451668	0.555716990
N	-2.568771778	5.905150137	-0.035115111
N	2.453575496	1.546628729	0.134800694
N	7.483651114	1.547040253	-0.168765062
N	4.976319247	5.907596159	0.098531663
N	-0.057180506	5.900396374	0.148297305
N	4.977809446	1.538118168	-0.071908514
N	6.241678982	3.724392052	-0.091035276
N	3.865520967	3.645978993	0.438702257
Cu	2.484341187	4.451565287	1.388341075
O	2.604671151	4.243426755	3.521819088
C	3.467158188	5.054239350	4.355184667
H	1.791289888	4.014515945	4.002334562
H	2.992296803	6.013972625	4.602833284
H	3.731223057	4.513197011	5.273119413
H	4.372457551	5.239576662	3.767472546

APPENDIX-A.4: PHONON INPUT

Cu_CO

&INPUTPH

!recover = .true. ,

outdir = './temp' ,

fildyn = 'dyn.mat' ,

trans = .true.,

asr = .true. ,

amass(1) = 10.8100,

amass(2) = 14.0070,

amass(3) = 63.5460,

amass(4) = 12.0110,

amass(5) = 1.0080,

amass(6) = 15.9990,

tr2_ph = 1.0d-12,

alpha_mix(1) = 0.7,

alpha_mix(2) = 0.4,

alpha_mix(3) = 0.1,

nat_todo = 6,

prefix = 'BN' ,

/

0.0 0.0 0.0

33 34 35 36 37 38

APPENDIX-A.5: DYNAMIC MATRIX (DYNMAT) INPUT

```
&input  
fildyn = 'dyn.mat',  
asr    = 'zero-dim',  
!asr   = 'simple',  
!asr   = 'crystal',  
!q(3) = 1,  
/  

```

APPENDIX-A.6: COPPER FCC CUBIC CELL OPTIMIZATION INPUT

```
&CONTROL  
calculation = 'scf',  
!restart_mode = 'from_scratch',  
outdir       = './temp',  
pseudo_dir   = '/home/olush/work/pseudopotentials',  
prefix       = 'cu',  
/  
  
&SYSTEM  
ibrav        = 2,  
celldm(1)    = 6.5973449,  
nat          = 1,  
ntyp         = 1,  
ecutwfc      = 50 ,  
ecutrho      = 350 ,
```

```
occupations = 'smearing',  
smearing     = 'gaussian',  
degauss      = 0.02 ,
```

```
nr1 = 30
```

```
nr2 = 30
```

```
nr3 = 30
```

```
nr1s = 24
```

```
nr2s = 24
```

```
nr3s = 24
```

```
/
```

```
&ELECTRONS
```

```
/
```

```
ATOMIC_SPECIES
```

```
Cu 63.54600 Cu.pbe-dn-kjpaw_psl.1.0.0.UPF
```

```
K_POINTS automatic
```

```
12 12 12 0 0 0
```

```
ATOMIC_POSITIONS crystal
```

```
Cu 0.000000000 0.000000000 0.000000000
```

APPENDIX-B: EXAMPLE OUTPUT SECTIONS

APPENDIX-B.1: DFT GROUND STATE OUTPUT

Program PWSCF v.6.3MaX starts on 20Aug2023 at 20:43:14

This program is part of the open-source Quantum ESPRESSO suite
for quantum simulation of materials; please cite

"P. Giannozzi et al., J. Phys.:Condens. Matter 21 395502 (2009);

"P. Giannozzi et al., J. Phys.:Condens. Matter 29 465901 (2017);

URL <http://www.quantum-espresso.org>",

in publications or presentations arising from this work. More details at

<http://www.quantum-espresso.org/quote>

BFGS Geometry Optimization

[...]

total energy = -903.74487549 Ry

Harris-Foulkes estimate = -903.74487625 Ry

estimated scf accuracy < 0.00000013 Ry

total all-electron energy = -6041.606592 Ry

The total energy is the sum of the following terms:

one-electron contribution = -2821.72655660 Ry

hartree contribution = 1459.26233814 Ry
xc contribution = -197.26402245 Ry
ewald contribution = 967.30521450 Ry
electric field correction = 0.00161930 Ry
one-center paw contrib. = -311.30223668 Ry
smearing contrib. (-TS) = -0.02123169 Ry

convergence has been achieved in 14 iterations

[...]

BFGS Geometry Optimization

bfgs converged in 1 scf cycles and 0 bfgs steps

(criteria: energy < 1.0E-04 Ry, force < 1.0E-03 Ry/Bohr)

End of BFGS Geometry Optimization

Final energy = -903.7448754855 Ry

Begin final coordinates

ATOMIC_POSITIONS (angstrom)

B -0.054261077 0.093953124 -0.084360200
B -1.318789733 2.271213142 -0.103062494
B 3.722241028 6.655859320 0.155056856
B 2.457439272 0.100763735 0.008596413

B	7.484529557	0.098143398	-0.110943420
B	1.172724397	2.253719176	0.198970120
B	-3.827427580	6.629676072	-0.010531998
B	-2.570154870	4.455352749	-0.079190899
B	4.968703821	0.093501084	-0.065794018
B	-0.084643786	4.436860958	0.203124595
B	1.196668446	6.651020043	0.184742024
B	-1.308681376	6.626251555	0.013196061
B	3.729785443	2.257529128	0.158938442
B	6.229074360	2.272753913	-0.114422685
B	4.997275882	4.447367565	0.134709118
N	-0.067577634	1.536710632	-0.067193917
N	3.718126528	8.091102356	-0.089980777
N	-3.826115164	8.080886373	-0.036610480
N	-1.327259695	3.722335892	-0.061812276
N	2.465761011	6.080921847	0.497427964
N	-1.314876261	8.079047067	-0.022905193
N	1.196045437	8.088571242	-0.062883713
N	1.031162433	3.625451668	0.555716990
N	-2.568771778	5.905150137	-0.035115111
N	2.453575496	1.546628729	0.134800694
N	7.483651114	1.547040253	-0.168765062
N	4.976319247	5.907596159	0.098531663
N	-0.057180506	5.900396374	0.148297305
N	4.977809446	1.538118168	-0.071908514
N	6.241678982	3.724392052	-0.091035276

N	3.865520967	3.645978993	0.438702257
Cu	2.484341187	4.451565287	1.388341075
O	2.604671151	4.243426755	3.521819088
C	3.467158188	5.054239350	4.355184667
H	1.791289888	4.014515945	4.002334562
H	2.992296803	6.013972625	4.602833284
H	3.731223057	4.513197011	5.273119413
H	4.372457551	5.239576662	3.767472546

End final coordinates

[...]

This run was terminated on: 20:45:19 20Aug2023

=====

JOB DONE.

=====

APPENDIX-B.2: DFT TRANSITION STATE NEB OUTPUT

Program NEB v.6.3MaX starts on 18Mar2024 at 7: 5:58

This program is part of the open-source Quantum ESPRESSO suite
for quantum simulation of materials; please cite

"P. Giannozzi et al., J. Phys.:Condens. Matter 21 395502 (2009);

"P. Giannozzi et al., J. Phys.:Condens. Matter 29 465901 (2017);

URL <http://www.quantum-espresso.org>",

in publications or presentations arising from this work. More details at

<http://www.quantum-espresso.org/quote>

[...]

initial path length = 4.8494 bohr

initial inter-image distance = 0.5388 bohr

string_method = neb

restart_mode = from_scratch

opt_scheme = broyden

num_of_images = 10

nstep_path = 100

CI_scheme = no-CI

first_last_opt = F

use_freezing = F

ds = 1.0000 a.u.

k_max = 0.1000 a.u.

k_min = 0.1000 a.u.

suggested k_max = 0.6169 a.u.

suggested k_min = 0.6169 a.u.

path_thr = 0.0500 eV / Å

[...]

----- iteration 71 -----

tcpu = 24227.0 self-consistency for image 2

tcpu = 24263.5 self-consistency for image 3
 tcpu = 24306.4 self-consistency for image 4
 tcpu = 24351.1 self-consistency for image 5
 tcpu = 24396.0 self-consistency for image 6
 tcpu = 24444.0 self-consistency for image 7
 tcpu = 24487.6 self-consistency for image 8
 tcpu = 24535.1 self-consistency for image 9

activation energy (->) = 2.129106 eV

activation energy (<-) = 0.205605 eV

image	energy (eV)	error (eV/A)	frozen
1	-12297.5792385	0.025588	T
2	-12297.5645808	0.033898	F
3	-12297.5225536	0.040972	F
4	-12297.5052723	0.041600	F
5	-12297.3222005	0.043000	F
6	-12296.9312089	0.039376	F
7	-12295.9072511	0.034211	F
8	-12295.4501323	0.029704	F
9	-12295.5965282	0.024186	F
10	-12295.6557378	0.042917	T

path length = 8.182 bohr

inter-image distance = 0.909 bohr

neb: convergence achieved in 71 iterations

NEB : 6h21m CPU 21h 6m WALL

49h

This run was terminated on: 13:55:30 18Mar2024

=====

JOB DONE.

=====

APPENDIX-B.3: DFT TRANSITION STATE NEB-CI OUTPUT

Program NEB v.6.3MaX starts on 21Mar2024 at 1:32:32

This program is part of the open-source Quantum ESPRESSO suite
for quantum simulation of materials; please cite

"P. Giannozzi et al., J. Phys.:Condens. Matter 21 395502 (2009);

"P. Giannozzi et al., J. Phys.:Condens. Matter 29 465901 (2017);

URL <http://www.quantum-espresso.org>",

in publications or presentations arising from this work. More details at

<http://www.quantum-espresso.org/quote>

[...]

initial path length = 9.3710 bohr

initial inter-image distance = 1.0412 bohr

string_method = neb

restart_mode = from_scratch

opt_scheme = broyden

num_of_images = 10

nstep_path = 100

CI_scheme = auto

first_last_opt = F

use_freezing = F

ds = 1.0000 a.u.

k_max = 0.1000 a.u.

k_min = 0.1000 a.u.

suggested k_max = 0.6169 a.u.

suggested k_min = 0.6169 a.u.

path_thr = 0.0500 eV / Å

[...]

----- iteration 27 -----

tcpu = 10551.4 self-consistency for image 2

tcpu = 10578.7 self-consistency for image 3
 tcpu = 10606.6 self-consistency for image 4
 tcpu = 10643.6 self-consistency for image 5
 tcpu = 10680.1 self-consistency for image 6
 tcpu = 10722.6 self-consistency for image 7
 tcpu = 10760.8 self-consistency for image 8
 tcpu = 10798.3 self-consistency for image 9

activation energy (->) = 2.070607 eV

activation energy (<-) = 0.147116 eV

image	energy (eV)	error (eV/A)	frozen
1	-12297.5792524	0.025095	T
2	-12297.5748155	0.010096	F
3	-12297.5570365	0.009196	F
4	-12297.5406051	0.042258	F
5	-12297.2932181	0.045865	F
6	-12296.5618174	0.039324	F
7	-12295.5086454	0.029532	F
8	-12295.6453138	0.040972	F
9	-12295.6606853	0.032142	F
10	-12295.6557617	0.045806	T

climbing image = 7

path length = 9.755 bohr
inter-image distance = 1.084 bohr

neb: convergence achieved in 27 iterations

NEB : 2h49m CPU 49h 3m WALL

0h

This run was terminated on: 4:33: 7 21Mar2024

JOB DONE.

APPENDIX-B.4: PHONON OUTPUT

Program PHONON v.6.3MaX starts on 24Apr2025 at 14: 7:44

This program is part of the open-source Quantum ESPRESSO suite
for quantum simulation of materials; please cite

"P. Giannozzi et al., J. Phys.:Condens. Matter 21 395502 (2009);

"P. Giannozzi et al., J. Phys.:Condens. Matter 29 465901 (2017);

URL <http://www.quantum-espresso.org>",

in publications or presentations arising from this work. More details at
<http://www.quantum-espresso.org/quote>

[...]

End of self-consistent calculation

Convergence has been achieved

Number of q in the star = 1

List of q in the star:

1 0.000000000 0.000000000 0.000000000

Diagonalizing the dynamical matrix

q = (0.000000000 0.000000000 0.000000000)

freq (1) = -22.638895 [THz] = -755.152264 [cm-1]
freq (2) = -17.241690 [THz] = -575.120863 [cm-1]
freq (3) = -16.614559 [THz] = -554.202044 [cm-1]
freq (4) = -15.741532 [THz] = -525.080999 [cm-1]
freq (5) = -11.825844 [THz] = -394.467690 [cm-1]
freq (6) = -10.336642 [THz] = -344.793260 [cm-1]
freq (7) = -9.032219 [THz] = -301.282387 [cm-1]
freq (8) = -7.993561 [THz] = -266.636501 [cm-1]
freq (9) = -5.089898 [THz] = -169.780713 [cm-1]
freq (10) = -4.474368 [THz] = -149.248863 [cm-1]
freq (11) = -3.442389 [THz] = -114.825723 [cm-1]
freq (12) = -3.026681 [THz] = -100.959196 [cm-1]
freq (13) = -2.114881 [THz] = -70.544842 [cm-1]

freq (14) = -1.010789 [THz] = -33.716305 [cm-1]
 freq (15) = -0.672152 [THz] = -22.420576 [cm-1]
 freq (16) = -0.605967 [THz] = -20.212873 [cm-1]
 freq (17) = -0.536116 [THz] = -17.882916 [cm-1]
 freq (18) = -0.180253 [THz] = -6.012591 [cm-1]
 freq (19) = -0.000000 [THz] = -0.000010 [cm-1]
 freq (20) = -0.000000 [THz] = -0.000009 [cm-1]
 freq (21) = -0.000000 [THz] = -0.000008 [cm-1]
 freq (22) = -0.000000 [THz] = -0.000008 [cm-1]
 freq (23) = -0.000000 [THz] = -0.000007 [cm-1]
 freq (24) = -0.000000 [THz] = -0.000006 [cm-1]
 freq (25) = -0.000000 [THz] = -0.000006 [cm-1]
 freq (26) = -0.000000 [THz] = -0.000005 [cm-1]
 freq (27) = -0.000000 [THz] = -0.000005 [cm-1]
 freq (28) = -0.000000 [THz] = -0.000005 [cm-1]
 freq (29) = -0.000000 [THz] = -0.000004 [cm-1]
 freq (30) = -0.000000 [THz] = -0.000004 [cm-1]
 freq (31) = -0.000000 [THz] = -0.000004 [cm-1]
 freq (32) = -0.000000 [THz] = -0.000004 [cm-1]
 freq (33) = -0.000000 [THz] = -0.000003 [cm-1]
 freq (34) = -0.000000 [THz] = -0.000003 [cm-1]
 freq (35) = -0.000000 [THz] = -0.000003 [cm-1]
 freq (36) = -0.000000 [THz] = -0.000003 [cm-1]
 freq (37) = -0.000000 [THz] = -0.000003 [cm-1]
 freq (38) = -0.000000 [THz] = -0.000003 [cm-1]
 freq (39) = -0.000000 [THz] = -0.000003 [cm-1]
 freq (40) = -0.000000 [THz] = -0.000002 [cm-1]
 freq (41) = -0.000000 [THz] = -0.000002 [cm-1]
 freq (42) = -0.000000 [THz] = -0.000002 [cm-1]
 freq (43) = -0.000000 [THz] = -0.000002 [cm-1]
 freq (44) = -0.000000 [THz] = -0.000002 [cm-1]
 freq (45) = -0.000000 [THz] = -0.000002 [cm-1]
 freq (46) = -0.000000 [THz] = -0.000002 [cm-1]

freq (47) = -0.000000 [THz] = -0.000002 [cm-1]
 freq (48) = -0.000000 [THz] = -0.000001 [cm-1]
 freq (49) = -0.000000 [THz] = -0.000001 [cm-1]
 freq (50) = -0.000000 [THz] = -0.000001 [cm-1]
 freq (51) = -0.000000 [THz] = -0.000001 [cm-1]
 freq (52) = -0.000000 [THz] = -0.000001 [cm-1]
 freq (53) = -0.000000 [THz] = -0.000001 [cm-1]
 freq (54) = -0.000000 [THz] = -0.000001 [cm-1]
 freq (55) = -0.000000 [THz] = -0.000001 [cm-1]
 freq (56) = -0.000000 [THz] = -0.000000 [cm-1]
 freq (57) = -0.000000 [THz] = -0.000000 [cm-1]
 freq (58) = -0.000000 [THz] = -0.000000 [cm-1]
 freq (59) = 0.000000 [THz] = 0.000000 [cm-1]
 freq (60) = 0.000000 [THz] = 0.000000 [cm-1]
 freq (61) = 0.000000 [THz] = 0.000000 [cm-1]
 freq (62) = 0.000000 [THz] = 0.000001 [cm-1]
 freq (63) = 0.000000 [THz] = 0.000001 [cm-1]
 freq (64) = 0.000000 [THz] = 0.000001 [cm-1]
 freq (65) = 0.000000 [THz] = 0.000001 [cm-1]
 freq (66) = 0.000000 [THz] = 0.000001 [cm-1]
 freq (67) = 0.000000 [THz] = 0.000001 [cm-1]
 freq (68) = 0.000000 [THz] = 0.000001 [cm-1]
 freq (69) = 0.000000 [THz] = 0.000001 [cm-1]
 freq (70) = 0.000000 [THz] = 0.000002 [cm-1]
 freq (71) = 0.000000 [THz] = 0.000002 [cm-1]
 freq (72) = 0.000000 [THz] = 0.000002 [cm-1]
 freq (73) = 0.000000 [THz] = 0.000002 [cm-1]
 freq (74) = 0.000000 [THz] = 0.000002 [cm-1]
 freq (75) = 0.000000 [THz] = 0.000002 [cm-1]
 freq (76) = 0.000000 [THz] = 0.000002 [cm-1]
 freq (77) = 0.000000 [THz] = 0.000002 [cm-1]
 freq (78) = 0.000000 [THz] = 0.000002 [cm-1]
 freq (79) = 0.000000 [THz] = 0.000003 [cm-1]

freq (80) =	0.000000 [THz] =	0.000003 [cm-1]
freq (81) =	0.000000 [THz] =	0.000003 [cm-1]
freq (82) =	0.000000 [THz] =	0.000003 [cm-1]
freq (83) =	0.000000 [THz] =	0.000004 [cm-1]
freq (84) =	0.000000 [THz] =	0.000004 [cm-1]
freq (85) =	0.000000 [THz] =	0.000004 [cm-1]
freq (86) =	0.000000 [THz] =	0.000004 [cm-1]
freq (87) =	0.000000 [THz] =	0.000004 [cm-1]
freq (88) =	0.000000 [THz] =	0.000005 [cm-1]
freq (89) =	0.000000 [THz] =	0.000006 [cm-1]
freq (90) =	0.000000 [THz] =	0.000006 [cm-1]
freq (91) =	0.000000 [THz] =	0.000007 [cm-1]
freq (92) =	0.000000 [THz] =	0.000007 [cm-1]
freq (93) =	0.000000 [THz] =	0.000008 [cm-1]
freq (94) =	0.000000 [THz] =	0.000009 [cm-1]
freq (95) =	0.000000 [THz] =	0.000009 [cm-1]
freq (96) =	0.000000 [THz] =	0.000011 [cm-1]
freq (97) =	6.589962 [THz] =	219.817486 [cm-1]
freq (98) =	7.515606 [THz] =	250.693633 [cm-1]
freq (99) =	8.589490 [THz] =	286.514536 [cm-1]
freq (100) =	13.940644 [THz] =	465.009824 [cm-1]
freq (101) =	15.733923 [THz] =	524.827174 [cm-1]
freq (102) =	16.463414 [THz] =	549.160363 [cm-1]
freq (103) =	30.165929 [THz] =	1006.227071 [cm-1]
freq (104) =	30.668602 [THz] =	1022.994436 [cm-1]
freq (105) =	31.071240 [THz] =	1036.425016 [cm-1]
freq (106) =	31.822726 [THz] =	1061.491887 [cm-1]
freq (107) =	33.313181 [THz] =	1111.208123 [cm-1]
freq (108) =	34.291559 [THz] =	1143.843292 [cm-1]
freq (109) =	39.021550 [THz] =	1301.618802 [cm-1]
freq (110) =	43.974269 [THz] =	1466.823715 [cm-1]
freq (111) =	68.298667 [THz] =	2278.198297 [cm-1]
freq (112) =	87.565530 [THz] =	2920.871682 [cm-1]

freq (113) = 89.618382 [THz] = 2989.347457 [cm-1]
 freq (114) = 97.732555 [THz] = 3260.007115 [cm-1]

Mode symmetry, C₁ (1) point group:

freq (1 - 1) =	-755.2 [cm-1] --> A	I+R
freq (2 - 2) =	-575.1 [cm-1] --> A	I+R
freq (3 - 3) =	-554.2 [cm-1] --> A	I+R
freq (4 - 4) =	-525.1 [cm-1] --> A	I+R
freq (5 - 5) =	-394.5 [cm-1] --> A	I+R
freq (6 - 6) =	-344.8 [cm-1] --> A	I+R
freq (7 - 7) =	-301.3 [cm-1] --> A	I+R
freq (8 - 8) =	-266.6 [cm-1] --> A	I+R
freq (9 - 9) =	-169.8 [cm-1] --> A	I+R
freq (10 - 10) =	-149.2 [cm-1] --> A	I+R
freq (11 - 11) =	-114.8 [cm-1] --> A	I+R
freq (12 - 12) =	-101.0 [cm-1] --> A	I+R
freq (13 - 13) =	-70.5 [cm-1] --> A	I+R
freq (14 - 14) =	-33.7 [cm-1] --> A	I+R
freq (15 - 15) =	-22.4 [cm-1] --> A	I+R
freq (16 - 16) =	-20.2 [cm-1] --> A	I+R
freq (17 - 17) =	-17.9 [cm-1] --> A	I+R
freq (18 - 18) =	-6.0 [cm-1] --> A	I+R
freq (97 - 97) =	219.8 [cm-1] --> A	I+R
freq (98 - 98) =	250.7 [cm-1] --> A	I+R
freq (99 - 99) =	286.5 [cm-1] --> A	I+R
freq (100 -100) =	465.0 [cm-1] --> A	I+R
freq (101 -101) =	524.8 [cm-1] --> A	I+R
freq (102 -102) =	549.2 [cm-1] --> A	I+R
freq (103 -103) =	1006.2 [cm-1] --> A	I+R

freq (104 -104) =	1023.0 [cm-1]	--> A	I+R
freq (105 -105) =	1036.4 [cm-1]	--> A	I+R
freq (106 -106) =	1061.5 [cm-1]	--> A	I+R
freq (107 -107) =	1111.2 [cm-1]	--> A	I+R
freq (108 -108) =	1143.8 [cm-1]	--> A	I+R
freq (109 -109) =	1301.6 [cm-1]	--> A	I+R
freq (110 -110) =	1466.8 [cm-1]	--> A	I+R
freq (111 -111) =	2278.2 [cm-1]	--> A	I+R
freq (112 -112) =	2920.9 [cm-1]	--> A	I+R
freq (113 -113) =	2989.3 [cm-1]	--> A	I+R
freq (114 -114) =	3260.0 [cm-1]	--> A	I+R

PHONON : 48m 5.91s CPU 49m50.97s WALL

APPENDIX-B.5: COPPER FCC CUBIC CELL OPTIMIZATION OUTPUT

Program PWSCF v.7.0 starts on 6Mar2024 at 13:31:16

This program is part of the open-source Quantum ESPRESSO suite for quantum simulation of materials; please cite

"P. Giannozzi et al., J. Phys.:Condens. Matter 21 395502 (2009);

"P. Giannozzi et al., J. Phys.:Condens. Matter 29 465901 (2017);

"P. Giannozzi et al., J. Chem. Phys. 152 154105 (2020);

URL <http://www.quantum-espresso.org>",

in publications or presentations arising from this work. More details at

<http://www.quantum-espresso.org/quote>

[...]

the Fermi energy is 14.5791 ev

! total energy = -213.09006327 Ry

total all-electron energy = -3309.969829 Ry

```

estimated scf accuracy < 5.1E-09 Ry
smearing contrib. (-TS) = -0.00091234 Ry
internal energy E=F+TS = -213.08915093 Ry

```

The total energy is F=E-TS. E is the sum of the following terms:

```

one-electron contribution = -23.50780590 Ry
hartree contribution      = 29.04991768 Ry
xc contribution           = -44.68462030 Ry
ewald contribution        = -84.08963293 Ry
one-center paw contrib.   = -89.85700948 Ry

```

convergence has been achieved in 6 iterations

Writing all to output data dir ./temp/cu.save/

[...]

APPENDIX-B.6: *h*BN FCC FIRST AXIS OPTIMIZATION OUTPUT

equation of state: murnaghan. chisq = 0.1127D-04

a0 = 4.7646 a.u., k0 =16774 kbar, dk0 = 3.85 d2k0 = 0.000 emin = -79.72625

a0 = 2.52131 Ang, k0 =1677.5 GPa, V0 = 27.04 (a.u.)^3, V0 = 4.01 A^3

#####

# Lat.Par	E_calc	E_fit	E_diff	Pressure	Enthalpy
# Ang	Ry	Ry	Ry	GPa	Ry

#####

2.09000	-78.95421	-78.95532	0.00111	3362.47	-75.43369
2.39000	-79.68514	-79.68206	-0.00308	372.27	-79.10229
2.49000	-79.72821	-79.72403	-0.00418	67.65	-79.60844
2.59000	-79.71147	-79.71669	0.00522	-116.30	-79.94321
3.49000	-78.66470	-78.66563	0.00093	-426.01	-80.74156

APPENDIX-B.7: *h*BN FCC SECOND AXIS OPTIMIZATION OUTPUT

```
# equation of state: murnaghan.      chisq = 0.1020D-08
# a0 = 16.3030 a.u., k0 = 0 kbar, dk0 = 4.39 d2k0 = 0.000 emin = -79.72867
# a0 = 8.62719 Ang, k0 = 0.1 GPa, V0 = 1083.29 (a.u.)^3, V0 = 160.53 A^3
#####
# Lat.Par      E_calc      E_fit      E_diff      Pressure      Enthalpy
# Ang          Ry          Ry          Ry          GPa          Ry
#####
6.03000      -79.71700      -79.71699      -0.00001      1.70          -79.67413
6.53000      -79.72394      -79.72397      0.00003      0.59          -79.70519
6.63000      -79.72476      -79.72476      0.00000      0.48          -79.70879
6.73000      -79.72544      -79.72542      -0.00002      0.39          -79.71183
7.63000      -79.72822      -79.72818      -0.00003      0.06          -79.72505
8.63000      -79.72861      -79.72867      0.00006      -0.00         -79.72861
9.63000      -79.72848      -79.72845      -0.00003      -0.01         -79.72968
```

APPENDIX-C: RAW DATA TABLES

APPENDIX-C.1: TABULATED RESULTS AND ENERGIES SPREADSHEET

Lay out	Label	Description	State	DFT (Ry)	ZPC (Ry)	Hvib (Ry)	T*Svib (Ry)	Gibbs (Ry)	Gases?	Gas (Ry)	Gas ZPC (Ry)	Gas Gibbs (Ry)	Total DFT (Ry)	Total Gibbs (Ry)	dE (Ry)	dE (kJ/mol)	dG (Ry)	dG (kJ/mol)
-	-	CH3OH (g)	CH3OH (g)	-64.81	0.10	0.004	0.004	-64.71	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
-	-	CO (g)	CO (g)	-60.01	0.01	0.004	0.005	-60.00	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
-	-	H2 (g)	H2 (g)	-2.33	0.02	0.006	0.007	-2.31	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
-	-	H (g)	H (g)	-0.93														
-	-	CH2O (g)	CH2O (g)	-62.39	0.06	0.006	0.006	-62.33	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
-	-	N2 (g)	N2 (g)	-56.43	0.01	0.003	0.004	-56.42	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
B	GS0	Surf + CH3OH(g)	GS0	-839.00	0.00	0.00	0.00	-839.00	CH3OH	-64.81	0.10	-64.71	-903.81	-903.71	0.0	0	0.0	0
B	GS1	CH3OH*	GS1	-903.85	0.11	0.01	0.01	-903.75	No	0	0	0	-903.85	-903.75	0.0	-54	0.0	-50
B	TS12		TS12	-903.70	0.10	0.01	0.01	-903.60	No	0	0	0	-903.70	-903.60	0.1	153	0.1	144
B	GS2	CH3O* + H*_Cu	GS2	-903.71	0.10	0.01	0.01	-903.61	No	0	0	0	-903.71	-903.61	0.1	137	0.1	132
B	GS3	CH3O* + H*	GS3	-903.84	0.11	0.01	0.01	-903.74	No	0	0	0	-903.84	-903.74	0.0	-38	0.0	-34
B	ts34_v2		TS34	-903.75	0.10	0.01	0.01	-903.66	No	0	0	0	-903.75	-903.66	0.1	78	0.1	69
B	GS4_b3	CH2O* + H* +	GS4	-903.77	0.10	0.01	0.01	-903.67	No	0	0	0	-903.77	-903.67	0.0	58	0.0	52
B	ts45_v2		TS45	-903.72	0.10	0.01	0.01	-903.63	No	0	0	0	-903.72	-903.63	0.1	117	0.1	109
B	GS5_n1	CH2O* + 2H*	GS5	-903.97	0.11	0.01	0.01	-903.86	No	0	0	0	-903.97	-903.86	-0.2	-207	-0.2	-199
B	GS6	CH2O*	GS6	-901.42	0.06	0.01	0.01	-901.36	H2	-2.333	0.020	-2.314	-903.75	-903.67	0.1	80	0.0	48
B	TS67	CHO* + H*_Cu	TS67	-901.33	0.05	0.01	0.01	-901.28	H2	-2.333	0.020	-2.314	-903.66	-903.59	0.2	198	0.1	156
B	GS7	CHO* + H*	GS7	-901.45	0.06	0.01	0.01	-901.39	H2	-2.333	0.020	-2.314	-903.79	-903.71	0.0	32	0.0	3
B	TS78		TS78	-901.36	0.05	0.01	0.01	-901.31	H2	-2.333	0.020	-2.314	-903.70	-903.62	0.1	153	0.1	114
B	GS8	CO* + 2H*	GS8	-901.51	0.07	0.01	0.00	-901.44	H2	-2.333	0.020	-2.314	-903.84	-903.76	0.0	-40	0.0	-59
B	GS9	CO* and 2H2(g)	GS9	-899.06	0.04	0.00	0.00	-899.02	2H2	-4.666	0.041	-4.628	-903.73	-903.65	0.1	110	0.1	84
B	GS10	Surf + CO(g) +	GS10	-839.00	0.00	0.00	0.00	-839.00	CO + 2H2	-64.677	0.053	-64.627	-903.67	-903.62	0.1	181	0.1	113
B	CH2O	CH2O (g) + H2 (g)		-839.00	0.00	0.00	0.00	-839.00	CH2O+H2	-64.719	0.076	-64.645	-903.72	-903.64	0.1	126	0.1	89
N	GS0	Surf + CH3OH(g)	GS0	-822.17	0	0	0	-822.17	CH3OH	-64.815	0.102	-64.713	-886.99	-886.88	0.0	0	0.0	0
N	GS1	CH3OH*	GS1	-887.06	0.11	0.01	0.01	-886.95	No	0	0	0	-887.06	-886.95	-0.1	-99	-0.1	-92
N	TS12		TS12	-886.98	0.09	0.01	0.01	-886.88	No	0	0	0	-886.98	-886.88	0.0	11	0.0	-1
N	GS2	CH3O* + H*_Cu	GS2	-887.11	0.10	0.01	0.01	-887.01	No	0	0	0	-887.11	-887.01	-0.1	-160	-0.1	-163
N	GS3_b5	CH3O* + H*	GS3	-887.01	0.10	0.01	0.01	-886.90	No	0	0	0	-887.01	-886.90	0.0	-28	0.0	-27
N	ts35_v2		TS35	-886.89	0.09	0.01	0.01	-886.80	No	0	0	0	-886.89	-886.80	0.1	129	0.1	114
N	GS5_b1	CH2O* + 2H*	GS5	-886.94	0.10	0.01	0.01	-886.84	No	0	0	0	-886.94	-886.84	0.0	64	0.0	56
N	GS6	CH2O*	GS6	-884.66	0.06	0.01	0.01	-884.60	H2	-2.333	0.020	-2.314	-886.99	-886.92	0.0	-12	0.0	-42
N	TS67	CHO* + H*_Cu	TS67	-884.57	0.05	0.01	0.01	-884.51	H2	-2.333	0.020	-2.314	-886.90	-886.83	0.1	113	0.1	75
N	GS7	CHO* + H*	GS7	-884.68	0.06	0.01	0.01	-884.62	H2	-2.333	0.020	-2.314	-887.01	-886.94	0.0	-32	-0.1	-69
N	TS78		TS78	-884.63	0.05	0.01	0.01	-884.59	H2	-2.333	0.020	-2.314	-886.97	-886.90	0.0	23	0.0	-22
N	GS8	CO* + 2H*	GS8	-884.74	0.05	0.01	0.01	-884.69	H2	-2.333	0.020	-2.314	-887.07	-887.00	-0.1	-110	-0.1	-154
N	GS9	CO* and 2H2(g)	GS9	-882.25	0.05	0.00	0.00	-882.20	2H2	-4.666	0.041	-4.628	-886.91	-886.83	0.1	94	0.1	70
N	GS10	Surf + CO(g) +	GS10	-822.17	0.00	0.00	0.00	-822.17	CO + 2H2	-64.677	0.053	-64.627	-886.85	-886.80	0.1	181	0.1	113
N	CH2O	CH2O (g) + H2 (g)		-822.17	0.00	0.00	0.00	-822.17	CH2O+H2	-64.719	0.076	-64.645	-886.89	-886.82	0.1	126	0.1	89