

**Modified Silica Supported Catalyst for 1,3-Butadiene
Production via Oxidative Dehydrogenation (ODH) of n-
Butane**

BY

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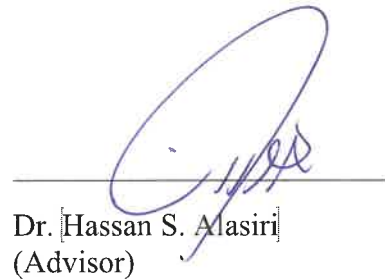
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[This project is dedicated to my loving parents, Engr. A.O. Lawal and Mrs. M.K. Lawal
for their unflinching love and support; and to all my teachers]

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LIST OF ABBREVIATIONS

AI	: Artificial Intelligence
ANN	: Artificial Neural Networks
BD	: 1,3-Butadiene
BET	: Brunauer–Emmett–Teller
DH	: Dehydrogenation
DDH	: Direct Dehydrogenation of n-Butane
FID	: Flame Ionization Detector
FR	: Feed Ratio
FS	: Fibrous Silica
GBR	: Gradient Boosting Regression
GC	: Gas Chromatograph
HRTEM	: High Resolution Transmission Electron Microscopy
ML	: Machine Learning
NuSVR	: Support Vector Regression with Nu Parameter
OC	: Oxygenate and Cracking
ODHB	: Oxidative Dehydrogenation of n-Butane
ODP	: Oxidative Dehydrogenation of Propane
PO	: Partial Oxidation
SAED	: Selected Area Electron Diffraction
SEM	: Scanning Electron Microscopy

TEM	: Transmission Electron Microscopy
TCD	: Thermal Conductivity Detector
TPD	: Temperature Programmed Desorption
TPR	: Temperature Programmed Reduction
XGBR	: eXtreme Gradient Boosting Regressor
XPS	: X-ray Photoelectron Spectroscopy
XRD	: X-ray Diffraction

ABSTRACT

Full Name : [Ridhwan Adedayo Lawal]

Thesis Title : [Modified Silica Supported Catalyst for 1,3-Butadiene Production via Oxidative Dehydrogenation (ODH) of n-Butane]

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The global 1,3-butadiene (BD) market is on a rising trajectory, with an expected value of about \$11 billion by 2027, driven mainly by the escalating demand from the automotive industry. Given this promising market outlook, this project was devised with a dual-pronged approach in effective catalyst development for on-purpose BD production. In the first approach, a novel fibrous silica (FS) supported bimetallic metal oxide catalyst is synthesized and investigated for the on-purpose production of BD via oxidative dehydrogenation of n-Butane (ODHB). Secondly, Artificial Intelligence (AI) techniques are employed to predict the dehydrogenation yield of mixed-metal oxide catalysts for ODHB. Specifically, Artificial Neural Networks (ANN), Support Vector Regression with Nu Parameter (NuSVR), eXtreme Gradient Boosting Regressor (XGBR), and Gradient Boosting Regression (GBR) machine learning algorithms were trained with a dataset of consistent experimental data to build chemometric models using reaction condition (temperature and oxygen to n—butane feed ratio) and metal composition of the catalyst as input features. The fibrous silica support was synthesized via the sol-gel hydrothermal technique, with metals anchored on the support through the wet co-impregnation method, to obtain 5 different catalysts with Ni wt.% loading ranging from 10 - 20% and Bi wt.% loading ranging from 10 - 30%. The as synthesized catalysts were characterized to assess

their properties using techniques including XRD, BET, TPR, SEM, TEM and XPS. The catalysts' performance for ODHB were investigated at temperatures ranging from 400 – 500 °C and oxygen to n-butane feed ratios from 1-4 using a fully integrated fixed-bed continuous flow reactor (BELCAT) system. The reaction products were analysed using an online GC system, and the conversion and selectivity were determined based on carbon balance. The 20Ni-10Bi/FS demonstrated the best performance with a butadiene yield of up to 20 % at 500 °C and O₂: n-C₄ ratio of 1. The developed AI models accurately predict the performance of the mixed metal oxides catalysts for ODH of n-butane, with prediction accuracy of 82%, 89%, 92%, and 95% using ANN, NuSVR, XGBR, and GBR models, respectively. Feature importance analysis also revealed that the amount of Ni loading in the catalyst(s) has the greatest influence on the yield of butenes and butadiene.

ملخص الرسالة

الاسم الكامل: رضوان لوال

عنوان الرسالة: السيليكا المعدلة المحفز المدعوم لإنتاج^٣، البيوتادين عبر التحميص التأكسدي للن بيوتان

التخصص: هندسة كيميائية

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في مسار صاعد، حيث تبلغ قيمته المتوقعة حوالي 11 مليار (BD) يسير السوق العالمي لمركب 1.3 بيوتادين" دولار بحلول عام 2027، مدفوعاً بشكل أساسي بالطلب المتزايد من صناعة السيارات. ونظراً لهذه التوقعات الواعدة حسب الغرض. في BD للسوق، فقد تم تصميم هذا المشروع باتباع نهج مزدوج في تطوير المحفز الفعال لإنتاج ودراسته من أجل (FS) النهج الأول، يتم تصنيع محفز أكسيد الفلز ثنائي المعدن الجديد المدعوم من السيليكا الليفية ثانياً، يتم استخدام تقنيات (ODHB) n-Butane حسب الغرض عن طريق نزع الهيدروجين التأكسدي لـ BD إنتاج على وجه ODHB. للتنبؤ بإنتاجية نزع الهيدروجين لمحفزات أكسيد المعادن المختلطة لـ (AI) الذكاء الاصطناعي Nu ودعم الانحدار المتجه باستخدام معلمة (ANN) التحديد، تم تدريب الشبكات العصبية الاصطناعية وخوارزميات التعلم الآلي لتعزيز (XGBR) وخوارزميات التعلم الآلي لتعزيز التدرج الشديد (NuSVR) باستخدام مجموعة بيانات من البيانات التجريبية المتسقة لبناء نماذج كيميائية. باستخدام حالة (GBR) الانحدار التفاعل (درجة الحرارة والأكسجين إلى نسبة تغذية البوتان) والتركيب المعدني للمحفز كميزات إدخال. تم تصنيع الحرارية المائية، مع تثبيت المعادن على الدعامة من خلال طريقة التشريب sol-gel دعامة السيليكا الليفية عبر تقنية Bi wt.٪ بالوزن٪ يتراوح بين 10 - 20٪ و Ni المشترك الرطب، للحصول على 5 محفزات مختلفة مع تحميل XRD، التحميل يتراوح من 10 - 30٪. تم توصيف المحفزات المصنعة لتقييم خواصها باستخدام تقنيات تشمل عند درجات حرارة تتراوح بين ODHB تم فحص أداء المحفزات لـ XPS، و TEM، و SEM، و TPR، و BET و درجة مئوية ونسب تغذية الأكسجين إلى البيوتان من 1-4 باستخدام نظام مفاعل التدفق المستمر ذو 400 - 500 عبر الإنترنت، وتم GC تم تحليل منتجات التفاعل باستخدام نظام (BELCAT) الطبقة الثابتة المتكامل بالكامل أفضل أداء مع إنتاجية بوتادين تصل Ni-10Bi/FS تحديد التحويل والانتقائية بناءً على توازن الكربون. أظهر 20 تبلغ 1. كما تتنبأ نماذج الذكاء الاصطناعي التي تم تطويرها بدقة O₂:n-C₄ إلى 20٪ عند 500 درجة مئوية ونسبة البيوتان، بدقة تنبؤ تبلغ 82٪، 89٪، 92٪، و 95٪ باستخدام n- ODHB بأداء محفزات أكاسيد الفلزات المختلطة على التوالي. كشف تحليل أهمية الميزة أيضاً أن كمية تحميل GBR، و XGBR، و NuSVR، و ANN نماذج النيكل في المحفز المحفزات لها التأثير الأكبر على إنتاجية البيوتين والبوتادين

CHAPTER 1

INTRODUCTION

Light alkane dehydrogenation is a process that involves the elimination of hydrogen atoms from short chain paraffins. This results in the formation of alkene and/or alkyne compounds which have greater reactivity and more diverse uses than alkanes. This process is particularly significant as a method for upgrading low-value raw materials into higher-value chemicals. The short-chain olefins obtained serve as primary raw material for chemical industries, enabling a production of a diverse array of consumer and industrial products. These include synthetic rubber, fuels, plastics, fertilizers, synthetic fibers, paints, and detergents. Utilizing light olefins as foundational components for the production of chemicals is particularly attractive because they are abundant, inexpensive, and environmentally friendly resources [1].

Traditionally, naphtha cracking and catalytic cracking of heavier feedstock like VGO (Vacuum Gas oil) are the dominant processes for the production of olefins. Cracking which involves the breaking down of long chain hydrocarbon molecules constitutes a significant majority, taking over 60% of the world's total production of ethylene, which is the most widely used olefin. Cracking is a common industrial process that is not limited to ethylene production alone. It serves as a common industrial technique for generating various other valuable olefins, including propylene and butenes. By subjecting the

feedstocks to controlled thermal or catalytic conditions, these processes facilitate the conversion of larger hydrocarbon molecules into smaller, more useful olefinic compounds. However, the yields of these olefins are contingent upon the nature of the feedstock and the operating conditions [2]–[4].

The increased production of ethylene has caused many on-purpose higher alkane production units to shut down. This is because the use of ethane as a feedstock in steam cracking, due to its lower cost and greater availability from natural gas, results in a decreased supply of butadiene and propylene as ethane yields relatively lower amounts of these compounds. The shale gas revolution is expected to further increase this trend [5].

The catalytic direct dehydrogenation (DDH) of propane to propene, as well as n-butane to butadiene, has served as an alternative to the cracking process, providing a more reliable and consistent source of olefins with environmental benefits compared to the traditional steam cracking processes, which can be affected by changes in the availability and quality of feedstocks [1], [6]. DDH of n-butane and propane has been commercialized, however the process is highly endothermic requiring temperatures in the excess of 600 °C [7], [8]. The high operating temperatures exposes the system to high risk of coke formation that comes with the extra burden of frequent catalyst regeneration. Ultimately, DDH is an energy-intensive process that necessitates the use of high temperatures to achieve acceptable conversion rates and selective olefin yields.

To reduce these risks associated with high operating temperatures in DDH, it becomes necessary that alternative catalysts or operating conditions that can achieve the industrially relevant conversion and selective olefin yields at lower temperatures. Oxidative dehydrogenation (ODH) process is an attractive solution that offers several

distinct advantages compared to the traditional DDH processes. Unlike the conventional dehydrogenation, ODH is not limited thermodynamically hence allowing for it to proceed at a relatively lower reaction temperature. In addition, catalyst deactivation by coke deposition is tempered due to the presence of oxygen [9]–[11]. This makes ODH a compelling choice for industrial application as it reduces energy requirements, reduces operational cost, improves catalyst life and improves operational safety.

Nevertheless, the development of selective and industrially relevant catalysts for propane oxidative dehydrogenation (ODP) and n-butane oxidative dehydrogenation (ODHB) poses a challenge. The objective is to produce propene and butadiene, respectively, while minimizing the generation of undesirable secondary or parallel products like carbon oxides and coke derived from deep oxidation. The challenge lies in designing catalysts that can promote the desired selective dehydrogenation reactions while suppressing the undesired side reactions. Achieving high selectivity towards propene and butadiene is crucial to enhance the overall efficiency and economic viability of the ODP and ODHB processes. Also, it is important that the developed catalysts demonstrate excellent activity and long-term stability during extended operational durations[1], [12].

Several catalysts have been explored for propane oxidative dehydrogenation [9], [12], [13] and n-butane oxidative dehydrogenation [1], [14]–[17]. Many of the catalysts even with the high activity that favors the yield of dehydrogenation products only give low selectivities of propylene for ODP and 1,3-butadiene for ODHB at best. The low selectivities are due to the formation of undesirable parallel and secondary products that result in lower selectivities for the desired propylene and 1,3-Butadiene (BD). Enhancing the selectivity of these catalysts is crucial to improve the overall efficiency and economic

viability of the light paraffin ODH. Hence, the focus for most of the research has been to explore novel catalyst formulations and strategies to enhance selectivity while maintaining high activity. The aim is to design catalysts that can effectively control the reaction pathways, promote the desired dehydrogenation reactions, and minimize the unwanted by-products formation.

The type of the support material used plays a significant role in influencing both the selectivity and activity of the catalyst used for dehydrogenation [18]–[20]. In the work by Tanimu et al., [19] for instance, several supports which include silica, alumina, and zincronia were investigated for BD production via ODHB using a Ni-Bi-O catalyst. The researchers found that the type of support material had a profound impact on the selectivity and activity of the catalyst. Silica support demonstrated the highest performance (activity and selectivity) towards butadiene production, indicating that the presence of the silica support greatly enhances the efficiency of the Ni-Bi-O catalyst in promoting the desired dehydrogenation reaction while minimizing unwanted side reaction. The observed performance was explained by the decreased oxygenate activity due to better dispersion of the active species enabled by the large surface area and reinforced interaction between active catalyst component and support.

Silica stands out as a remarkable support material for catalysts, possessing several advantageous properties. It is known for its inert nature, affordability, and versatility in shaping into various appealing morphologies. Among these morphologies, fibrous silica and mesoporous silica deserve special attention due to their exceptionally high surface areas. The high surface area of fibrous and mesoporous silica supports offers significant benefits in catalysis. Firstly, it enhances the accessibility of the catalytically active sites,

allowing for efficient interaction between the reactant molecules and the catalyst. This increased accessibility promotes higher reaction rates and improved overall catalytic performance. Additionally, using silica as a support material helps mitigate the issue of particle sintering [21], [22]. These improvements in properties have been demonstrated to significantly enhance catalyst performance [23].

1.1 Industrial Technologies

The endothermic dehydrogenation reaction necessitates elevated reaction temperatures (600-700 °C) to achieve industrially relevant conversion. However, operating at such elevated temperatures presents several challenges. The elevated temperatures give rise to numerous undesirable parallel reactions, such as cracking and other secondary reactions. These other reactions not only reduce the selectivity of the desired olefin but also lead to the formation of unwanted by-products, affecting the overall process efficiency. To address these challenges effectively, it is crucial to develop catalysts that exhibit high selectivity and stability under the prevailing operating conditions.

In industrial settings, dehydrogenation reactions are commonly conducted using transition metals such as vanadium, chromium, platinum, and tin supported on alumina as catalysts. Alumina is a commonly preferred support material for the reaction compared to other support materials such as titania, silica and zirconia due to its alumina's excellent mechanical strength, thermal stability, and its unique characteristics that facilitate catalyst re-generations [24]. However, it is important to consider some potential drawbacks associated with alumina, particularly the presence of acidic sites. These acidic sites on alumina can promote unwanted reactions, like cracking and isomerization, leading to the formation and deposition of coke [25].

Currently, there exist a range of commercial processes available for light paraffin dehydrogenation. These processes utilize mainly platinum-based catalysts and chromia/alumina catalysts. The Oleflex, the Linde/BASF PDH and the STAR, are examples of processes that use platinum-based catalysts. The FBD process and the CATOFIN process employ chromia/alumina catalysts. Each process has its own advantages and disadvantages, such as differences in efficiency, cost, and environmental impact [24]. Table 1.1 summarizes these commercialized dehydrogenation technologies, including catalysts used, reactor types, reaction conditions, and reported selectivities (S) and conversions (X) .

Table 1.1: Commercial Propane and Butane DDH Processes

Process	STAR	Catofin	FBD	Oleflex	Linde/BASF
Catalyst	Pt/Sn/Zn/Ca/Al	CrO _x /Al ₂ O ₃	CrO _x /Al ₂ O ₃	Pt/Sn/Al ₂ O ₃	Pt-Sn/Zr
T/°C	550-590	590-650	550-600	550-620	500-600
P (bar)	1.1-1.5	0.3-0.5	5-6	2-5	>1
Propane X/ mol %	40	48-65	40	25	30
n-Butane X/ mol %	-	60-65	50	35	-
Propene S/ Mol %	89	82-87	89	89-91	90
iso-Butene S/ Mol %	-	93	91	91-93	-

1.2 Aim and Objectives

This research aims to improve the oxidative dehydrogenation of n-butane to produce butadiene by developing novel catalysts. Specifically, it focuses on on modifying silica support material for nickel-bismuth bimetallic oxide catalysts to create a fibrous morphology with a high surface area. Additionally artificial intelligence techniques are employed in the study to predict the performance of catalysts in in oxidative dehydrogenation of n-butane.

Objectives:

- To synthesize Fibrous silica support with increased surface area using a microemulsion method.
- To prepare a range of catalysts with varying nickel and bismuth loadings from 10 - 20% and 10 – 30% respectively on the fibrous silica support.
- In order to analyze the catalysts and assess their physical and chemical properties, characterization techniques including XRD, BET, SEM, and TPR would be carried out to determine metal dispersion, pore size distribution and surface area, surface characteristics as well as reducibility respectively.
- Performance evaluation of the synthesized catalysts in the ODHB using a fixed-bed reactor.
- To compare the performance of the synthesized catalyst supported on modified silica in terms of the n-butane conversion and butadiene selectivity.
- To develop and optimize machine learning models based on experimental data to predict the dehydrogenation yield of ODHB using supported mixed metal catalysts.

1.3 Scope

This work is limited to the synthesis of the catalysts supported on fibrous silica; characterization of the catalysts in order to assess their chemical and physical properties; and evaluation of the catalysts' performance in ODHB for butadiene production. Artificial Neural Networks (ANN), Support Vector Regression with Nu Parameter (NuSVR), eXtreme Gradient Boosting Regressor (XGBR), and Gradient Boosting

Regression (GBR) machine learning algorithms would be trained with a dataset of consistent experimental data to build chemometric models to predict dehydrogenation yield using reaction temperature, feed ratio and metal loading compositions as input features.

CHAPTER TWO

LITERATURE REVIEW

2. Dehydrogenation Process Overview

The dehydrogenation of light alkanes plays a crucial role in the production of valuable chemicals and the development of sustainable energy sources. The process of converting light alkanes into more valuable compounds contributes to the development of a more sustainable and resource-efficient chemical industry while also supporting the transition towards cleaner and greener energy alternatives. Dehydrogenation converts alkanes (paraffins) to alkenes (olefins) by removing hydrogen from the alkane molecule [26]. In recent years, there has been considerable interest in the dehydrogenation of light paraffins due to its potential for the production of valuable chemicals and the development of more sustainable energy sources. In the petrochemical industry, this process finds extensive application for the production of olefins, which are primary raw materials utilized in the manufacturing of various chemical products, which include plastics, synthetic fibers, and rubber [1]

The dehydrogenation process is characterized by its endothermic nature, requiring high operating temperatures ranging from 500 to 700 °C, and low pressures typically between

0.1 and 1 atm. However, this process is not without its challenges. One of the main challenges arises from the occurrence of undesired side reactions during the process as the dehydrogenation reaction is often accompanied by undesired side reactions, such as cracking of the alkene product, leading to the formation of unwanted by-products like methane and ethylene [27]. These by-products can hinder the efficiency and selectivity of the process, requiring careful consideration and optimization to mitigate their formation and enhance the overall performance of the dehydrogenation process. A representative example of the dehydrogenation of alkanes can be depicted by the equation:



Oxidative dehydrogenation (ODH) however, is a variation of the dehydrogenation process that involves the use of an oxidizing agent, such as air (oxygen) or more recently CO_2 [18], [28], [29], to facilitate the elimination of hydrogen from the alkane molecule. As proven by the overall lower Gibbs energy of the products, the products for ODH are thermodynamically more stable than those obtained via direct dehydrogenation. Hence, the ODH process can proceed at relatively lower reaction temperatures, typically between 350 °C and 550 °C, with lower pressures, typically between 0.1 and 0.5 atm, than traditional dehydrogenation [1], [11]. ODH has several other advantages over traditional dehydrogenation, including higher selectivity towards the desired alkene product, lower energy consumption, and reduced deposition of carbon on the catalyst surface. A representative example of the ODH of paraffins can be depicted by the equation:



Controlling the selectivity of the oxidative dehydrogenation (ODH) reaction for light alkanes poses a significant challenge. When light paraffins are subjected to ODH, the

reaction can yield not only olefins but also undesirable by-products such as carbon dioxide, carbon monoxide, and soot. Enhancing the selectivity of the reaction becomes crucial to industrial applications. This can be achieved by employing catalysts that effectively promote the desired reaction pathway while suppressing the formation of undesired by-products. Catalysts capable of selectively producing olefins are particularly valuable in this regard. In order to promote the selectivity of the dehydrogenation products, ODH of light alkanes is typically carried out using heterogeneous catalysts. The catalysts used for this process are typically metal based (transition metals and noble metals), such as nickel [19], platinum [30], Boron [31], [32], chromium[33] mixed metal oxides, such as those containing molybdenum[34], [35] and vanadium [18], [36] and are supported on various materials, such as alumina [37], silica [20], and zeolites [38] using ODP as a typical example.

2.1 Experimental Studies in Oxidative Dehydrogenation of Butane

Experimental studies on ODHB have been an active research area for several decades [26]. Literature reports generally suggest that butene selectivity values for diverse catalytic systems display a maximum limit of 50-60% at conversions exceeding 20%. However, the selectivity spectrum varies from 0 up to 100% and depends on the catalyst type and reaction conditions that were applied. The butene selectivity is observed to increase steeply only at very low conversion rates that are not industrially relevant as depicted in Figure 2.1[1].

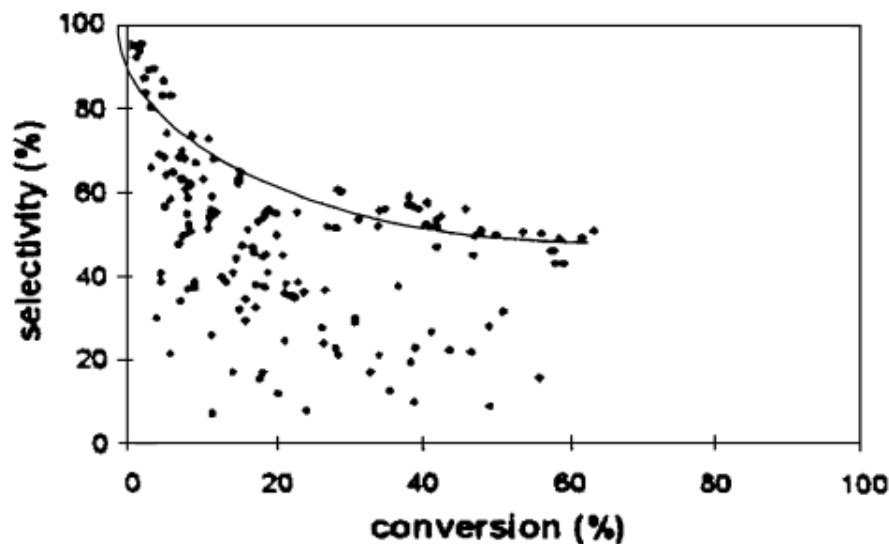


Figure 2. 1: C4 olefin selectivity versus conversion for n-Butane oxidative Dehydrogenation Reactions, adapted from [1]

One of the early studies on this topic was conducted by Shenoy and Rao [39]. The authors explored the properties of Bismuth Molybdate – Aluminium phosphate catalysts for ODHB. Their findings showed early on that metal oxide catalysts were promising candidates for the conversion of light alkanes to corresponding alkenes from the high conversion and selectivity that they demonstrated. This study served as an important milestone in understanding the potential of these metal oxides as catalysts in the ODH.

In subsequent studies, researchers have focused on optimizing the composition of catalysts and refining the reaction conditions to enhance the overall efficiency of the dehydrogenation process. A notable area of exploration has been the investigation of mixed metal oxide catalysts [40], [41]. Tanimu et al. [40] conducted a comprehensive investigation into the use of mixed metal oxides, specifically the (Ni, Fe, Co)-Bi- oxide species supported on γ -Al₂O₃ catalyst for ODHB. Their research revealed that the mixed oxide catalysts displayed superior performance compared to single metal oxide catalysts. Additionally, substituting Ni with Fe and Co partially led to improvements in both

activity and selectivity of the catalysts. Furthermore, by substituting nickel (Ni) with iron (Fe) and cobalt (Co), notable enhancements in both catalyst activity and selectivity were achieved. Of particular interest was the catalyst composition consisting of 10 wt.% Ni, 5 wt.% Co, 5 wt.% Fe, and 30 wt.% Bi-O/ γ -Al₂O₃ demonstrated an excellent n-butane conversion of 30% and BD selectivity of 46.3% . These findings highlight the promising potential of mixed metal oxide catalysts for efficient ODHB processes.

In addition to catalyst composition, there has also been increased interest in developing catalysts that can operate under mild conditions, such as lower oxygen: butane ratios and temperatures for oxidative dehydrogenation of butane. This is because conventional metal oxide catalysts require high temperatures and pressures to achieve high conversion and selectivity, which can result in operational inefficiencies. To address this issue, researchers have explored the use of alternative catalytic systems, such as carbon nanotubes [42], [43] and other pure and modified carbonaceous materials [44], [45], as catalysts for ODHB. These materials have shown promising performance, while also providing a more sustainable and cost-effective alternative to conventional metals/metal oxide catalysts.

Moreover, some researchers have also explored the use of an alternative oxidants for ODHB [46], such as carbon dioxide (CO₂) which has the potential to be a greener alternative as it utilizes CO₂ as a reactant, thus mitigating its contribution to global warming [29], [38], [47]. Use of some other oxidising agents have also been investigated like nitrous oxide (N₂O) [48], [49]. Utilization of these oxidants is attractive and can provide a more environmentally friendly and sustainable alternative to conventional oxidants like oxygen. For example, Ovsitser and Kondratenko [48] investigated the use of

dispersed VO_x/MCM-41 catalyst for ODH of light paraffin using N₂O and O₂ as the oxidants. They found that replacing O₂ with N₂O improved olefin selectivity specifically for ODHB with the formation of carbon oxides significantly suppressed.

Another trend in ODHB research has been the study of how the type of reactor used for the process affects the yield and product distribution, the type of reactor used can offer several advantages [50]. Soler and co-workers [51] conducted a comprehensive study to examine the influence of reactor type on ODHB over V/MgO catalysts. The authors compared a fluidized-bed (FBR), an in situ redox fluidized-bed (IRFBR) and adiabatic fixed-bed reactors. They showed that the performance increased in that order. Best performance was obtained using the in situ redox fluidized bed reactor where 1,3-butadiene selectivity up to 44% was recorded at a conversion of 58% and relatively low reaction temperature of 550 °C showing that high selectivities to 1,3-butadiene can be obtained if good separation between the reduction and oxidation zones is achieved. These findings underscore the significance of selecting an appropriate reactor type to optimize the performance of the ODH process.

In addition to experimental studies, multiscale modelling and computational modeling have also been used to gain deeper insights into the mechanisms and catalyst properties associated with the oxidative dehydrogenation of butane [52]–[54]. A recent review by Skubic et al [55], presents the most influential efforts towards multiscale modelling light alkane dehydrogenation reactions.

Overall, the studies on ODHB have yielded notable advancements in elucidating the catalytic properties of metals/metal supported on diverse materials. These studies have not only contributed to the development of better performing catalysts for ODHB, but

also provided insights into the optimization of reaction conditions for enhanced performance. In the following section extensive literature on various metal groups employed as catalysts for ODHB and ODP in numerous studies will be discussed, outlining their distinct characteristics, advantages, and limitations in terms of their performance for these target reactions. By examining the strengths and weaknesses of each metal group, we can gain valuable insights into the design and selection of catalysts for these industrially significant processes.

2.2 Noble Metal Catalysts for Light Paraffin ODH

The catalysts in this group use noble metals, such as platinum, palladium, and rhodium, as active species, which are highly efficient in combustion. Under certain conditions however, such as reduced contact times and minimal oxygen supply noble metal catalysts can facilitate the dehydrogenation of alkanes. However, it is worth noting that at lower temperatures, the selectivity of noble metals may not be optimal for this process. Nevertheless, these noble metal catalysts can be effectively utilized for selective oxidation reactions at higher temperatures, typically reaching 1000 °C [56]. Platinum is the most widely used noble metal catalyst for the oxidative dehydrogenation of light alkanes. There are a few reported cases of other noble metals demonstrating excellent activity for example palladium in n-butane dehydrogenation [57]. Platinum has several advantages over other noble metals including lower cost, high thermal stability, and resistance to poisoning by sulfur-containing compounds which makes it suitable for use in harsh industrial environments.

Although platinum catalysts have been used for direct catalytic dehydrogenation (DDH) of n-butane with selectivities of up to 96% [58], they are not as promising for 1,3-

butadiene production via ODH of n-butane. However, excellent performances have been noticed for ODH of propane as seen in Table 2.1. The selectivity of propene can be enhanced through several strategies, including increasing the alkane-oxygen ratio, elevating the reaction temperature, or incorporating suitable promoters like tin [59]. These approaches contribute to achieving nearly complete conversion of oxygen, albeit with the drawback of catalyst deactivation primarily caused by coking and sintering [60]. To address this challenge, the integration of active noble metals within a passive support material proves beneficial. The support layer plays a crucial role in mitigating catalyst deactivation by limiting deep oxidation reactions, preventing metal sintering, and minimizing coke formation at elevated temperatures. By providing a protective environment and promoting catalyst stability, the passive support enables prolonged catalytic activity and enhances the overall performance of the system.

2.3 Non-Noble Metal Catalysts for Light Paraffin ODH

The research on use of non-noble metal as catalysts for ODH of light paraffins has been ongoing in recent years, driven by the need to lower the cost and increase the sustainability of this process. This category mainly comprises redox-type catalysts that use heterogeneous redox-type mechanisms and are based on reducible metal oxides. Popular in this group is the use of supported transition metal oxides, where the active species oxidizes an alkane's C-H bond and is then re-oxidized by O₂ to return to an active state [61]. Vanadia-based catalysts for example are known to easily switch between +III and +V oxidation states, and this ability accounts for their observed catalytic activity. However, obtaining high selectivity of alkenes with these catalysts remains a great challenge because of the higher reactivity of alkenes compared to alkanes [61]. In this

section some of the major successes recorded in the use of non-noble metals as catalysts for ODH of light alkanes are highlighted [62], [63].

Table 2. 1: Comparison of Supported Platinum Based Catalysts for ODHB and ODP

Catalyst	Reaction Temperature (°C)	Feed Composition	X (%)	Propene Selectivity (%)	CO selectivity (%)	Contact time (min)	Reference
Pt-Sn/SAPO-34	550	C ₄ H ₁₀ :O ₂ = 2:1	70	90 (BD+Propene)	4.41	720	[64]
Pt-Sn/SAPO-34	550	C ₃ H ₈ :O ₂ = 2:1	62.94	97	0.61		[59]
Pt/Sn-CeO ₂			15.1	63.9		240	[65]
0.5Pt-5Sn/Si-beta	550	C ₃ H ₈ /O ₂ =2	48	79	21	-	[66]
Pt/Al ₂ O ₃	650		60	20	48	-	[67]
Pt-SnO ₂ /Al ₂ O ₃ +SiO ₂	700	30% C ₃ H ₆ , 10% O ₂ , 60% N ₂	55	35	5	-	[68]
0.5% Pt+M ₂ P ₂ O ₇ /α-Al ₂ O ₃ (M=Co, Mn)	678	30% C ₃ H ₆ , 10% O ₂ , 60% N ₂	58	33.9	11	GHSV=3 600 h ⁻¹	[68]

X: propane conversion

2.4 Catalysts Based on Oxides of Metals in Transition Series

Compared to noble metals, this category of catalysts provides benefits in terms of the activation of alkanes at lower temperatures, resulting in generally superior performance. The ODH of lower paraffins with metal oxides in the transition series that are supported on a carrier material follows the Mars Van Krevelen mechanism which described in section 2.5. In this mechanism, lattice oxygen within the catalysts is used to oxidize the paraffin, which is then re-oxidized by molecular oxygen in the gas phase [16].

The oxidative dehydrogenation (ODH) process of lower paraffins using metal oxide catalysts supported on carrier materials operates according to the Mars Van Krevelen

mechanism. In this mechanism, the oxygen present within the catalysts' lattice structure participates in the oxidation of the paraffin, which is subsequently re-oxidized by molecular oxygen in the gas phase. The effectiveness of the catalyst is influenced by several factors, including the type of support utilized, the loading and dispersion of the transition metal, and the characteristics of the active oxygen species, as well as the redox properties and acid-base behavior. These factors collectively determine the catalyst's performance and its ability to facilitate the ODH reaction efficiently.

2.4.1 Catalysts Containing Vanadium

Catalysts from group V metals such as Vanadium and their oxides have been intensively investigated for their performance in the ODH of light alkanes over the past years [69], [70]. They have demonstrated excellent performance. The excellent activity of supported VO_x catalysts has been attributed to the ease with which the vanadium species on the catalyst surface can be reduced. This reducibility facilitates the activation of the catalyst and promotes the desired dehydrogenation reactions. The selectivity of the dehydrogenation products on the other hand is influenced by the acid-base property of the catalyst material [71], [72]. Table 2.2 reports the performance comparison of the vanadium-based catalysts for ODH catalyst reported in the open literature.

Wang and co-workers achieved an overall butene selectivity of 57% at n-butane conversion of 47.4% at 550 °C reaction temperature using $\text{VO}_x/\text{MCM-41}$ to catalyze the reaction. Similarly, Xu et al., [73] observed a 30.3% conversion of n-butane at 600 °C using 5%- $\text{V}_2\text{O}_5/\text{MgO-Al}_2\text{O}_3$. In another study by Volpe et al., [74] where VO_x was deposited onto several support materials such as NaY, USY, $\alpha\text{-Al}_2\text{O}_3$, and $\gamma\text{-Al}_2\text{O}_3$ to act as an active metal. Among the catalysts tested, VO_x/USY exhibited superior catalytic

activity with a general selectivity for butenes of 68% and an n-butane conversion of 8.2% at 520 °C. For these analyses, oxygen-free environment in a fixed-bed reactor was employed.

The effect of dopants that improve the catalytic performance of these vanadium-based catalysts on ODHB like molybdenum [75], [76] and Cerium [77] have also been investigated by researchers including Khan and co-workers, [77] , they found that VO_x/γ-Al₂O₃ catalyst modified with cerium will give significantly low levels of coke formation at a 5 seconds reaction time and 450 °C. This results in a butene selectivity of 62.4% at a conversion rate of 10.7%. It is believed that the presence of cerium decreases the acidity of the catalyst thereby limiting coke formation and the potential for deep oxidation reactions. These findings suggest that the catalyst will be well-suited for use in continuous circulating fluidized bed operations. Moreover, the group has also investigated the kinetics of the reactions using the catalyst [78].

Table 2. 2: Comparison of vanadium based catalyst for ODHB

Catalyst	T(°C)	X	S BD (%)	S (%)	Contact time	Ref
Mo-V-MgO(720)*	500-620	64	50.7	-	-	[76]
VO _x /CeO ₂ -γAl ₂ O ₃	575	10.94	2.7	60.5	5	[78]
VO _x /Ce-meso-Al ₂ O ₃	450	10.7	-	62.4	5s	[79]
VO _x /MCM-41	550	47.4	-	57	1h	[80]
V ₂ O ₅ /MgO-Al ₂ O ₃	600	30.3	-	64.3	-	[81]
VO _x /USY	520	8.2	-	68	4 min	[74]

X: n-butane conversion

S: overall selectivity of butenes

S BD: 1,3-butadiene selectivity

* Calcined at 720 °C

For ODP, extensive work has been conducted by the research community to investigate the use of supported vanadium as catalysts [82]. Selective heterogeneous catalysts for ODP have been extensively investigated, leading to the widespread use of catalysts that have the active specie to be vanadium oxide. The activity of the catalysts has been improved over time through studies conducted on the surface mechanism involved [83]. In Table 2.3, performance of some catalysts that have been investigated recently are highlighted.

The VO_x catalysts activity is directly proportional to the amount of V_2O_5 present. Nevertheless, the reaction rates per V-atom attain their highest levels on VO_x domains that are medium size, since it provides a compromise between the surface activity of the VO_x species and their accessibility to reactants. Similarly, selectivity towards the desired alkenes follows the same trend, with an optimal point found for moderate levels of the active phase loading. This is because the monolayer structure of the catalyst is most developed at this point. Additionally, the formation rate of olefins per V-atom is dictated by the surface density of vanadia, which peaks at moderate surface densities [68], [70], [84].

Numerous studies have explored the influence of the support on the performance of VO_x in alkane oxidative dehydrogenation [85]–[88]. Typically, catalysts containing V oxide supported on silica exhibit higher selectivity towards propane ODH than those supported on alumina, and the latter exhibit higher selectivity than those supported on titania. This is primarily due to the reduced extent of parallel combustion reaction (of propane), particularly at low loadings of the active specie (i.e. vanadia), as highlighted by various researchers [87], [89], [90].

The addition of various additives (such as Mo, Zn, Ca, Mg, P, Cr, K, Nb, Ni, and Au) in significant amounts relative to V, can alter the acid-base character and reducibility of supported VO_x catalysts [62], [87], [91]–[93]. These modifications can impact the performance of the catalyst in ODH of light paraffins [91], [92]. In instances where an increase in acid sites is detected, as a result of the addition of electronegative additive ions, the overall activity of the catalyst is enhanced at the expense of selectivity towards the desired olefin. Conversely, the introduction of alkali and alkaline earth additives results in reduced activity but increased selectivity towards propylene in ODP [87], [93].

Table 2. 3: Comparison of ODH of propane from literature using vanadium based catalyst based on conversion (X) and propylene selectivity (S)

Catalyst	T(°C)	X	S (%)	Ref
VO _x /CaO·γ-Al ₂ O ₃ (1:1)	525-600	65.1	85.89	[94]
7.5VO _x /ZrO ₂	550	25	93	[95]
7.5VO _x /γ-Al ₂ O ₃ ZrO ₂	550	28	85	[95]
7.5V/γ-Al ₂ O ₃	500-550	26	90	[73]
VO _x /γ-Al ₂ O ₃	475-550	11.73	85.89	[96]
VO _x /SiO ₂	400-600	26.5	88.3	[97]

In more recent studies, the use of supported vanadium catalysts with oxidants other than O₂ have been investigated such as CO₂ [98] , N₂O [48] CS₂ [99]. While these investigations have generally shown good catalyst performance, catalyst performance comparisons have become more difficult to make due to the differences in catalyst composition and conditions in which the reactions are carried out as reported in the literature, however, some generally excellent performances have been recorded. Nonetheless, researchers such Arinaga and co-workers [99] have reported impressive results, achieving an olefin selectivity of 85% with a propane conversion of 9.4%. They investigated the ODP over 1V/Al₂O₃ catalyst at 550 °C using C₂S as a soft oxidant and

showed how superior catalyst performance was observed with the C₂S oxidant compared to when O₂ was used for the same process.

2.4.2 Catalysts Containing Chromium (Cr)

Supported Cr-based catalysts, such as CrO_x/Al₂O₃ have shown excellent performance in DDH of n-butane and propane for production of the corresponding olefins, this explains why the catalyst have been widely adopted in various industrial processes currently available [24], [100], [101]. As a result, despite the safety concerns associated with handling chromium-based catalysts, researchers are exploring their performance for oxidative dehydrogenation reactions. These catalysts exhibit high thermal stability and can be easily prepared by simple methods. For ODP, a wide range of catalysts have been formulated and tested and the recorded performances are highlighted. For ODHB however, most of the results for the catalysts developed and tested as reported in the literature have high selectivity for isobutene and not 1,3-butadiene [102]–[105]. Therefore, most of the discussion in this section will be on ODP.

An application worthy of note in ODHB however is in a recent study conducted by Zhen-Hong and co-workers [106], the performance of various CrO_x catalysts loaded on CeZr support material for the ODHB process was investigated. It was found that the interaction between the CrO_x species and support material could be affected by CeZrO₂ solid solutions with varying Ce/Zr molar ratios. This suggests that by controlling the Ce/Zr ratio, it is possible to tailor the surface properties and electronic structure of the support material, leading to enhanced catalytic activity and selectivity in various oxidation reactions. The CrO_x species were made up of both Cr³⁺ and Cr⁶⁺ species, and it was determined that the redox Cr⁶⁺ species were important precursors for the formation

of active sites in the ODH process. Amongst the different catalysts tested, 10%CrO_x/Ce_{0.5}Zr_{0.5}O₂ catalyst was found to be the most effective. Utilizing this catalyst with an 11-second contact time resulted in a 25% conversion rate with an impressive 75% 1,3-butadiene selectivity.

Several studies have been conducted on ODP using supported chromium-based catalysts, and the performance of these catalysts has been found to be promising. However, comparing the results in the literature can be challenging because various studies employ different oxidizing agents, reactor type/configurations, catalyst supports, and reaction conditions. Regardless, a general idea of the performance of the reported catalysts relative to one another can be discerned. Table 2.4 highlights the findings of some recent studies.

The effect of varying Chromium content in the catalyst have been investigated [107], [108]. In [107], the authors observed the effect of different chromium loadings from 1 wt% to 12 wt% on the ODP using Cr/Nano-MgO catalyst. Optimal performance was observed at a 5% loading, however they also discovered that the prepared catalyst had formation of Cr₅O₁₂ and MgCrO₄. The propylene selectivity observed was due to the Cr₅O₁₂ present. MgCrO₄ was not selective towards propylene formation, but instead favoured the generation of acetone.

Chromium ion has the ability to easily switch between multiple oxidation states when exposed to high temperatures. This has been recognized as crucial for the remarkable catalyst performance noticed [109]. When activated propane molecules come into contact with CrO_x's active oxygen, which is in a higher Cr oxidation state, the Cr oxidation state in CrO_x decreases, leading to the production of propene and water [110].

Table 2. 4: ODP using supported chromium catalysts

Catalyst	T (°C)	Feed Composition	Oxidizing Agent	X	S(%)	Ref
5%Cr/Nano-MgO	450	C ₃ /O ₂ = 2:1	O ₂	10.8	84	[107]
15wt%Cr/ZrO ₂	550	-	CO ₂	22	74	[108]
FeCr50	550	-	CO ₂	14.2	71	[111]
10%Cr/ γ -Al ₂ O ₃	450	-	O ₂	16.7	54.1	[112]
3Cr/SiO ₂ -5	650	C ₃ /CO ₂ = 2:1	CO ₂	20	70	[113]

Moreover, a noticeable trend in the most recent research works for the use of Cr-based catalyst for ODH of lower alkanes generally has been directed towards optimizing their performance using CO₂ as a mild oxidant. This trend can be attributed to the commercial and environmental advantages associated with CO₂ utilization. CO₂ has a higher thermodynamic limit, making it an attractive option for achieving enhanced catalytic performance. Additionally, utilizing CO₂ as an oxidant offers the potential to reduce anthropogenic CO₂ emissions, aligning with sustainability goals. By exploring the potential of CO₂ as an oxidant in ODH reactions, researchers aim to develop more efficient and environmentally friendly catalytic processes for alkane conversion[109], [110], [114].

2.4.3 Supported Mixed Metal Oxides and Others

As one of the most investigated approaches to improve the ODH process efficiency remains the design of more effective catalysts, a promising route using this approach is modifying catalysts by introducing an additional metal (or more) to the catalyst composition. This addition has been shown to alter the surface properties of the catalyst,

leading to changes in activity, selectivity, and stability. For example, researchers have investigated the use of bimetallic supported nickel-bismuth catalysts for ODH of n-butane, which have shown higher selectivity and stability compared to monometallic Nickel or Bismuth catalysts. The addition of bismuth to the catalyst composition can modify the surface properties of the nickel catalyst, leading to an increased concentration of active sites and a reduction in the coke formation during the reaction [19], [40], [115]. In Table 2.5 a performance comparison of the catalysts of selected mixed-metal oxides is presented.

In a study conducted by Jermy [116] and his group the ODHB using different Ni:Bi ratios for the Ni-Bi/ γ -Al₂O₃ catalysts and varying O₂ to n-butane (Feed) ratios were investigated for BD production. According to the findings, Bismuth introduction influenced the catalysts' reduction behavior and enhanced the reduction of surface species of nickel oxide. The study also discovered that the inclusion of bismuth resulted in further decrease in the reduction temperature, leading to lower temperatures. The study found that a catalyst with both bismuth modification and highly loaded nickel oxide on γ -Al₂O₃ had high activity and selectivity for ODHB (27% conversion; 47% BD selectivity). The authors proposed the improved performance of the catalyst observed to be a direct consequence of the effects of bismuth and nickel on the surface properties of the catalyst material. The exact mechanism by which the addition of another metal to a catalyst enhances the activity of the ODHB and 1,3-butadiene selectivity is not yet fully understood, it is hoped that further research in this area would help to elucidate the phenomenon.

For propane ODH, the research trend is towards the use of alternative mild oxidizing agents other than oxygen especially CO₂ – ODP. Many of the overall best performing catalysts reported in terms of activity, selectivity and stability are supported multi-metallic oxides [117]–[122]. In a report by Xing et al., [30] they describe the successful development of a Platinum-Cobalt-Indium ternary nanoalloy supported on CeO₂, that demonstrated remarkable performance. At 550 °C the catalyst exhibited 50% conversion of propane, propylene selectivity of 95%, high stability, and CO₂ use efficiency. The presence of cobalt species in the catalyst contributed to a high density of states close to the Fermi level, hence decreasing the high energy barrier for carbon dioxide reduction. By combining Pt with In and Co, the researchers were able to enhance propylene selectivity and CO₂ reducibility, respectively, resulting in an overall improvement in the catalyst's performance.

In another interesting work by Gomez et al., [121] bimetallic catalysts for CO₂-ODP to produce propylene was investigated. Platinum and Palladium-based bimetallic catalysts with Nickel, Cobalt, and Iron, as well as nonprecious metal combinations, were evaluated using flow reactor. They showed that bimetallic catalysts based on Pt performed better than Pd-based catalysts based on activity measurements of both site-specific turnover frequency (TOF) values and mass-based propane conversion. Ni outperformed Fe and Co as the most active transition metal examined with Pt and Pd. The bimetals with Ni and Co were more stable in addition to being more active compared to monometallic Pt and Pd. It was also observed that the Co_xNi_y catalysts were active and selective for the propane reforming pathway, while the Fe_xNi_y catalysts favoured CO₂-ODP selectivity. The

selectivity of propylene using Fe_xNi_y catalyst was observed to diminish by increasing the Ni atomic ratio above 1 in the bimetallic composition.

Table 2. 5: Selected mixed-metal catalysts reported for ODH

Catalyst	T (°C)	Feed Composition	Oxidizin g Agent	X (%)	S (%)	Condi tions	ref
20wt% Ni- 30wt%Bi- O/SBA-15	450	$\text{O}_2/\text{n-C}_4/\text{N}_2 = 20/10/78$	O_2	28.9	47.5	total flow 31.2 ml/min	[20].
20wt%Ni- 30wt%Bi- O/SiO ₂	450	$\text{O}_2/\text{n-C}_4/\text{N}_2 = 20/10/78$	O_2	35.6	41.6	total flow 31.2 ml/min	[19]
30wt%Bi- 20wt%Ni-O/ γ - Al ₂ O ₃	500	$\text{CO}_2/\text{n-C}_4=2$	O_2	23	47	-	[116]
Mo-V-MgO	570	$\text{O}_2/\text{n-C}_4=1.9$	O_2	64.1	51	-	[76]
20%(10Ni5Fe5 Co)-30%Bi- O/ γ -Al ₂ O ₃	450	$\text{O}_2/\text{n-C}_4=2$	O_2	30	46.3	-	[40]
Bi-Ni-O/ γ - Al ₂ O ₃ (30 wt% Bi-20 wt% Ni)	450	$\text{O}_2/\text{n-C}_4=2$	O_2	26.9	39	-	[19]
Ni-Mo/Al ₂ O ₃	450	$\text{O}_2/\text{n-C}_4=2$	O_2	71	25	-	[46]
Mo-doped VMgO	630	$\text{n-C}_4/\text{O}_2=1.5/1$	O_2	30	42	GHSV = 58800 h- l	[75]
1.8%Ni- 6.5%Mo/Al ₂ O ₃	450	$\text{CO}_2/\text{n-C}_4=2$	CO_2	7.5	45	GHSV = 6000 h-1	[46]
1.8%Ni- 6.5%Mo/Al ₂ O ₃	450	$\text{CO}_2/\text{n-C}_4=2$	N_2O	6.8	61	GHSV = 6000 h-1	[46]

n-C₄: n-butane

2.5 Light Alkane ODH Reaction Mechanism

The mechanism of ODH reaction is different depending most importantly on the specific alkane and type of catalyst used. For instance, in the presence of vanadium oxide

supported on silica or alumina which is one of the extensively studied catalysts. The heterogenous reaction typically proceeds via the following steps:

1. Physisorption: Adsorption of the alkane molecule onto the catalyst surface: The alkane molecule is adsorbed onto the surface of the catalyst, where it undergoes activation through weak bonding with the metal sites.
2. Formation of an alkyl radical: The alkane molecule is converted into an alkyl radical through hydrogen abstraction by a reactive oxygen specie, such as O^{2-} and O_2^- present in the metal oxide catalyst lattice.
3. β -elimination: Formation of a double bond: The alkyl radical then undergoes a β -hydride elimination, in which a H atom is transferred from a neighbouring C atom to the metal catalyst, resulting in double bond formation to produce the alkene.
4. Desorption of the alkene product: The alkene product is then desorbed from the surface of the catalyst, leaving the active sites accessible for the next cycle of the reaction.
5. Diffusion of products from surface of catalyst into the bulk. The cycle is complete by the replacement of the lattice oxygen with oxygen from in the feed stream.

Based on these steps, various proposals for the ODH reaction models have been made, including the Mars Van Krevelen model (Redox model), Langmuir Hinshelwood model, Eley Rideal model, Rake model, and power law model. In the case of ODH reactions using transition metal oxide catalysts, studies have found that the kinetics typically follow the Mars Van Krevelen model, which involves a redox mechanism. In this model, oxygen species within the catalyst (lattice oxygen) actively participate in the oxidative dehydrogenation reaction by activating the C-H bond and extracting H molecules from the alkane substrate, resulting in water formation as a by-product that is then eliminated

through surface dehydration. The catalyst becomes reduced during the reaction and must be oxidized again by molecular oxygen present in the gas phase [56], [82], [97], [123]. Figure 2.2 is a depiction of the mechanism for oxidative dehydrogenation of propane over MnWO_4 catalyst where active O^{2-} species within the catalyst lattice activate the C-H bond in propane according to the described Mars Van Krevelen model.

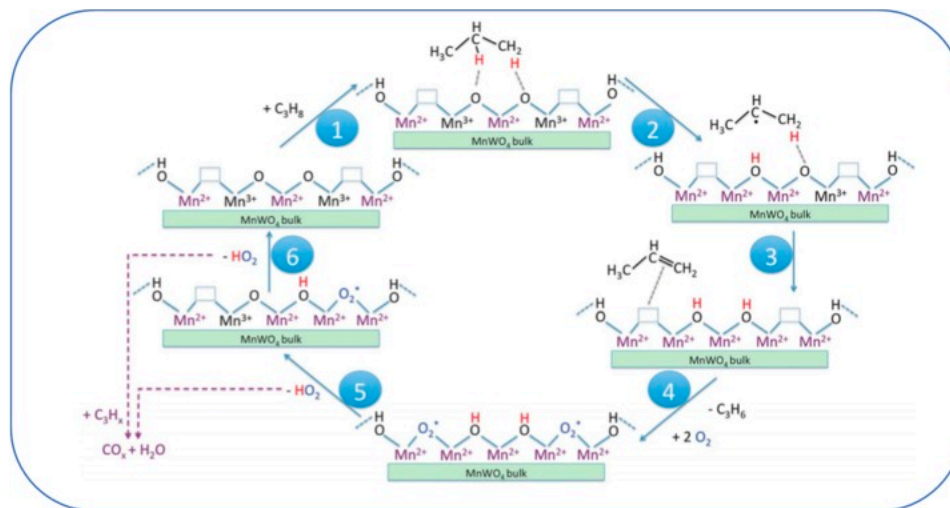


Figure 2. 2: Mars Van Krevelen mechanism for oxidative dehydrogenation of propane over MnWO_4 catalyst adapted from [12]

In the context of ODHB, researchers have also proposed reaction networks based on the catalyst's acidic or basic properties. For catalysts with dominant basic sites, olefins (1-butene and 2-butenes) are produced directly from n-butane, while 1,3-butadiene is formed by further dehydrogenation of these intermediary olefins as a consecutive product, however whether 1,3-butadiene is formed via the 1-butene route or the 2-butene route has been a subject of debate amongst researchers [1]. Recent studies have however shown that although the catalyst used can influence which path would be favoured, the 1-butene route appears to be the most favourable route for 1,3-butadiene production [20], [124]. Figure 2.3 shows a possible 1-butene pathway for ODHB to produce 1,3-butadiene

suggested by Tanimu et al., [20]. The range of products and intermediates are grouped into 3 namely: the dehydrogenation group (DH) consisting of 1-butene, cis-2-butene, trans-2-butene and 1,3-butadiene; the oxygenate and deep cracking products (OC) consisting of methane, ethane, ethylene, propane, propylene, carboxylic acids and carbon dioxide; and the partial oxidation products (PO) consisting of H_2 and CO.

On the other hand, for catalysts with many acidic sites, olefins and diolefins are initially produced from n-butane, with CO_x formed as a consecutive product of deep oxidation. The rate of hydrogen removal from n-butane is crucial in determining overall reaction rate, while the selectivity is governed by the second hydrogen removal/desorption step of the olefinic intermediate. Notably, catalysts with basic character exhibit a higher olefinic intermediate desorption rate compared to those with acidic character [1], [15], [78].

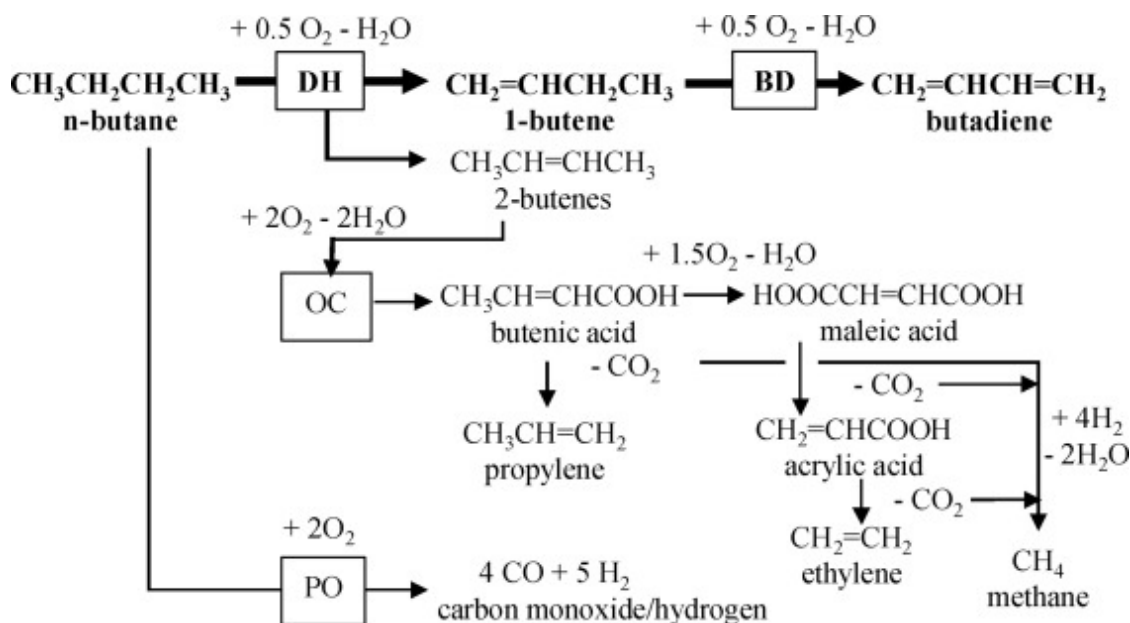


Figure 2. 3: Reaction scheme for oxidative dehydrogenation of n-butane to 1,3-butadiene [20]

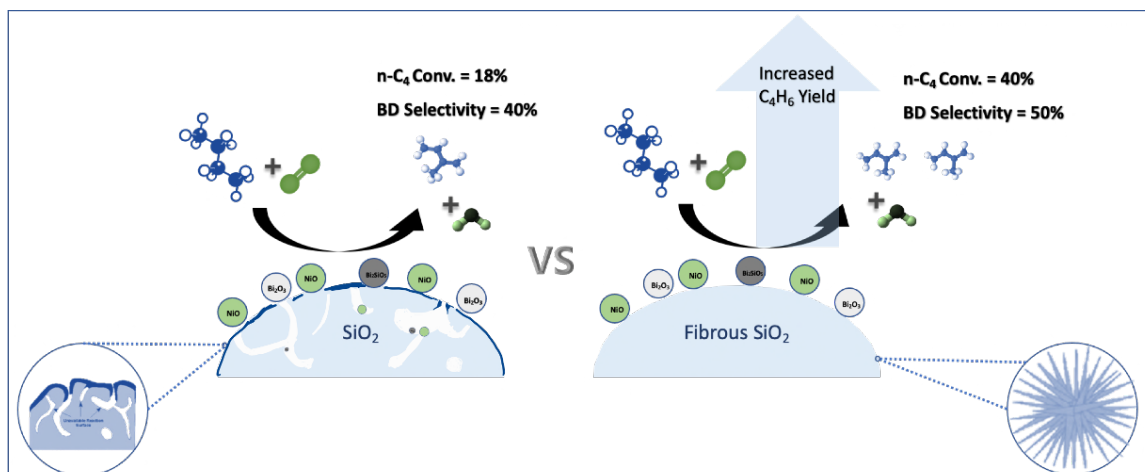
CHAPTER 3

FIBROUS SILICA SUPPORTED BI/NI OXIDE CATALYSTS FOR OXIDATIVE DEHYDROGENATION OF N-BUTANE

ABSTRACT

Oxidative dehydrogenation of n-butane to was investigated over a series of catalysts having Nickel loading between 10 – 20 wt % and Bismuth loading between 10 – 30 wt% deposited on fibrous silica support (Ni-Bi/FS). Conducted at atmospheric pressure, the experiments employed a fixed-bed reactor at temperatures between 400 °C and 500 °C, and different oxygen to n-butane feed ratios of 1:1, 2:1 and 4:1. Characterization techniques, including XRD, BET, SEM, and TEM were utilized to analyze catalyst properties. The study revealed a correlation between the formation of NiO and Bi₂SiO₅ phases, influencing dehydrogenation activity and 1,3-butadiene selectivity, respectively. Notably, the 20Ni-10Bi/FS catalyst exhibited superior performance, giving the highest butadiene yield of 20% at at a reaction temperature of 500 °C oxygen to n-butane feed ratio of 1:1

Graphical Abstract



3. Introduction

1,3-Butadiene (BD) stands out as the most important conjugated diene. Its significance is underscored by its role as a primary feedstock in the manufacturing of several important synthetic elastomer including polybutadiene rubber, styrene butadiene rubber, and acrylonitrile butadiene styrene resins which are important for the production of automobile tires [1]. It is worth noting that a projected incremental market growth of 6.15%, corresponding to 10.77 billion dollars, is forecasted between 2021 and 2026. This growth is mainly attributed to the increasing demand from the automobile industry [125]. The main source of 1,3-butadiene historically came from the dehydrogenation of naphtha and larger hydrocarbons for production of ethylene that results in the production of 1,3-butadiene, light alkanes and other olefins as by products. However, there has been a shift towards producing ethylene via dehydrogenation of light alkanes, thanks to the abundant supply of natural gas. The yield of propylene and C₄ olefins are however lower via this route [2]–[4].

Hence, with the shale gas revolution which implies a more economical supply of light alkanes that can serve as raw materials for ethylene production, there is the need for new on-purpose production techniques for 1,3-butadiene [126]. Catalytic direct dehydrogenation of butane to produce 1,3-butadiene (DDH) using chromium supported on alumina or platinum based catalysts is a developed technology and has been commercialized under several patents [24]. DDH is, however, a thermodynamically limited reaction that requires very high reaction temperatures usually greater than 600 °C

[7]. The process also possesses a challenge of formation of carbon deposits which cause frequent catalyst deactivation.

Oxidative dehydrogenation of butane (ODHB) offers a promising alternative for the on-purpose production of 1,3-butadiene. The incorporation of an oxidizing agent in the feed stream ensures the formation of more stable products thereby enhancing the thermodynamically feasibility of the route. Additionally, the reaction proceeds at lower temperatures, which in turn, reduce the tendency for coke formation on the catalyst surface [1], [120], [127]. Several studies [1], [14]–[16] have been conducted by researchers to investigate the performance of several metals as catalysts for ODHB. These studies have explored supported platinum [64], and oxides of transition metals like vanadium [79], [80], [128], chromium [106], and nickel [129] as well as combination of these metals as mixed metal catalysts [46], [75], [128], [130], [131].

Nevertheless, despite these advances, ODHB process experiences some drawbacks that have hindered its widespread industrial adoption. These include by-product formation like the risk of deep oxidation of the reactants, intermediates and products to form unwanted carbon oxides [1], [120]. In response to these challenges, finding catalysts that can exhibit excellent selectivity towards 1,3-butadiene production even at high n-butane conversion rates have been the focus of recent research endeavours. A study conducted by Jermy et al., (2015) [131] showed the improved effect of the addition of bismuth oxide to the nickel oxide species supported on alumina for the oxidative dehydrogenation of n-butane to selectively produce 1,3-butadiene. 30wt% Bi and 20 wt% Ni on the alumina support was found to demonstrate high BD selectivity of about 47% at a reaction temperature of 450 °C. In a recent work by Tanimu et al., (2023) further studies using

atomistic simulations were carried out to elucidate the role of BiOx in the catalyst for the observed improved performance [124]. The work showed that Bi species present in the catalyst suppresses the formation of 1-Butene and 2-Butene while the selectivity of BD increases.

The acid-base surface characteristics and the redox property of a material plays a pivotal role in determining its performance as an excellent catalyst for oxidative dehydrogenation of n-butane. The choice of support material employed can significantly affect the acid-base characteristics of the catalyst. Moreover, an important corollary of employing a suitable support material lies in its ability to enhance the dispersion of the active species. This improved dispersion, in turn, facilitates efficient access of the reactants to these active sites. Consequently, this phenomenon leads to a marked improvement in the overall catalytic activity [1], [132]. Tanimu and co-workers in a follow up study [133] investigated the effect of different supports including Al₂O₃, SiO₂ and ZrO₂ for the bismuth oxide-nickel oxide catalyst system for ODHB, the mixed metal catalyst system using the silica support demonstrated the best performance for 1,3-butadiene production. Notably, the 20Ni-30Bi supported on calcined silica catalyst configuration exhibited the best performance with BD selectivity and conversion up to 41.6 % and 35.6 % respectively.

Conventional porous silica serves as a choice material for catalyst supports due to its exceptional thermal properties and mechanical properties, its ability to take on various morphologies, large surface area and tuneable pore sizes [21]. However, the silica supported catalysts though showing good selectivity towards BD, displayed relatively low activity for ODHB compared to the other commonly used supports like alumina and

zirconia [133]. When silica is modified to have a fibrous morphology and used as a catalyst support, it improves the surface characteristics of the catalyst and allows access for more metal nanoparticle species to be deposited on accessible sites on the surface and within the pores, hence improving catalytic activity [23]. An illustrative example of this is demonstrated by fibrous silica nanospheres (KCC-1) whose dendritic nature have contributed to its excellent performance as a catalyst support for shift conversion reaction using gold nano particles [134] when compared with conventional porous silica.

In this work, a catalyst containing different percentage loadings of Ni:Bi ratio dispersed on as synthesized fibrous silica composite (Ni-Bi/FS) was synthesized using the templated sol-gel method for the support preparation and wet co-impregnation technique for the metal impregnation. The XRD, TEM, FESEM, N₂ adsorption–desorption, and TPD techniques were used to gain insight into the physicochemical properties of the catalysts. The performance of the catalyst for ODHB was then evaluated in a fixed bed reactor and compared.

3.1 Experimental

This section provides a comprehensive account of the methodology that was used in this work, ranging from the synthesis of the support and catalyst, characterization of the prepared catalysts, and evaluation of the catalyst performance in ODHB.

3.1.1 Catalyst Synthesis

Fibrous silica support was produced using sol-gel hydrothermal synthesis, which was previously reported by Soltani et al., [135], [136]. First, urea (59.9 mmol) and CTAB (8.23 mmol) were mixed in 250 mL of distilled water and stirred for fifteen minutes at 25 °C. Subsequently a mixture of 15 ml tetraethyl orthosilicate and 250 ml cyclohexane is

added, and the mixture is stirred for another 15 minutes before adding 18 ml butanol. The mixture is stirred for another 20 minutes and then transferred to a Teflon-lined autoclave. The autoclave is heated at 120 °C in an electric oven for 6 hours, then allowed to cool down to 27 °C afterwards. The white gel-like product is separated using a centrifuge and undergoes multiple washes times with ethanol then water. The product is dried in an oven at 80 °C overnight after which it is subjected to calcination in air at 550 °C for 6 hours to obtain fine white powders of the synthesized support and labelled FS.

Nanoparticles of Ni and Bi were deposited on the prepared support using the wet co-impregnation technique to obtain the Ni-Bi/FS catalyst. In a typical procedure to prepare a catalyst containing a 20 wt% Ni and 30 wt% Bi based on 5 g of support, 4.955 g of the nickel precursor ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was dissolved in 150 mL of distilled water in a beaker. Then 3.465 g of the bismuth precursor ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) was added to the solution. The resulting solution was stirred using a magnetic stirrer for 30 minutes at 500 rpm. 5 g of the prepared FS support was then introduced to the solution and stirring continued for 2 hours to ensure that a homogenous mixture is obtained. Afterwards, water was expelled from the mixture by gradual evaporation at 50 °C on a hotplate with continuous stirring. The resulting solid was kept overnight in an oven at 100 °C.

The resulting catalyst was crushed into a fine powder and subjected to a two-step calcination procedure to improve the crystallinity, expel any leftover nitrates, water molecules or organic compounds; and also, to achieve full stabilization. First the temperature was raised to 350 °C at a rate of 10 °C per minute and maintained for 1 hour. For the next step, then temperature is raised to 590 °C at a rate of 15 °C per minute and held at the temperature for 2 hours. Afterward it was allowed to cool to room temperature

in the furnace. The resulting catalyst was pelletized into granules ranging from 500 – 850 μm in size and tagged 20Ni-30Bi/FS. In a similar way 10Ni-10Bi/FS, 15Ni-10Bi/FS, 20Ni-10Bi/FS, and 20Ni-20Bi/FS were prepared.

3.1.2 Characterization and Performance Evaluation of Catalysts

- XRD analysis was conducted to identify the crystal structure of both the fibrous silica support and the synthesized catalysts.
- SEM, TEM and SEM-EDX were conducted to analyze the surface features, morphology, elemental composition and microstructure of the fibrous silica support and the catalysts supported on FS. Information about the particle size and shape of the catalysts were also obtained from this analysis.
- Ammonia TPD (NH_3 TPD) was conducted to measure the acidic properties and strength of the catalysts.
- XPS analysis was conducted to confirm the catalyst elemental compositions and their oxidation states.
- The BET surface area of the modified silica support and the supported catalysts were measured using nitrogen adsorption, which can provide information on their porosity, pore size distribution and surface area.
- The performance of the catalysts for ODHB was evaluated in a fixed bed reactor system and the product stream composition was analysed using an online Agilent gas chromatograph unit downstream the reactor.

3.1.3 Analyses of BET Surface Area and Distribution of Pore Size

The Micrometrics ASAP 2020 apparatus was utilized to find out the surface area and pore characteristics of the freshly synthesized catalysts and FS supports. Prior to

adsorption measurements of a sample, a 0.05 g portion of the sample will be degassed under a nitrogen stream at 240 °C for 3 hours. Nitrogen adsorption isotherms will be acquired at liquid Nitrogen temperature of 77K, and the determination of pore size distribution will be done using the Barrett-Joyner-Halenda method applied to the adsorption branch.

3.1.4 Investigating Crystal Structure using X-ray Diffraction

The Rigaku Miniflex II desktop X-ray diffractometer was employed to identify the crystalline phases of the freshly synthesized catalysts. The diffraction angle to be scanned varied from 2θ of 5 to 90 degrees, utilizing Cu K α radiation ($\lambda=1.5406\text{\AA}$) and operation will be at 40 kV and 30 mA, with a step size of 0.02 degrees and speed of 1°/min. However, the region showing the relevant peaks was between 2θ values of 25 to 55 as shown in the results' discussion section.

3.1.5 Temperature Programmable Analysis (TPD and TPR)

The BEL-CAT-A-200 chemisorption instrument was utilized to conduct TPR to investigate the reducibility of the catalyst and ammonia TPD to investigate the acidic character of the catalysts experiments. The apparatus includes a quartz type sample holder equipped with a furnace, as well as TCD and mass spectrometer for analysis.

3.1.6 Exploring Microstructure with Transmission Electron Microscopy (TEM)

The JEM-2100 F model ultra-high-resolution TEM was employed to analyze the catalysts and supports at the nanoscale. This was to examine their microstructure and properties and provide valuable insights into the morphologies of FS and Ni-Bi/FS catalysts.

3.1.7 Analysis and Imaging Using Scanning Electron Microscopy (SEM)

TESCAN MIRA's Low Vacuum and Variable Pressure Ultra-High Resolution Scanning Electron Microscope (LMU) will be used to examine the surface features and generate high resolution images of the fibrous silica supports and synthesized catalyst surfaces.

3.2 Catalyst Performance Testing

The ODHB reactions were conducted using BELCAT, fixed bed reactor of the continuous flow type. It comprises a single tubular quartz reactor connected to a stainless-steel furnace through a thermowell in the reactor furnace wall. The freshly synthesized and pelletized catalyst sample (about 0.3 g) with uniform particle size between 500 μm to 850 μm were packed into the reactor and subjected to a pre-treatment step under flowing air to activate and stabilize it. The products formed during the reaction were continuously analysed by a GC system (Agilent, 7890N) downstream of the reactor equipped with one FID for hydrocarbon and oxygenate analysis, and two TCD detectors for N_2 , CO , O_2 , H_2 , and CO_2 , analysis. The products were identified by comparison to standard samples. The n-butane conversion and 1,3-butadiene with by-product selectivity were calculated based on carbon balance. The following equations were used to calculate the conversion, product selectivity and yield.

$$\text{Butane conversion (\%)} = \frac{\text{moles of butane fed} - \text{moles of butane in the product}}{\text{moles of butane fed}} \times 100 \quad (\text{i})$$

$$\text{Selectivity of product i (\%)} = \frac{\text{moles of i product}}{\text{Butane conversion}} \times 100 \quad (\text{ii})$$

$$\text{Yield of product i (\%)} = \frac{\text{Butane conversion} \times \text{selectivity of product i}}{100} \quad (\text{iii})$$

All tests were performed under identical conditions, including a constant total gas volumetric flowrate (consisting of nitrogen, n-butane, and air in the ratio of 18:1.2:12 mL min⁻¹, respectively for a O₂:n-C₄ ratio of 2:1) at a rate of 31.2 ml/min. A constant catalyst to feed (n-butane) ratio of 0.42 h·gcat/mol-C₄ will be maintained. The O₂:n-butane feed ratio was regulated by varying the flow of the air stream into the reactor inlet mixture to a desired value. The adjustment was made in accordance with calculations based on the air cylinder containing a 21% oxygen and 79% nitrogen by volume. Finally, the reactions were carried out at three distinct temperatures, specifically 400 °C , 450 °C and 500 °C.

3.3 Results and Discussion

3.3.1 Powder X-ray diffraction pattern

Powder X-ray diffraction pattern of different concentrations of Ni and Bi loading on the fibrous silica support as shown in Figure 3.1. The fibrous silica support shows no crystallinity pattern, but once 10 wt.% of Ni and Bi were loaded on the FS, it showed sharp crystalline peaks corresponding to NiO, Bi₂SiO₅, and Bi₁₂SiO₂₀ phases. But there was no individual peak corresponding to bismuth oxide. The phases of Bi₂SiO₅ and Bi₁₂SiO₂₀ were formed by the interaction of Bi with support FS. However, these phases have been confirmed by our previous work as well as the ICSD pattern [14], [137]. With further increased Ni loading from 10 to 20 wt.% with 10 wt.% of Bi, the intensity of the NiO phases (+ on Figure 3.1) increased with decreasing Bi₁₂SiO₂₀ phases. The individual phase of Bi₂O₃ was formed along with increasing the intensity of Bi₂SiO₅, while Bi loading increased from 10 to 30 wt.% on the fibrous silica support.

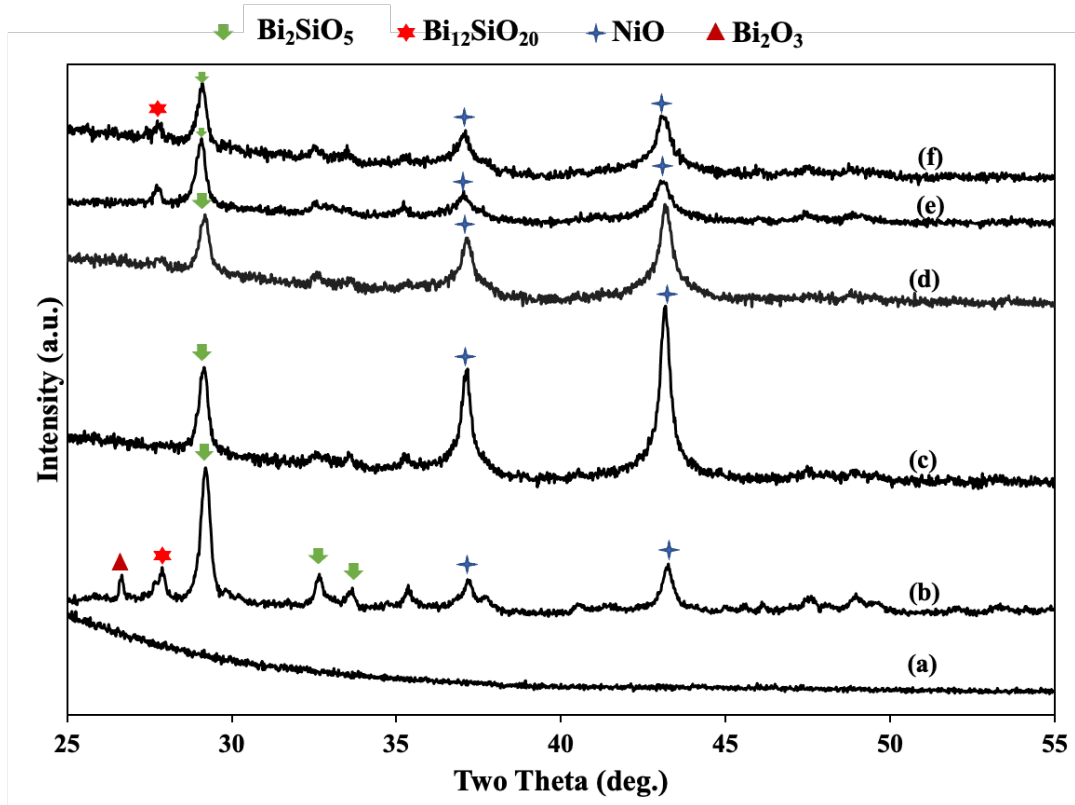


Figure 3. 1: XRD pattern of synthesized catalysts and FS Support, (a) FS, (b) 20Ni-30Bi/FS, (c) 20Ni-10Bi/FS, (d) 15Ni-10Bi/FS, (e) 20Ni-20Bi/FS (f) 10Ni-10Bi/FS

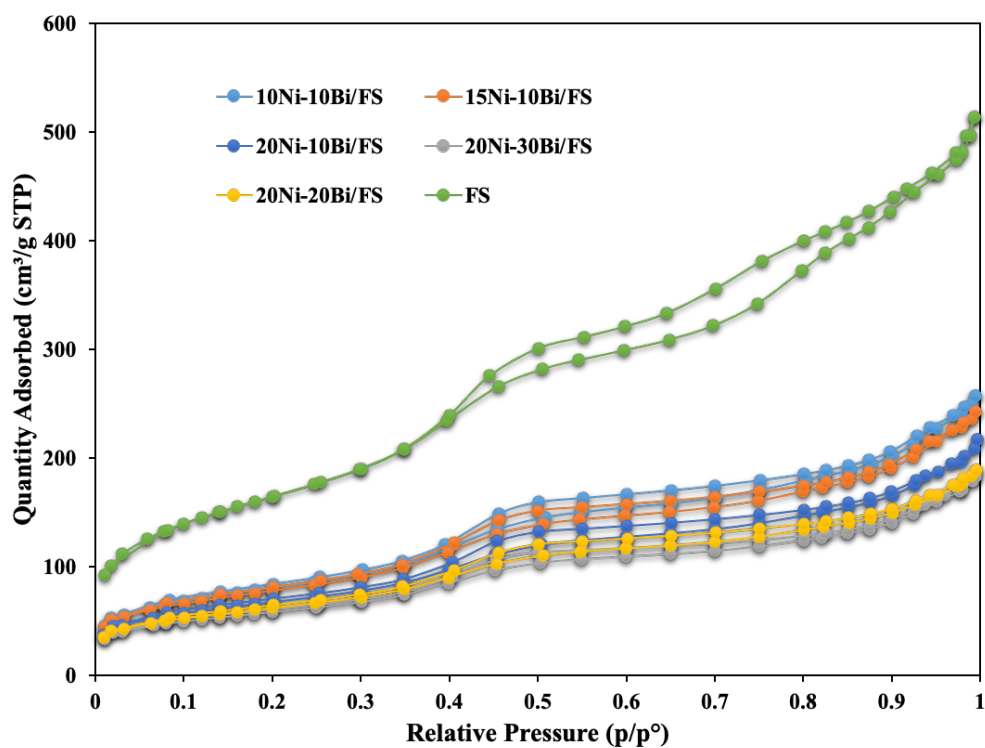
3.3.2 BET Surface Area Measurement

The effect of surface area, pore size, and pore volume of the synthesized catalysts was analyzed by N₂ sorption techniques (Figure 3.2). Synthesized catalysts showed a type IV isotherm with an H3-type hysteresis loop, which indicated that these samples possessed a mesoporous structure in the range of relative pressure (P/P_o) from 0.6 to 1.0 [138]. It can be seen that the nitrogen adsorption quantity was higher for the FS support than the Ni-Bi-O/FS catalysts. This result suggested that FS had a higher surface area and pore volume than Ni-BiO/FS catalysts (Table 3.1). These pore distribution properties for the support and all the catalysts are calculated using the BJH (Barrett, Joyner, and Halenda) method

Table 3. 1: Textural properties of the catalysts

Catalyst	FS	10Ni-10Bi/FS	15Ni-10Bi/FS	20Ni-10Bi/FS	20Ni-30Bi/FS
Surface area					
BET Surface Area (m ² /g)	593	291	281	244	210
t-Plot Micropore Area (m ² /g)	31	13.6	15.2	13.1	13.6
Pore volume					
Total pore volume (m ³ /g)	0.836	0.421	0.399	0.357	0.301
t-Plot micropore volume (cm ³ /g)	0.010	0.0038	0.0047	0.0043	0.0047
Mesopore volume (cm ³ /g)	0.826	0.417	0.394	0.353	0.2963
Average pore diameter (nm)	4.72	4.69	4.63	4.79	4.70

The surface area and pore volume of the support FS decreased by 50% when 10 wt.% Ni and Bi were impregnated on FS (10%Ni-10Bi/FS) (Table 1). This is due to the introduction of metal oxide within the mesoporosity of the support FS. Impregnation of metal does not affect the mesoporosity of the FS. It shows a sharp pore size distribution peak for both FS and Ni-Bi-O/FS, with an average pore diameter of 4.7 nm(Figure. 3.3)

Figure 3. 2: N₂ sorption of synthesized catalysts

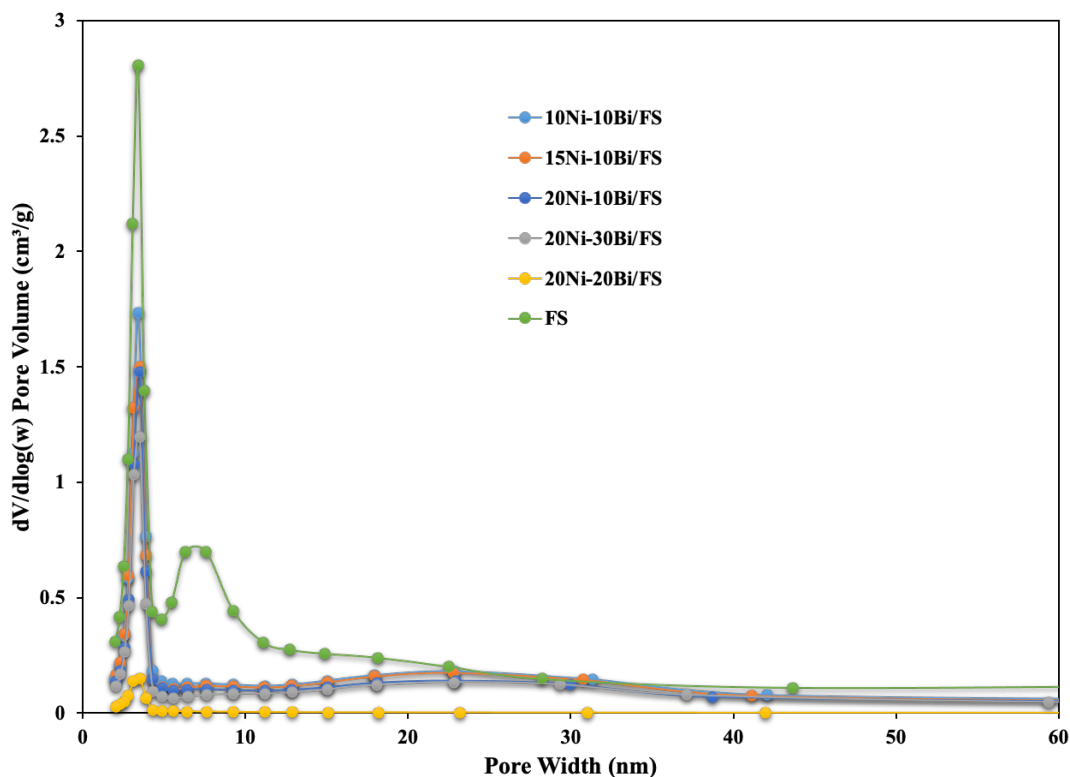


Figure 3. 3: Pore size distribution of synthesized catalysts

3.3.3 Temperature Programmed Reduction (TPR)

The temperature-programmed reduction profiles of Ni-Bi/FS catalysts are shown in Figure 3.4. Ni-Bi/FS catalysts generally show a wide reduction peak between 400–700 °C except the 10Ni-10Bi/FS catalyst that has a shorter and smaller peak between 400 – 550 °C indicating that it has the least amount of reducible NiO on the surface of the catalyst and weakest attraction between support and active phase among the catalysts investigated. This reduction peak is mainly responsible for the reducibility of NiO on the support [19]. XRD results of Ni-BiO/FS suggest that Ni forms as NiO and Bi interact with support from Bi_2SiO_5 and $\text{Bi}_{12}\text{SiO}_{20}$. But the reduction peaks corresponding to Bi_2SiO_5 and $\text{Bi}_{12}\text{SiO}_{20}$ were not observed in the TPR profile. This suggests that NiO dispersed on the stable Bi_2SiO_5 , $\text{Bi}_{12}\text{SiO}_{20}$, and FS surfaces. As the Ni concentration

increased in the Ni-Bi-O/FS catalyst, the peak intensity increased, and the peak slightly shifted towards higher temperatures. The shifting of the peak indicates a possible synergistic interaction between NiO and the Bi_2SiO_5 [137]. The shift of the peak associated with the 15Ni-10Bi/FS catalyst suggests a stronger metal-support interaction within the catalyst compared to the 20Ni-10Bi/FS and 20Ni-30Bi/FS catalysts. This could be due to better dispersion of the NiO phase over the support from lower metal loading.

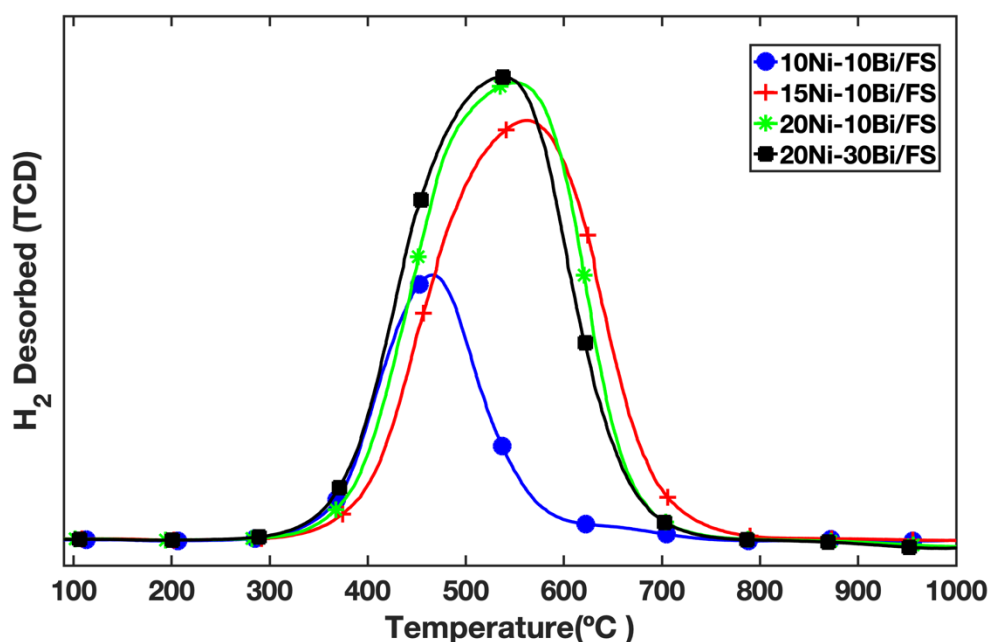


Figure 3. 4: TPR profiles of synthesized catalysts

3.3.4 Ammonia Temperature Programmed Desorption

The temperature programmed desorption to examine the acidic character of the catalysts and support was performed. The desorption profiles are shown in Figure 3.5. The profiles for all the materials can be deconvoluted into two distinct peaks, the first is between 100 °C and 250 °C and appears to be more dominant in all catalysts while the second is between 300 °C and 450 °C which is more dominant in the support. These peaks are identified as delineation of weak acid sites and moderate acid sites respectively.

However, as shown in the bar chart presented in Figure 3.6 the total acidity of all the catalysts are low. It has been shown in previous studies that the presence of weak acid sites on the catalyst surface enables for 1-butene intermediate adsorption on the catalyst surface to facilitate further dehydrogenation [19], [40] to produce 1,3-butadiene.

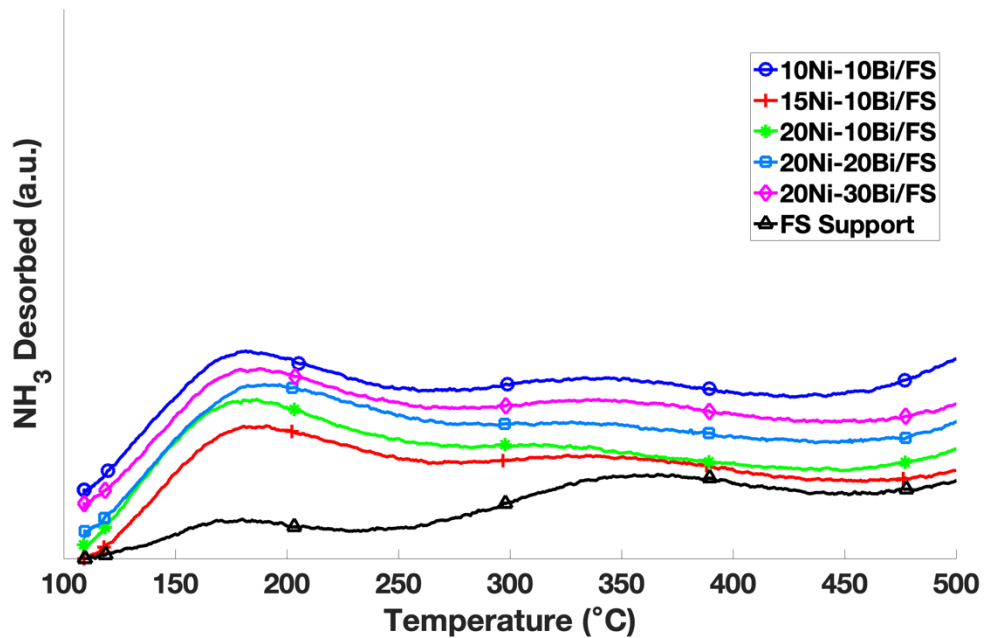


Figure 3. 5: Ammonia temperature programmed desorption profiles

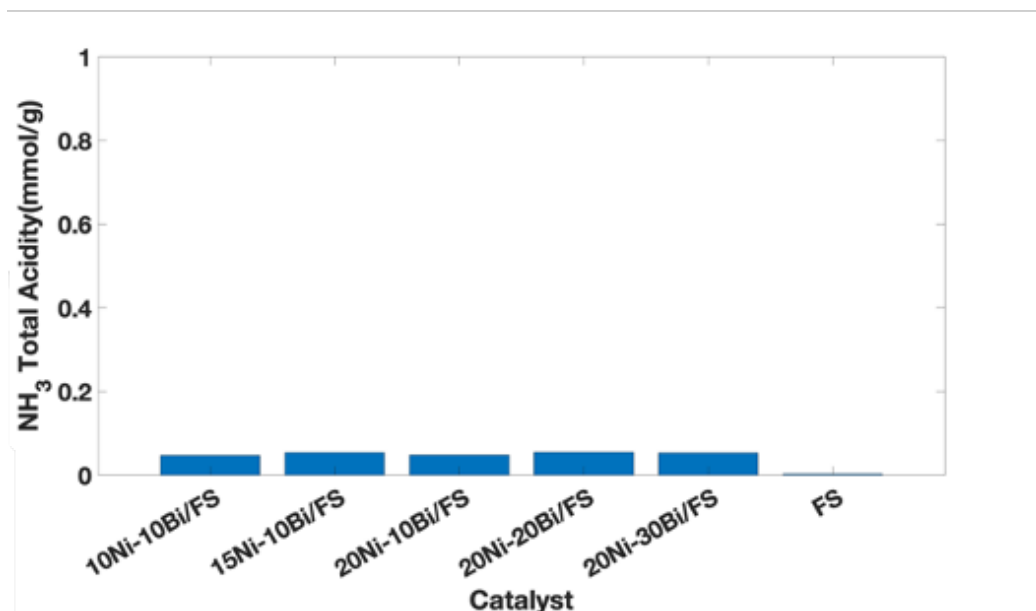


Figure 3. 6: Bar chart showing the total acidity of the catalysts and FS support

3.3.5 Electron Microscopy

Scanning electron microscopy (SEM) images of synthesized catalyst shows that colloidal nano sphere with average diameter of 0.5 μ m (Figures 3.7a and b). SEM images possess dendrimetric fibers, which were confirmed by TEM analysis (Figures.3.7a and b). These dendrimetric fibers are organized in three dimensions to form a sphere, which allows for a high surface area. The HRTEM clearly shows that organized fibers emanate from the core of the particles and spread uniformly in all directions. The dendritic morphology of the fibrous silica support was not affected by the loading of the Ni-Bi-O/FS (Figure. 3.8d). SAED pattern of the catalyst 20Ni-10Bi/FS shows the well dispersion of particles on the support (Figure. 3.8f).

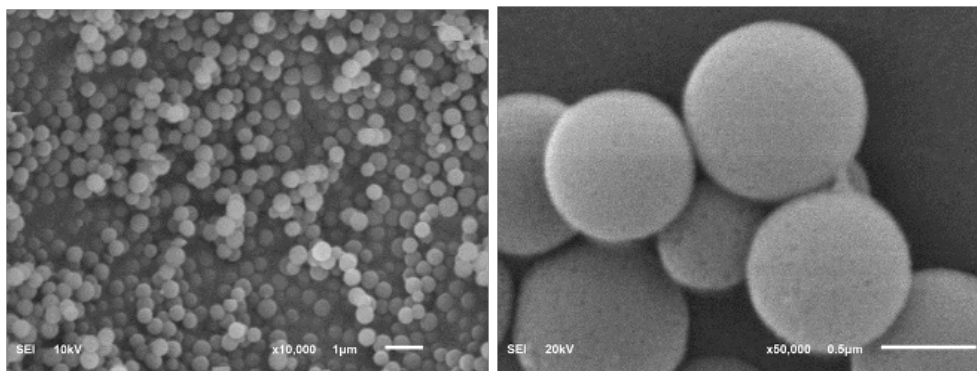


Figure 3. 7: SEM images of synthesized fibrous silica nanospheres

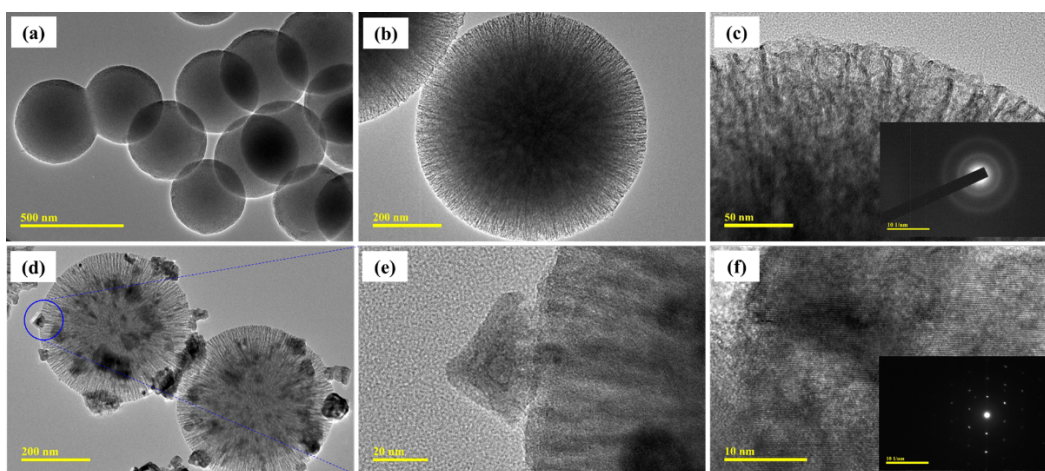


Figure 3. 8: TEM images of synthesized catalysts

3.3.6 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was employed to investigate chemical composition of metal oxide and their electronic state in the catalyst system. The XPS spectra of 20Ni-10Bi/FS catalyst for Bi 4f_{7/2} it shows that the chemical state of Bi can be identified as Bi³⁺ in two different chemical composition (Figure 3.9). The major peak at 156.0 eV is assigned to be for Bi³⁺ from Bi-O-Si bonds in Bi₂SiO₅. The peak at 162.0 eV is also for the Bi³⁺ state, but it forms Bi-O-Bi bonds in Bi₂SiO₅ [1]. This result suggests that Bi is present in two chemical environments in Bi₂SiO₅. Evidence from XRD results also shows the formation of the Bi₂SiO₅ phase in 20Ni-10Bi/FS. The Ni 2p_{3/2} spectra for

20Ni-10Bi/FS catalyst is shown in the Figure 3.9. The spectrum of the Ni 2p region shows that two typical Ni^{2+} 2p_{3/2} and Ni^{3+} 2p_{3/2} peaks were identified at binding energies of 854.0 and 556.3 eV, respectively [139], [140]. The oxidation state of Ni in +2 and +3 refers to the presence of stoichiometric and non-stoichiometric NiO [141]. The non-stoichiometric sites are known as defect sites. These defect sites are formed due to a charge imbalance between oxygen and Ni (the ratio of O to Ni). This could be because of an interaction between NiO and Bi_2SiO_5 [137].

The O1s XPS spectra of the 20Ni-10Bi/FS catalyst show two distinct peaks. The peak at the lower binding energy of 525.0 eV is assigned to lattice oxygen in the metal oxide crystal structure. The major peak at 533.6 eV is attributed to the surface oxygen of the catalyst. The surface oxygen species are the defect sites, which might help in improving the catalytic activity.

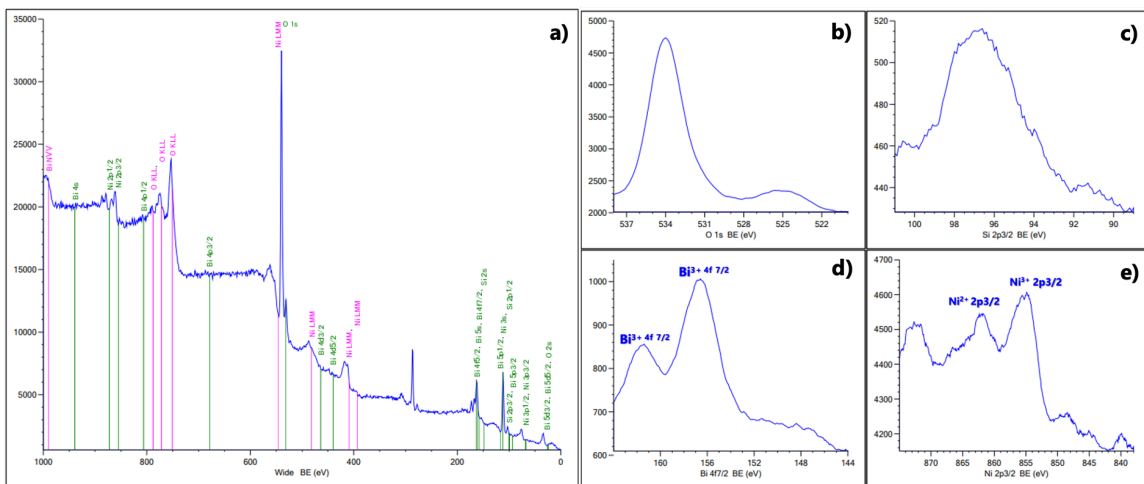


Figure 3. 9: XPS result spectra for 20Ni-10Bi/FS catalyst showing; a) Wide Band Energy b) Oxygen 1s c) Silicon 2p_{3/2} d) Bismuth 4f_{7/2} e) Nickel 2p_{3/2}

3.4 Catalyst Performance Evaluation

Table 3.2 provide an overview of the performance of the fibrous silica supported catalysts, showing varying composition of the Ni and Bi loaded on the support during the

evaluation for oxidative dehydrogenation of n-butane. The accuracy of the conversion and product selectivity values reported are based on reproducibility re-run experiments that were carried out. It showcases the conversion of n-butane and general product distribution obtained using each catalyst under different reaction temperatures (400 °C and 500 °C) and oxygen: n-butane ($O_2:n-C_4$) feed ratios of 1:1 .

Table 3. 2: Comparing the performance of the catalysts at different reaction temperatures and temperatures (400°C and 500°C) and oxygen-to-butane feed ratios ($O_2:n-C_4$) of 1:1

	10Ni-10Bi		15Ni-10Bi		20Ni-10Bi		20Ni-30Bi		20Ni-20Bi		No Catalyst	
Temp. (°C)	400	500	400	500	400	500	400	500	400	500	400	500
n-C ₄ conv. (%) ± 1.4	11.4	32.1	12.5	29.9	23.1	40.1	17.2	34.0	12.0	28.9	0.2	1.4
Selectivity (%) ± 1.1												
DH	94.0	75.6	90.0	74.7	83.5	71.6	90.6	70.6	94.3	75.2	100.0	69.3
1-C ₄ ⁼	13.1	7.5	12.2	6.6	10.2	8.2	13.8	6.3	12.7	7.4	38.1	24.9
2-C ₄ H ₈	41.7	14.5	38.4	15.6	28.4	13.4	30.8	11.2	41.8	17.2	61.9	39.2
BD	39.2	53.5	39.4	52.5	44.9	50.0	46.1	53.0	39.7	50.6	0.0	5.3
OC	1.6	6.5	4.5	7.5	2.5	7.1	2.2	8.7	1.1	7.5	0.0	18.8
BD/DH	41.7	70.8	43.7	70.3	53.8	69.8	50.8	75.1	42.1	67.2	0.0	7.6
(1-C ₄ ⁼ +BD)/DH	55.6	80.8	57.3	79.2	66.0	81.2	66.0	84.1	55.6	77.1	38.1	43.5
BD/(1-C ₄ ⁼ +BD)	75.0	87.7	76.3	88.8	81.5	85.9	77.0	89.3	75.7	87.2	0.0	17.5
BD yield	4.5	17.2	4.9	15.7	10.4	20.0	7.9	18.0	4.8	14.6	0.0	0.1

DH = Dehydrogenation selectivity (selectivity of all C-4 olefines); BD = 1,3-butadiene; OC = Oxidative cracking selectivity; 1-C₄⁼ = 1-butene; 2-C₄H₈ = 2-butene.

A general trend of improved n-butane conversion is observed across all catalyst as the temperature is increased from 400 °C to 500 °C. The conditions of a 500 °C reaction temperature and oxygen to n-butane feed ratio of 1:1 appears to be the most promising of all the conditions tested for 1,3-butadiene production using all the fibrous silica supported catalysts analysed. The catalyst containing a moderate loading of 20 wt.% Ni and 10 wt.% Bi (20Ni-10Bi/FS) particularly gave the best 1,3-butadiene yield of 20 % at the said condition with n-butane conversion of 40.1% and BD selectivity of 50% when compared to the lower and higher loading catalysts. The full product distribution using the 20Ni-10Bi/FS catalyst is shown in Table 3.3. The performance of all the other catalysts evaluated and details about the product distribution are shown in appendix A.

Notably, in the absence of any catalyst (blank test), negligible n-butane conversion of 1.4 % was observed further emphasizing the role of the catalysts. In addition, the analysis also reveals the catalyst's ability to promote the second step dehydrogenation. When no catalyst was used 92 % of the dehydrogenation products comprise of 1-butene and the two 2-butene isomers. However, the least DH selectivity (20Ni-20Bi/FS catalyst) obtained amongst all the catalysts tested had 67.2% of its dehydrogenation products to be BD and the remaining 32.8% to be other butenes.

The product distribution also shows that the 2-butene ($2\text{-C}_4\text{H}_8$) first step dehydrogenation product has a higher tendency to be desorbed into the gaseous phase when compared to 1-butene. The stronger adsorption of 1-butene to the catalyst surface is an indication of the n-butane $\rightarrow$ 1-butene $\rightarrow$ BD reaction route being more favoured by the catalyst for compared to the n-butane $\rightarrow$ 2-butene $\rightarrow$ BD. This finding is in perfect agreement with results from our previous work [124] where an atomistic scale simulation approach was utilized to gain insight into the dehydrogenation pathway for n-butane dehydrogenation.

This moderate loading of the catalyst has the highest amount of active NiO phase stabilized by the Bi_2SiO_3 phase as shown in the XRD analysis (Figure 3.1). The high BD selectivity of the 10Ni-10Bi/FS and 20Ni-30Bi/FS catalyst can be attributed to the higher Bismuth silicate to NiO phase ratio and also presence of the additional $\text{Bi}_{12}\text{SiO}_{20}$ in both catalysts. The relatively lower amount of NiO phase compared to the bismuth silicate phases in these catalysts is responsible for the lower n-butane conversion obtained despite the high 1,3-butadiene selectivity.

Table 3. 3: Performance of 20Ni-30Bi/FS catalyst at different temperatures and oxygen-to-butane feed ratios (O₂:n-C₄) of 1:1, 2:1 and 4:1 showing product distribution

Temp. (°C)	400	400	400	450	450	450	500	500	500
O ₂ :n-C ₄ Feed Ratio	1:1	2:1	4:1	1:1	2:1	4:1	1:1	2:1	4:1
n-C ₄ conv. (%)	23.1	20.1	19.0	34.2	33.8	31.8	40.1	41.7	39.8
Selectivity (%)									
DH	83.5	87.5	85.9	80.3	76.1	77.2	71.6	68.8	63.9
1-C ₄ ⁼	10.2	12.8	14.1	11.6	13.2	15.1	8.2	11.7	12.0
2-C ₄ H ₈	28.4	28.6	28.5	19.9	18.6	20.7	13.4	14.5	17.2
BD	44.9	46.1	43.3	48.8	44.4	41.4	50.0	42.6	34.7
OC	2.5	3.6	4.9	4.1	8.6	7.1	7.1	9.0	13.0
BD/DH	53.8	52.7	50.4	60.8	58.3	53.6	69.8	61.9	54.2
(1-C ₄ ⁼ +BD)/DH	66.0	67.4	66.8	75.2	75.6	73.2	81.2	78.9	73.1
BD/(1-C ₄ ⁼ +BD)	81.5	78.3	75.5	80.8	77.1	73.3	85.9	78.4	74.2
BD yield	10.4	9.3	8.2	16.7	15.0	13.1	20.0	17.8	13.8

DH = Dehydrogenation selectivity (selectivity of all C-4 olefines); BD = 1,3-butadiene; OC = Oxygenate and Cracking selectivity; 1-C₄⁼ = 1-butene; 2-C₄H₈ = 2-butene.

The observed trend for the varying feed ratio indicated that lower oxygen-to-butane feed ratios generally supported higher selectivity towards BD. This is due to higher oxygen concentrations promoting other undesired reactions like deep oxidation or combustion pathways over the desired dehydrogenation reaction, further affecting the 1,3-butadiene selectivity of the reaction. These underscore the intricate relationship among these variables, emphasizing the need for precise reaction parameter selection to optimize 1,3-butadiene yield in oxidative dehydrogenation of n-butane using the fibrous silica supported catalysts.

In Table 3.4 a comparison of the performance of previously reported silicious materials as support to immobilize 20 wt.% Ni and 10 wt.% Bi in ODHB is shown.

Table 3. 4: Comparing the Performance of 20 wt.% Ni and 10 wt.% Bi supported on different types of silicious materials at O₂:n-Butane of 2:1

Reference	[115]	[115]	[115]	This Work	
Support	SiO ₂ Gel	SiO ₂ Foam	SiO ₂ Sol	FS	FS*
Temp. (°C)	450	450	450	450	500
nC ₄ conv. (%)	17.6	34.1	35.7	33.8	40.1
Selectivity (%)					
BD	32.9	38.8	35.0	44.2	50.0
DH	67.5	69.0	57.4	76.1	71.6
1-C ₄ ⁼	18.0	12.2	11.1	13.1	8.2
2-C ₄ H ₈	16.6	18.8	11.3	18.6	13.4
OC	26.7	30.5	41.2	8.6	7.1
BD yield	9.6	13.2	12.5	15.0	20.0

* O₂:n-Butane = 1:1

DH = Dehydrogenation selectivity (selectivity of all C-4 olefines); BD = 1,3-butadiene; OC = Oxygenate and cracking selectivity; 1-C₄⁼ = 1-butene; 2-C₄H₈ = 2-butene.

3.4.1 Effect of Bismuth Loading on Catalyst

Figure 3.10 shows the profile for the n-butane conversion, BD selectivity and dehydrogenation selectivity of the catalysts as the amount of Bi loading is increased on the catalyst from 10 wt.% to 30 wt.% with the Ni loading maintained at 20 wt.%. These catalysts' performance were at the identified optimal operating conditions—500 °C reaction temperature and oxygen to n-butane feed ratio of 1:1.

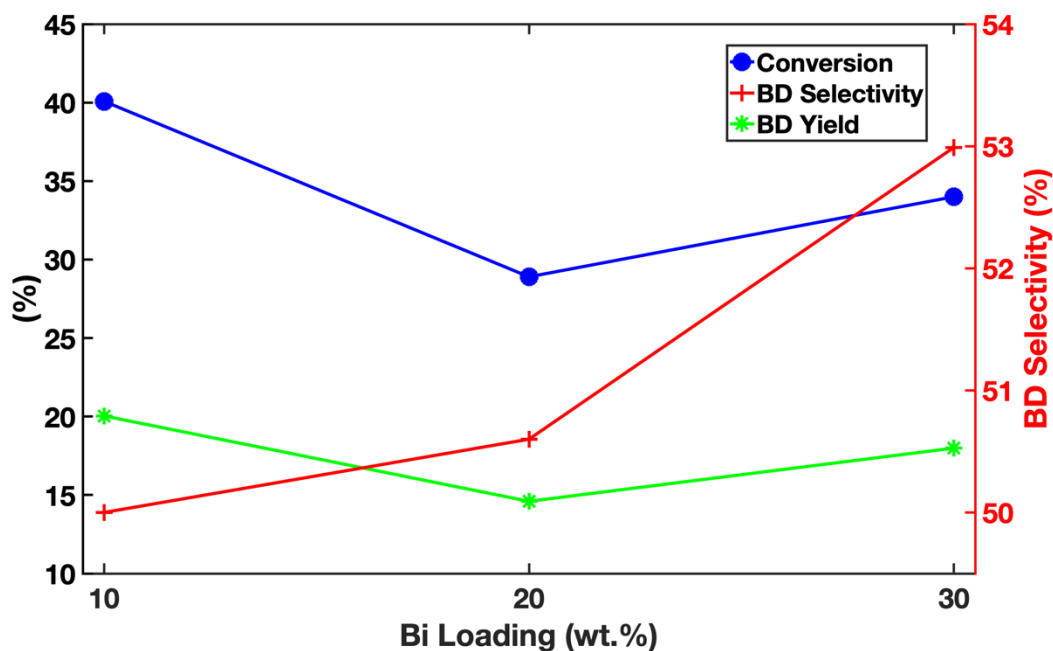


Figure 3. 10: Effects of Bi loading for 20Ni-Bi/FS at 500 °C and O₂: n-C₄ ratio of 1:1

From the analysis, a direct correlation can be noticed between the amount of Bi loading on the catalyst and the BD selectivity. The BD selectivity increased slightly with increasing amount of Bi loading from 10 – 30%. The increasing amount of Bi loading had a direct correlation with the amount of the Bi₂SiO₅ phase formed as shown in the XRD results. This silicate phase has been proven to stabilize the NiO phase and improve the selectivity of 1,3-butadiene [142]. The n-butane conversion however displays an interesting pattern. At low Bi loading, the 20Ni-10Bi/FS catalyst has the highest n-butane conversion. A dip is observed for the medium loading then a slight increase for the heavy loading. The low Bi loading had an optimum distribution of the NiO and Bi₂SiO₅ phases formed with a ratio of NiO:Bi₂SiO₅ of 2 which was large when compared to the low loading and high loading catalysts that have ratios of 0.6 and 0.34 respectively. The Bi loading affects the phase distribution of the phases formed and hence the amount of active NiO phase formed. In the catalysts where the NiO active phase formed were lower compared to the

Bi₂SiO₅ phase, lower catalytic activity was observed. The decline in dehydrogenation selectivity at high Bi loading can be attributed to the formation of more oxidative cracking products at the high Bi loading.

3.4.2 Effect of Nickel Loading on Catalyst

Figure 3.11 shows the profile for the n-butane conversion, BD selectivity and dehydrogenation selectivity of the catalysts as the amount of Ni loaded on the catalyst is increased from 10 wt.% to 20 wt.% with the Bi loading maintained at 10 wt.%. These catalysts' performance were at the identified optimal operating conditions—at 500 °C and oxygen to n-butane feed ratio of 1:1.

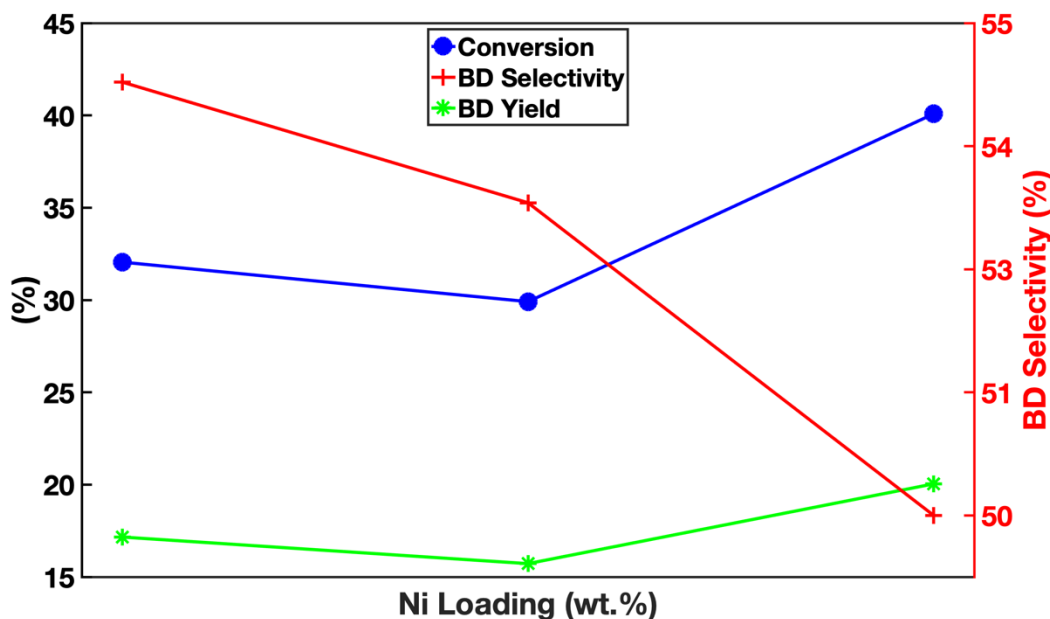


Figure 3. 11: Effects of Bi Loading for Ni-10Bi/FS at 500 °C and O₂: n-C₄ ratio of 1:1

There is negligible impact on the conversion of n-butane with the low and medium loading of Ni however when the Ni loading is increased up to 20% the increase in the n-butane conversion is noticeable due to the evidently larger amount of the NiO active phase in the high Ni loading catalyst as seen in the XRD.

3.5 Conclusion

Novel fibrous silica supported Ni-Bi-O supported catalysts demonstrated outstanding performance for oxidative dehydrogenation of n-butane to produce 1,3-butadiene. Different Ni/Bi loading ratios which affected the distribution of the NiO and Bi₂SiO₅ phases formed were evaluated. The modified silica supported catalysts showed enhanced activity and BD yield. The good selectivity towards BD is as a result of the formation of the highly crystalline Bi₂SiO₅ phase which confirmed through XRD that stabilizes the stoichiometric NiO phase. The 10 wt.% Ni and 10 wt.% Bi supported on the fibrous silica catalyst had the highest BD selectivity owing to the presence of this silicate phase in the largest amount amongst the catalyst, thus, enhancing the selectivity towards BD and suppressing the formation of deep cracking products. However, the 20Ni-10Bi/FS catalyst gave the highest BD yield at reaction temperature of 500 °C and oxygen:n-butane feed ratio of 1:1. The catalyst had the highest amount of crystalline NiO active phase formed relative to the Bi₂SiO₅ phase amongst all the catalyst.

CHAPTER 4

PREDICTING THE PERFORMANCE OF SUPPORTED MIXED-METAL OXIDES CATALYSTS FOR OXIDATIVE DEHYDROGENATION OF n-BUTANE USING ARTIFICIAL INTELLIGENCE

ABSTRACT

The development of efficient and selective catalysts for the oxidative dehydrogenation (ODH) of n-butane to produce butenes and 1,3-butadiene with high performance has been subject of intense research in recent years. Herein, we report a novel approach for predicting the performance of mixed metal oxides supported on Al_2O_3 for ODH using artificial intelligence (AI). Specifically, Artificial Neural Networks (ANN), Support Vector Regression with Nu Parameter (NuSVR), eXtreme Gradient Boosting Regressor (XGBR), and Gradient Boosting Regression (GBR) machine learning algorithms were trained with a dataset of consistent experimental data to build the chemometric models using reaction temperature, feed ratio of O_2 :n- C_4 , and catalyst composition as input features to predict the yield of ODH products as a measure of catalyst performance. The

results show that the AI-based models can accurately predict the performance of mixed metal oxides catalysts for ODH of n-butane, with prediction accuracy of 82%, 89%, 92%, and 95% using ANN, NuSVR, XGBR, and GBR models, respectively. Feature Importance Analysis also revealed that the amount of Ni loading in the catalyst(s) has the greatest influence on the yield of butenes and 1,3-butadiene. These findings demonstrate that accurate predictions of catalyst performance can be made even with simple and easily accessible features, thus paving the way for the development of more efficient catalyst design and discovery methods.

4. Introduction

Catalysts are the driving force behind the paradigm shift toward the development of efficient and environmentally friendly chemical processes for the conversion of materials and wastes into useful fuels and chemicals. This is because catalysts influence a chemical reaction and have a major effect on the distribution of reaction products. A green future would require the development of chemical processes involving a net input of only environmentally friendly chemicals and materials. Hence, the requirement for catalysts that can control the production of base chemicals and fuels from sustainable sources. Also required are catalysts that follow reaction paths that minimize unwanted by-products [143].

Catalyst discovery through experimentation, however, poses a formidable challenge for researchers, given the vast number of materials and an even greater multitude of potential material combinations to explore as well as wide range of operating conditions. This is further compounded by the diminishing resources available for research. However, machine learning (ML) offers a promising solution to ease this burden. By leveraging on sophisticated algorithms, ML can rapidly sift through the vast design space, predicting and optimizing catalyst performance with remarkable efficiency. Through the analyses of vast amounts of data, ML algorithms can uncover hidden patterns, correlations, and insights that might elude traditional experimental approaches. This enables researchers to prioritize and focus their efforts on the most promising catalyst candidates, significantly reducing the time, cost, and resources required for exploration [143]–[145].

Oxidative dehydrogenation (ODH) is an important process for upgrading low-value short-chain alkanes into higher-value alkenes. The obtained short-chain alkenes serve as major raw material for chemical industries to produce a wide range of consumer and industrial products, including synthetic rubber, fuels, plastics, fertilizers, synthetic fibers, paints, and detergents [120]. The use of light alkanes as building blocks for the production of chemicals is particularly attractive because they are abundant, inexpensive and environmentally friendly resources [143].

Oxidative dehydrogenation of n-butane (ODHB) to produce 1,3-butadiene is an attractive alternative compared to conventional dehydrogenation (DDH) and has been trending subject of research. This is because ODHB is not limited thermodynamically and hence, can proceed at a relatively lower reaction temperature. In addition, catalyst deactivation by coke deposition is tempered due to the presence of oxygen [9]–[11]. This offers several advantages including decreased operational cost and longer catalyst life.

However, developing selective and industrially relevant catalysts for ODHB to C4 olefins while minimizing the formation of unwanted by-products such as carbon oxides (CO_x) and coke, remains a main challenge. Several catalysts have been explored by researchers for ODHB [1], [14]–[17], however, even with the high activity that favour the yield of dehydrogenation products only gives low selectivity to C4 olefins.

For many catalytic applications, excellent catalysts have been discovered with time and experimentation. However, a systematic way to provide information on the intrinsic catalytic property that results in the observed catalytic performance has not been proven. In this regard, ML has shown promise as a valuable tool for such purposes [146], [147]. ML techniques in combination with big data have resulted in advancements in catalysts

discovery [148]–[150]. However, a necessary condition for the success of a ML model to represent a system is the quality of the data used to develop the model. Quantum mechanics integrated with ML has been applied for several important catalytic processes including accurate screening of catalysts[148], [151], prediction of yield and accurate conversion estimation of catalytic reaction.

Research in heterogeneous catalysis using ML can be traced back to the early 1990s. The early works used neural networks (NN) to study the relationship between reaction conditions and catalyst properties with experimentally determined catalyst performance [145], [152], [153]. Kito et al [152] were one of the first to make attempts in this area of research. In their work, the authors concluded that a NN with only one hidden layer is useful to directly predict product distribution in a catalysed reaction. They studied the catalytic performance of 18 promoted and unpromoted SnO₂ catalysts for the selective dehydrogenation of ethylbenzene using a NN comprising 9 units in the input layer, a single hidden layer with 8 units and a 5-unit output layer. The NN demonstrated excellent estimates of the styrene selectivity and other by-products.

Sasaki et al., (1995) demonstrated that artificial neural networks (ANN) can accurately estimate catalytic activity and optimize experimental conditions [154]. Similarly, Serra et al., (2003) demonstrated that a developed ANN model needed only little experimental data to give accurate predictions that can be relied upon [145]. They considered input parameters such as reactor temperature, reaction time, and partial pressure to investigate the isomerization reaction of n-octane on platinum-chlorinated alumina catalyst using ANN to accurately foretell the conversion and yield. Their findings revealed an interesting relationship between experimental errors in the training data and the reliability

of predictions. Experimental errors minimally affected prediction accuracy, except when the standard deviation surpassed 2. Higher variability introduced errors that significantly deviated predictions. Keeping the standard deviation below 2 yielded reliable and consistent results, emphasizing the importance of minimizing experimental variability.

Ghasemzadeh et al., (2018) created ANN to model the reaction on a silica membrane reactor utilized for methanol steam reforming process [155]. The ANN achieved a remarkable prediction accuracy of 99% despite not considering the physical interactions and governing equations. The results obtained from ANN closely aligned with the original data. This further emphasizes the efficacy of ML approach in capturing the underlying patterns and relationships within complex reaction systems without explicitly incorporating the detailed physics governing the system.

The use of ML techniques for accurate catalyst performance prediction is not limited to ANNs alone. Several studies have demonstrated the effectiveness of other ML algorithms in predicting catalyst performance using simple features. In a study by Nguyen et al. [156], the random forest regression technique was employed to predict the C₂ yield in the oxidative coupling of methane reaction. They utilized a dataset comprising 12,708 high-throughput experimentation data points. Input features were 11 comprising catalyst composition, reaction temperature, feed flow rate, contact time, and feed ratio. Despite the simplicity of these features, the random forest regression model achieved a high cross-validation score of 0.88.

Chowdhury et al., investigated various ML algorithms, including support vector regression (SVR), Gaussian process (GP), and ANN, for predicting the surface adsorption energies of three chemical species on a catalyst (2018) [157]. They focused on geometric

data of the active catalyst species and used several descriptors for prediction. The study revealed that the models did not consider sophisticated features such as coordinate-based descriptors. Despite this limitation, the ML methods, including SVR, GP, and ANN, were able to provide useful insights and predictions. This finding emphasizes the successful application of diverse ML techniques in catalyst performance estimation, even when simple features are employed.

The above studies have demonstrated that ML techniques beyond ANN can be effectively employed for catalyst performance estimation using simple features. The success of random forest regression in predicting C2 yield and the application of SVR, GP, and ANN in predicting surface adsorption energies underscore the versatility of ML methods in this domain. By considering different ML techniques and their respective strengths, we can enhance the understanding of catalyst performance and develop accurate predictive models.

Experimentally determining the performance of large number of catalyst composition in ODHB can be extremely time-consuming. There is the need for an AI model that can accurately predict catalyst performance in ODHB especially, when there is an endless possibility of metal combinations to be tested as potential catalysts.

In this work, ML models are developed to predict the product yield in oxidative dehydrogenation of n-butane using Al₂O₃-supported mixed metal oxides catalysts with high accuracy. The models are based on simple and inexpensive input features which include reaction temperature, feed ratio, and catalyst composition. The data comprises 184 points of purely experimental data obtained using BELCAT system, a fully integrated continuous flow type fixed-bed reactor unit.

4.1 Machine Learning Concepts

Machine learning is often used interchangeably with AI to describe the same thing. This cannot be always correct as AI represents a larger application and ML is only a subfield of AI that involves algorithms that can be employed in categorizing data and accurately predicting future happening [158]. As shown in Figure 4.1, deep learning refers to a certain class of algorithms built on ANN while data science is an umbrella term for activities relating to data. Finding nonlinear connections between independent and dependent factors remains the prime purpose of ML, which also uses classification and regression to forecast precise classifications. A dependent variable is predicted using ML models as a function of independent factors. The two main actors in prediction and decision-making are deep learning (DL) and ML algorithms, which teach a computer to become an expert device. AI, however, is the parent field utilized to demonstrate human intellect in a computer [158], [159].

ML depends on creating statistical models that adapt to the input data and has lately shown to be a potent tool for the effective discovery of nuanced patterns in complicated data which would normally prove difficult for human parse [160], [161]. In what are known as interpolative tasks, trained ML models may be used to generate predictions when fed with inputs that fall inside the boundaries of the training dataset. This comprises novel pairings of existing well-known elements including catalysts, ligands, and additives. The predictive ability of a ML model declines as structural differences between the training and test data rise, making extrapolative tasks problematic since they include predictions about inputs that are not within the boundaries of the training data. The three main parts of ML are: Data gathering, featurization and modelling. The

following discussion in this study will be according to these aspects as they relate to heterogeneous catalysis, especially the ODHB [162]. In Table 4.1 details of some notable ML applications in heterogeneous catalysis are highlighted.

Classification using ML can be seen as predicting the groups that a feature falls into while regression predicts constant numerical values. The prediction of catalytic performance in new regimes from current experimental data is the simplest ML application in catalysis informatics. For this, operating parameters (such as temperature and pressure) and macroscopic characteristics of evaluated catalysts (such as surface area, phase, composition, and particle size) are often used as features to replicate the catalytic performance [163].

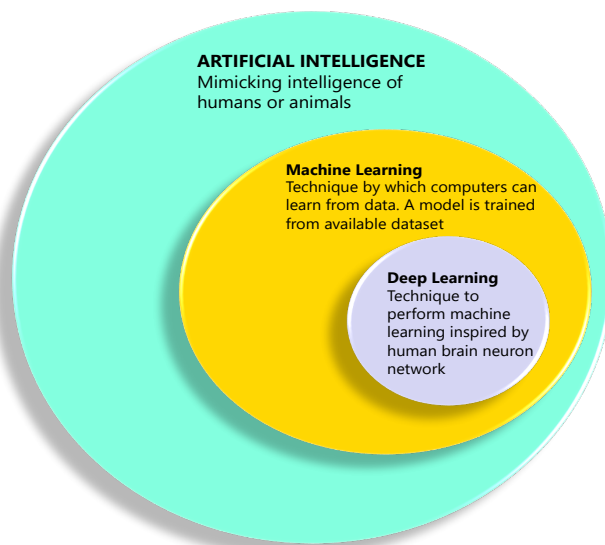


Figure 4. 1: Illustration of the connection between machine learning and artificial intelligence [159]

Other common applications of ML in heterogeneous catalysis include catalyst discovery [164], [165], characterization of catalyst structural features [166], construction of complex catalyst phase diagrams [167], predicting catalytic performance in un-experimented conditions[156], [157], [168], [169], accurate evaluation of reaction

energetics which is vital in kinetic modelling for catalyst screening [170], [171], catalyst active site identification [164], [172], [173], sorting through reaction networks involving thousands of pathways [174], transition state search [175]–[177], expediting Quantum Mechanical calculation and structural optimizations [178]. These wide relevance of ML in heterogeneous catalysis is tied to reliable data availability.

Table 4. 1: Notable applications of machine learning (ML) in heterogenous catalysis

APPLICATION	ML TECHNIQUE	CATALYST MATERIAL	DETAILS OF FINDINGS	REFERENCES
CATALYST DISCOVERY	Active ML Regression	Cu-Al alloy	ML reduced computational cost of determining optimal Cu-Al ratios before confirmation with DFT calculations	[164]
	Unsupervised ML technique Hierarchical agglomeration algorithms	Zn-Mg bases Ternary Nitrides	Discovery of 7 new Zn and Mg based ternary nitrides.	[165]
PHASE DIAGRAM CONSTRUCTION	Convolutional Neural Network	Tested with Platinum-based	Coverage effects of material were accurately modelled	[167]
CATALYST PERFORMANCE PREDICTION	Random Forest Regression	20 different catalysts 216 different reaction conditions Catalyst form: $M_1-M_2-2M_3O_4/\text{support}$. M1 are transition metals and lanthanide elements; M2 and M3 constitute tungstates or molybdates		[156]
	Unsupervised: Gaussian	6 Different catalysts groups	ML in addition revealed complex	[168]

	Mixture model (GMM)	identified based on changing CH ₄ /O ₂ ratio	patterns and trends in OCM data	
	Supervised - Artificial Neural Networks	Manganese based	Reliable and accurate prediction of the Performance of Manganese ores as oxygen carriers for chemical looping	[169]
EVALUATION OF REACTION ENERGETICS OF HETEROGENEOUS CATALYZED REACTIONS	Theory-infused neural network (TinNet)	Pt-based bimetallics (with transition metals) doped with a third metals	1.Accurate estimation of chemical reactivity of transition-metal surfaces using ML 2.Develop strategies for catalyst design	[170]
	SISSO Multitask learning	Accurate prediction of adsorption energies on all potential surface sites of materials.	Transition metals and Bimetallics formed from Transition metals	[171]
IDENTIFY CATALYST ACTIVE SITES	Two separate Neural networks	Reliable estimation of CO adsorption energy on irregular material surface. Accurately predict formation energy of HOCO on uneven gold surfaces.	Au	[172]
	Neural Networks	Active sites CO ₂ reduction using Nickel gallium bimetallic Catalysts.	Nickel-gallium bimetallics	[173]
FINDING TRANSITION STATE AND QUANTUM MECHANICAL CALCULATION AND STRUCTURAL	Gaussian Process Regression (GPR)	Optimization of adsorption systems	Faster and cheaper computation yielding more accurate results than traditional method	[175]
	GPR	Quantum mechanical calculation and structural		[176]

OPTIMIZATIONS		optimizations		
	GPR	Used the model to accelerate the rate of convergence of Nudged Elastic Band Calculations		[177]
	Sparse Interpolation with Smolyak Construction	Accurate and cost-effective Construction of Potential Energy Surface (PES)		[178]

4.2 Models used for Machine Learning in Heterogeneous Catalysis

4.2.1 Unsupervised ML Models

Algorithms for unsupervised learning attempt to draw patterns from the data. They utilize information based on features already learned to determine the group any provided unseen data belongs to. K-Means clustering is a popular clustering technique. Using this technique, data points that are identical make a cluster. Its name, "k," comes from the k different clusters and by finding the average of all points in a cluster, the cluster head is determined [179].

For the study and design of heterogeneous catalysts, the accurate predictive correlations between geometric structure, electronic structure and the adsorption characteristic of a catalyst site must be established [180]. There is currently no standardized method for systematically finding how electronic configurations affect a catalyst's adsorption capabilities, it may or may not be evident which features are responsible for an observed performance. Recently, unsupervised ML approach has proved valuable for the identification of electronic structure descriptors. Esterhuizen et al. [181] showed using principal-component analysis that unsupervised learning provides a simple method for creating interpretable and precise electronic-structure descriptors for materials' catalytic properties that can be linked to composition and geometric structure.

Due to the ability of unsupervised models to learn unclassified data, the models prove valuable in the search for new catalysts. Sun et al. [165], recently used unsupervised ML to build a substantial stability map of ternary metal nitrides, a chemical region with a wealth of potential uses that has yet to be fully investigated due to challenging synthesis conditions. In addition to seven novel zinc and magnesium based ternary nitrides being successfully synthesized, their studies showed hundreds of intriguing new ternary nitrides. They also explained the thermochemical and electrical causes of the stability of ternary nitride using ML. This research demonstrates the potential of ML-assisted in silico materials discovery to remarkably increase the library of catalysts already available.

4.2.2 Supervised ML Models

Using the training dataset as a starting point, supervised learning algorithms build patterns that are then applied to the test dataset. They are mainly used for the detection of outliers in data, classification, and prediction [179]. Support vector machine and Decision Tree (DT) are examples of supervised learning models. Decision trees are sequential structures that identify the unknown data and develop rules from the known data. Hence, by ensuring the greatest separation between the classes, the learning algorithms of the Support Vector Machine reduce any errors in regression analysis and classification [158]. One of the most popular weak learners for ensemble techniques is the DT. A simple predictor that is just marginally more accurate compared to a random predictor is referred to as a weak learner. To simultaneously reduce the model's variance and bias, tree-based ensemble approaches use several weak DT models that evolve in tandem. Ensemble

methods are a conglomeration of algorithms that use more than one base learner to make more advanced models [182].

The conglomeration of several DTs gives rise to a Random Forest. Hence, in comparison to using a single decision tree, ensemble approaches integrate many decision trees to generate higher predicting performance. The ensemble model's power comes from the synergy created when two or more techniques are combined to produce a single and more powerful technique. Basically, weak learners can be synergized to give birth to stronger learners [183].

Random forest (RF) is a tree-based ensemble method that reduces the variance of decision trees. Numerous data subsets are created from the available training sample randomly selected with substitutes. The unique property of the random forest technique is that the tree is grown utilizing a random selection of features as opposed to using all. It uses a voting procedure, similar to other ensemble learning techniques, to enhance the performance of numerous weak tree estimators [179], [184]. The original dataset is utilized to generate N bootstrapped sample sets, which are then used to train a random forest.

Abdelbasset et al. [185] in a recent work demonstrated the power of ensemble methods. They developed three ML models and combined them to simulate and optimize the heterogeneous catalytic conversion of waste cooking oil to biodiesel. They utilized the model to predict optimal properties that gave a biodiesel yield of 96.7%. The utilized features were catalyst loading, feed ratio, reaction time and temperature with a biodiesel percent yield as the only target variable selected. The models were Boosted Multi-layer perception, Boosted Linear Regression, and Forest Randomized Tree. The results showed

that the boosted multi-layer perceptron was superior compared to the others in terms of the accuracy of prediction.

4.3 Research Methodology

The collected experimental dataset was pre-processed to prepare it for use in ML models. Four separate ML algorithms were selected and trained on the data to predict n-butane dehydrogenation yields. The performance of the model was evaluated, and potential limitations and areas for improvement were made evident. Finally, a feature importance analysis was conducted to investigate which features have the most influence on the dehydrogenation yield.

4.3.1 Dataset Gathering and Description

To gather the data used in this work, the catalyst performance in ODHB reaction was investigated utilizing the BELCAT system [8] which is a fully integrated fixed-bed continuous flow type reactor. The system consists of a single tubular quartz reactor that is connected to a stainless-steel furnace assembly through a thermowell present in the reactor furnace wall. Analysis of the reaction products was conducted using an online GC system (Agilent, 7890N) equipped with one FID for hydrocarbon and oxygenate analysis and two TCD detectors for N₂, O₂, CO, CO₂, and H₂ analysis. The products were identified by comparing them to standard samples, and the product yield was calculated based on carbon balance. Equations 4.1 to 4.3 were used for the evaluation of the n-butane conversion, DH selectivity and DH yield

In a typical procedure, the wet co-impregnation technique was employed for synthesizing the catalysts. Metal precursors (over 98% purity) were utilized to obtain active metal loading of between 0 – 30 wt. %. To activate the catalysts, a two-step calcination

procedure was implemented consisting of an initial stage of 350 °C for 1 hour (with a heating rate of 10 °C per minute) followed by a second stage at 590 °C for 2 hours (with a heating rate of 15 °C per minute), respectively. For the performance evaluation in ODHB 300 mg of the catalysts having pellet size in the range of 500 – 850 microns were used. Further experimental details including the detailed procedures followed for catalyst preparation, catalyst characterisation, and the conditions and equipment used for the evaluation of the catalyst performance can be found in our previous work [186].

The dataset obtained comprised 184 noiseless datapoints comprising 31 different catalysts and bare Al₂O₃ support with no metal loading tested for the ODHB reaction at different temperatures, and feed ratios. The performance measure used is the yield of dehydrogenation products (i.e. C₄ olefins which include 1-butene, 2-butene and 1,3-butadiene). The reaction temperature range was between 400 – 500 °C and the feed ratio is between 1 – 4 mol/mol for O₂:C₄. The catalyst composition is in percentage weight loading of Nickel (Ni), Iron (Fe), Cobalt (Co), Bismuth (Bi), Molybdenum (Mo), Tungsten (W), Zinc (Zn) and Manganese (Mn).

$$\text{Butane conversion (\%)} = \frac{\text{moles of butane fed} - \text{moles of butane in the product}}{\text{moles of butane fed}} \times 100 \quad (1)$$

$$\text{DH selectivity (\%)} = \frac{\text{moles of DH product}}{\text{Butane conversion}} \times 100 \quad (2)$$

$$\text{DH yield (\%)} = \frac{\text{Butane conversion} \times \text{DH selectivity}}{100} \quad (3)$$

DH here represent dehydrogenation products which comprise 1-butene, cis-2-butene, trans-2-butene and 1,3-butadiene

4.3.2 Data Analysis

A concise statistical overview of the dataset is presented in Table 4.2. In Figure 4.2 a visual representation showcasing the distribution of the features used for the model development is presented. These visuals are instrumental in identifying areas with limited data, highlighting where availability of additional data can potentially increase the predictive accuracy of the machine learning models.

Table 4. 2: Statistical Measures Describing the Input and Output Features of the Dataset

	Inputs										Output
	T	FR	Ni	Fe	Co	Bi	Mo	W	Zn	Mn	Yield
count	184.00	184.00	184.00	184.00	184.00	184.00	184.00	184.00	184.00	184.00	184.00
min	400.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.64
max	500.00	4.00	30.00	20.00	20.00	30.00	20.00	30.00	20.00	20.00	22.61
mean	436.41	2.25	10.16	2.28	2.04	22.77	2.22	1.63	1.71	1.47	9.03
σ	41.88	1.09	7.94	4.65	4.63	11.75	5.27	5.96	4.78	4.74	5.05
min and max represent the minimum and maximum value of a particular feature in the dataset;											

min and max represent the minimum and maximum value of a particular feature in the dataset;

FR represents feed ratio

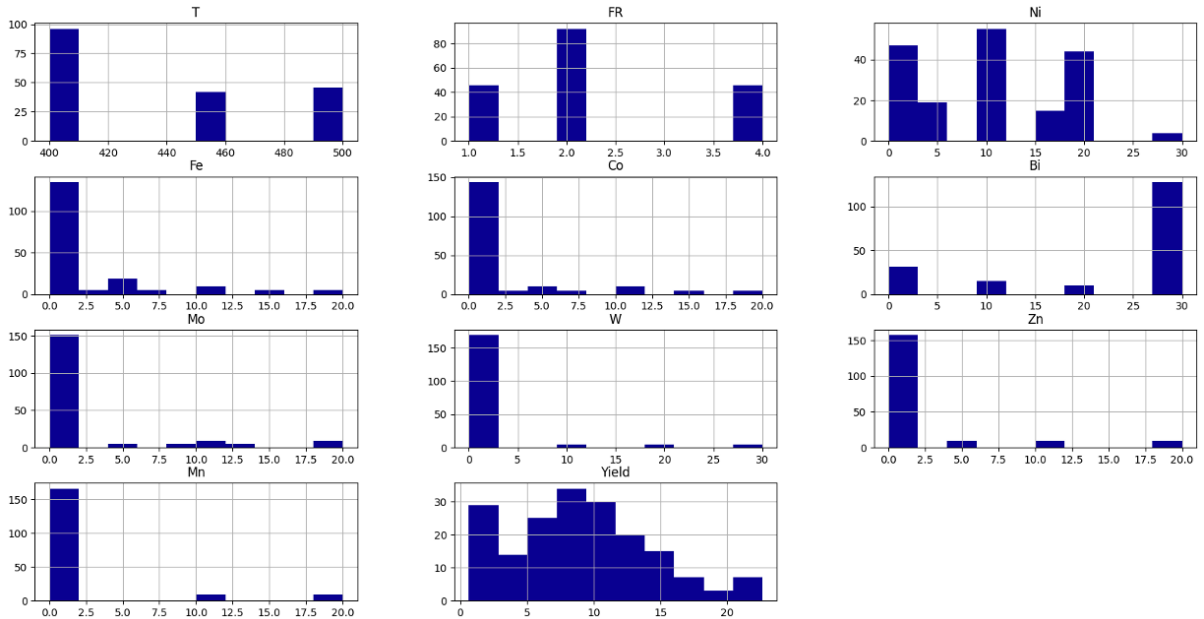


Figure 4. 2: Distribution of Data for the input variables which include Reaction temperature, Feed Ratio, Nickel Loading, Iron Loading, Cobalt Loading, Bismuth Loading, Molybdenum Loading, Tungsten Loading, Zinc Loading, Manganese Loading and the Yield which is the Target Variable

Figure 4.3 shows the pair plot illustrating the relationship between the dehydrogenation yield with each of the input features used in this study, showcasing any existing connections between them. Pair plots offer visual insights into linear relationships among variables, thereby helping to uncover patterns or relationships. In Figure 4.3, the target variable is compared against all input variables. Analyzing these results guides the selection of appropriate chemometric techniques for predicting dehydrogenation yield from the considered features.

The analysis reveals that no robust linear correlation exists between the input features and dehydrogenation yield. However, weak positive correlations emerge for Co loading, Ni loading, Bi loading, and Reaction Temperature with the yield, while W loading and Mo loading display weak negative correlations. The absence of strong correlations suggests the need for sophisticated chemometric techniques to model the relationship between the input variables and the target variable. This consequently ensures a reliable and accurate prediction of the target variable using the developed model.

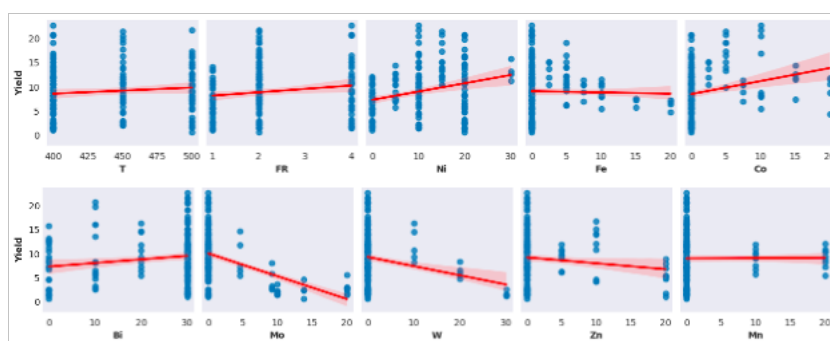


Figure 4. 3: Pair plot of the Dehydrogenation Yield Against All The Input Variables

4.3.3 Data Driven Modelling

All the features described previously were used to develop the chemometric models for predicting the dehydrogenation yield in ODHB. In Figure 4.4, an insight into the

relationship existing between the features is shown using Pearson's correlation. The Pearson's correlation coefficient (PCC) between each input feature (input-input) and between the dehydrogenation products yield and each input feature (output-input) is shown. Pearson correlation is widely used in regression methods to investigate the linear relationship that exist between two features in a dataset. The degree of correlation between two features is indicated by the values located at the intersection of the column corresponding to one feature and the row corresponding to the other feature. For example, the value 0.0075 is an indication of a weak relationship between the amount of Mn loaded and the dehydrogenation yield. In this case, the correlation of the input feature with the target variable as well as with each other is shown.

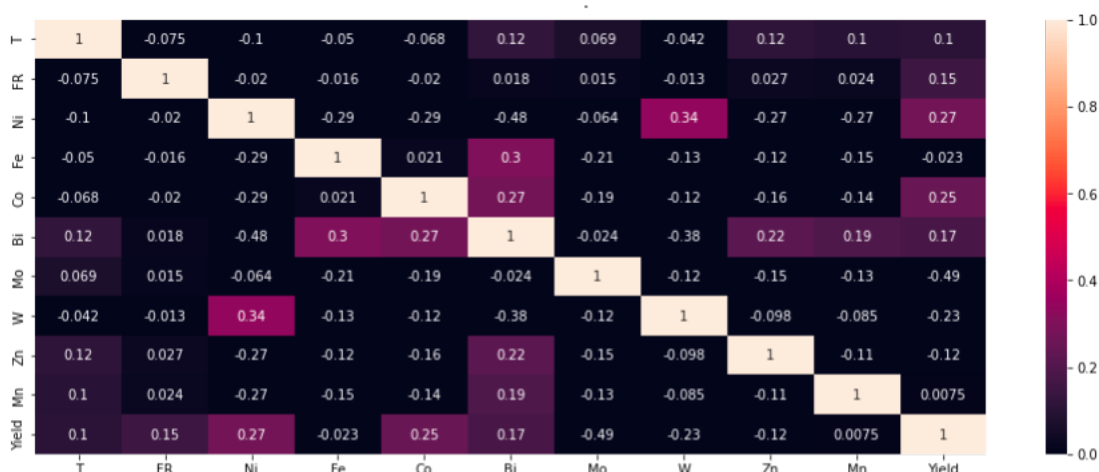


Figure 4. 4: Pearson Correlation Coefficients for Dehydrogenation Yield and Input Features (Reaction Temperature, Feed Ratio, Nickel Loading, Iron Loading, Cobalt Loading, Bismuth Loading, Molybdenum Loading, Tungsten Loading, Zinc Loading, Manganese Loading).

Examining the interrelatedness between features before model development is essential. Detecting any existing issues in how features relate to each other beforehand is critical as they can adversely impact model performance. A notable concern arises when two input features exhibit strong correlation, typically above 0.8, leading to multicollinearity

issue[187]. The low correlation coefficient values between the features, with 0.34 between Ni and W being the largest indicate that no two features have any direct linear relationship. This indicates that there is low risk for multicollinearity in the dataset. However, for a robust model with reliable predictions, it also implies that all the 10 input features would have to be used for training the chemometric models.

To develop the models, the entire dataset was split into optimal training and testing set of 80% and 20%, respectively. As a pre-processing step, the values of the features were normalized to range from 0 to 1. This is mainly to reduce the impact of different scales of the data on the training process and to improve the numerical stability of the model. For each model also, data stratification using the output variable as criteria was employed when splitting the data into the training and test set by several random splits using different seeds. Then the model was trained on each of the splits with different combination of hyper-parameters. This was in order to determine the optimum split that has a training set which would serve as a good representation of the dataset along with a parameter combination that would result in a high-performance chemometric model.

To assess the performance and validity of each model, various metrics including root mean squared error (RMSE) and coefficient of determination (R-Squared) were employed. The R-squared values were obtained from cross plots of the DH yields predicted by each model plotted against the experimental DH yields and were used to represent the percentage accuracy of the models' predictions. The test set was only used at the end to check the model's performance and was not used during the model development and training process. The equations for the performance metrics used in the data pre-processing and model training stages are as follows

$$\begin{aligned}
\text{I. R-Squared} &= 1 - \frac{\sum_{i=1}^n (X'_i - X_i)^2}{\sum_{i=1}^n (X'_i - \bar{X}_i)^2} \\
\text{II. RMSE} &= \sqrt{\frac{\sum_{i=1}^n (X'_i - X_i)^2}{n}} \\
\text{III. PCC} &= \frac{\sum_{i=1}^n (X'_i - X_i)(Y'_i - Y_i)}{\sum_{i=1}^n (X'_i - \bar{X}_i)^2 (Y'_i - \bar{Y}_i)^2}
\end{aligned}$$

Note that X is the actual value for variable X in dataset, X' is the Predicted value for variable X , and n is the Total number of sample points

4.3.4 Artificial Neural Network (ANN) Model Development

Using the training set, the ANN model was optimized by tuning the hyper-parameters. Evaluation of the model's performance was based on the test set which was not used during the training process, thus reducing any bias that may arise when testing the model's performance. The hyper-parameters that were tuned using the training set include the number of hidden layers and the number of neurons in the hidden layers. After running several iterations, the optimal topology resulting from the parameters that generated the least errors was retained and finally examined using the test set.

Table 4.3 gives a depiction of the search space explored in building the model. The parameters were determined in separate levels to improve the computational cost effectiveness. However, while varying a parameter to determine the optimum, some variance was maintained with some of the other parameters to account for their interdependence. For example, when checking for the optimum number of hidden layers, the search result is an average over a subset of the different optimizers, the number of epochs and the number of neurons in the hidden layers.

Table 4. 3: Range of Hyper-Parameters Explored for ANN model

Parameter	Range
Number of Neurons	$1 \leq x \leq 100$
Number of Hidden layers	$1 \leq x \leq 3$
Number of Iterations (Epochs)	$1 \leq x \leq 1000$
Loss Function	RMSE
Optimizer	Adam, Nadam, SGD

4.3.5 Nu Support Vector Regression (NuSVR) Model Development

The dataset was divided into training and test sets with an 80:20 ratio after the data pre-processing procedure described previously. The training set was then used to fit the model. To find the optimal hyper-parameters of the NuSVR model, a grid search was performed using 5-fold cross-validation. The grid search explored different combinations of C and gamma values to find the best model performance using the Linear Kernel, Gaussian i.e. Radial Basis Function (RBF) Kernel and Polynomial Kernel. Table 4.4 shows the grid search space employed. The GridSearchCv module available on scikit-learn python library was employed to carry out an exhaustive search over the specified parameter grid in order to determine the optimal hyper-parameters for the model. At the end, the model's performance was evaluated using the test set.

Table 4. 4: Range of Hyper-Parameters Explored for the NuSVR Model

Parameter	Range
C	$0.01 \leq x \leq 100$
Gamma	$0.1 \leq x \leq 100$
Kernels	Linear, Polynomial, RBF
Loss Function	RMSE
Accuracy	R-squared

4.3.6 Gradient Boosting Regressor (GBR) and eXtreme Gradient Boosting Regressor (XGBR) Model Development

For both ensemble models, the data pre-processing steps were applied and the optimum 80:20 train/test split was used for model development. The model performance was

optimized by tuning hyper-parameters using the GridSearchCV module available in the scikit-learn ML library. Different numbers of trees (estimators), learning rates, and maximum tree depths were explored for each model. The grid search space explored is summarized in Table 4.5.

To avoid overfitting, k-fold cross-validation with 5 folds was applied to only the training set during the parameter tuning and training process. The test data was not used during this process, but only at the end to evaluate the performance of each model.

Table 4. 5: Range of Hyper-Parameters Explored for the GBR and XGBR Models

Model	Parameter	Range
GBR	Number of Trees	$100 \leq x \leq 400$
	Learning Rates	$0.05 \leq x \leq 1.0$
	Maximum Depth of Trees	$3 \leq x \leq 5$
XGBR	Number of Trees	$100 \leq x \leq 400$
	Learning Rates	$0.05 \leq x \leq 1.0$
	Maximum Depth of Trees	$3 \leq x \leq 5$

4.3.7 Shapley Additive exPlanations (SHAP)

SHAP is a commonly used technique for understanding the way a ML technique makes its predictions. This technique, introduced in 2017 by Lundberg and Lee [188], offers an integrated approach that prioritizes the input features for individual predictions by machine learning models. SHAP operates by determining Shapley values. The Shapley value associated to a feature is an indication of the influence that the feature in question has on the prediction outcome. Leveraging co-operative game theory principles, SHAP technique has gained popularity due to its lucid properties as a result [189]. Using an additive feature attribution method, the technique estimates the contribution and relative impact of each input feature toward the final model prediction.

4.4 Results and Discussion

In this section, the outcomes of our study are presented and discussed. Instructive results on the prediction of dehydrogenation yield from the ODHB over alumina supported bimetallic catalysts using the ML techniques that have been described in section 3. The outcomes in addition to confirming the viability of the adopted techniques also give insight into variables that promote dehydrogenation. The prediction accuracies of the different models were compared and insight into how the model works is also presented.

4.4.1 Final ANN Model

The ANN model was developed as per the following method. The optimized hyper-parameters for the ANN model are shown in Table 4.6. The performance of this final model was evaluated using the test set which comprises 20% of the original 184 data points. It is worthy of note that this test set was not used at all during the training and development of the model. The performance of the model is shown in Figure 4.5 where a cross plot of the predicted and experimentally measured DH yield is shown. Each point on the plot represents a single observation. The regression coefficient (R-squared value) obtained for the fit based on the unseen test data is 0.82 and RMSE of the predicted values from the measured is 0.305.

Table 4. 6: Details of Hyper-Parameters in Final ANN Model

Parameter	Range
Number of Hidden layers	3
Number of Hidden Layer Neurons	Layer 1 = 30; Layer 2 = 20; Layer 3 = 100
Number of Iterations (Epochs)	1000
Optimizer	Adam

The performance of the model on the entire dataset was also investigated and an R-squared value of 0.87 is observed.

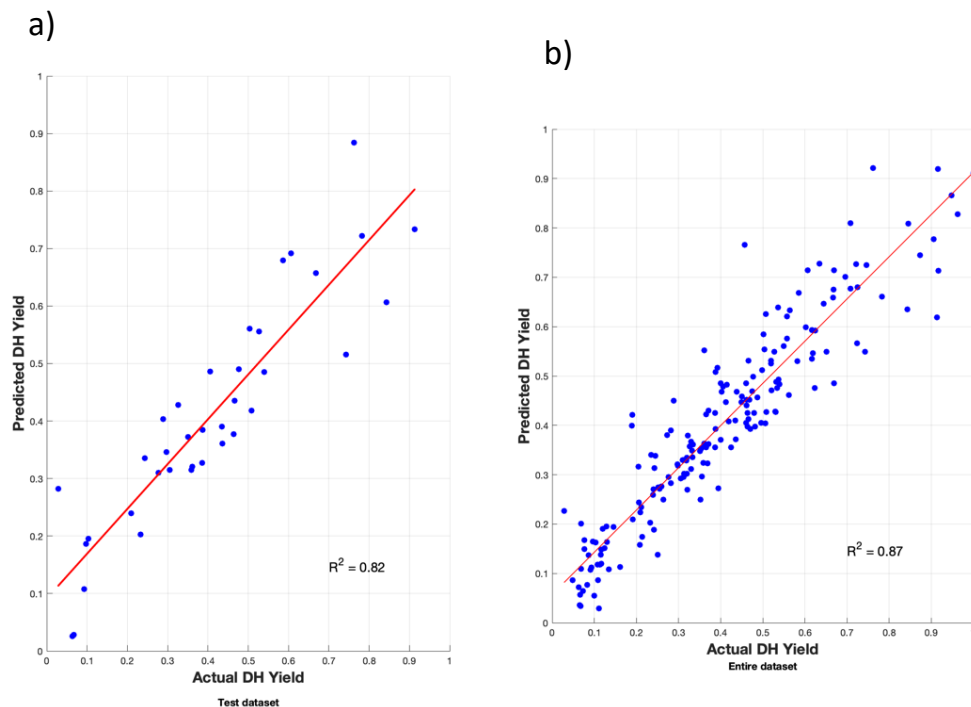


Figure 4. 5: Cross plot of Measured DH Yield and Predicted Yield using the ANN Model. The graph displays the results for both the test dataset (a) and the entire dataset (b).

4.4.2 Final NuSVR Model

Based on the methodology for developing the NuSVR model earlier described, the best parameters found using the scikit-learn GridSearchCv module were $C=1$ and $\gamma=1.4$, with a training score of 0.85. The combination was chosen to balance model complexity and predictive performance, with the aim of achieving the best possible generalization performance on unseen test data. This best model was then evaluated on the test set, resulting in an R-squared value of 0.89 and an RMSE of 0.065. These results suggest that the model has a good predictive performance and can accurately predict the dehydrogenation yield from the input features.

To further demonstrate the model's accuracy, Figure 4.6 displays a comparison of the model's performance when evaluated on the test set as well as the entire dataset. The

cross plots show that the model achieves high accuracy in both cases, further confirming its ability to predict the target variable.

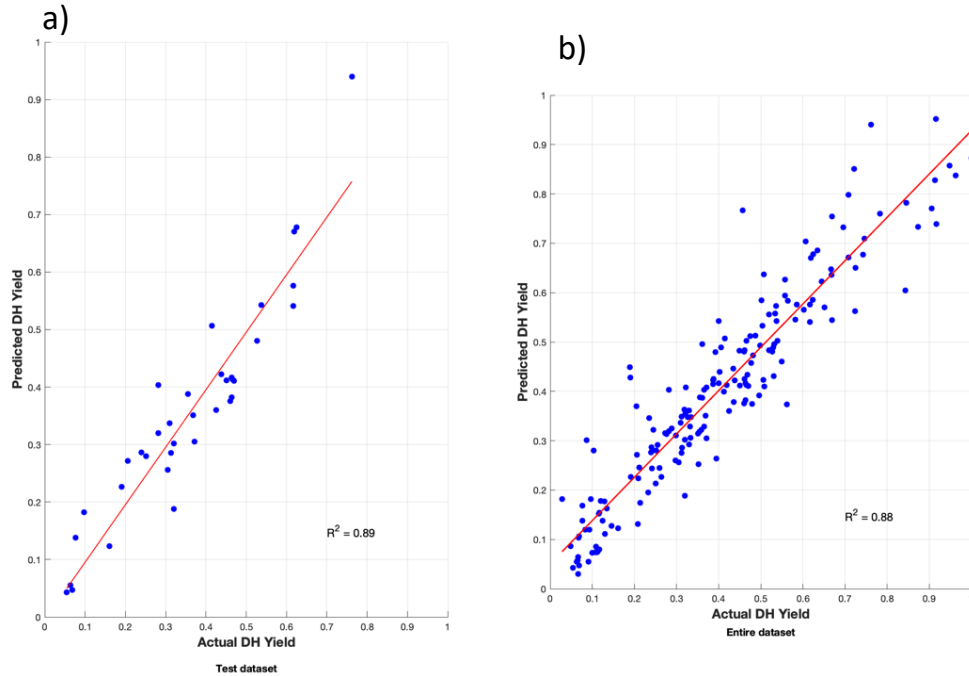


Figure 4. 6: Cross plot of Measured DH Yield and Predicted Yield using the NuSVR Model. The graph displays the results for both the test dataset (a) and the entire dataset (b).

4.4.3 GBR and XGBR Final Models

By following the methodology described earlier (section 4.3.6) for developing the GBR and XGBR models, a thorough search grid analysis was conducted as summarized in Table 4.7 to determine the optimal model configuration using the training set. After evaluating the hyper-parameter combinations, the search process identified the optimal hyper-parameter combination that was used to build the final GBR and XGBR models. These optimal hyper-parameter combinations are highlighted in Table 4.7. With these specific parameter values, the GBR model achieved an impressive score of 0.998 when evaluated on the training set. Similarly, the XGBR model yielded a high score of 0.988, also based on the training set evaluation.

Table 4. 7: Hyper-Parameters for GBR and XGBR Mode

Model	Parameter	Range
GBR	Number of Trees	100
	Learning Rates	0.15
	Maximum Depth of Trees	5
	Weights L1 regularization Term	0.9
XGBR	Number of Trees	300
	Learning Rates	0.2
	Maximum Depth of Trees	3

Using the test data, the performance of both models was evaluated. The GBR model has a score of 0.94 for the predicted yields of the test dataset. Similarly, the XGBR model had a score of 0.89. Figures 4.7 and 4.8 show cross plots of the predicted and experimental yield to demonstrate the performance of the GBR and XGBR models respectively. In addition, the cross plot of the predicted and experimental yield for the entire dataset is also included to show the overall performance of the models.

The GBR model gave a dehydrogenation product yield prediction accuracy of 94% on the test data and prediction RMSE of 0.054 while the XGBR gave 92% accuracy and prediction error of 0.059 (RMSE). These demonstrate the ability of the models to give accurate predictions of the dehydrogenation product yield using simple and clear descriptors.

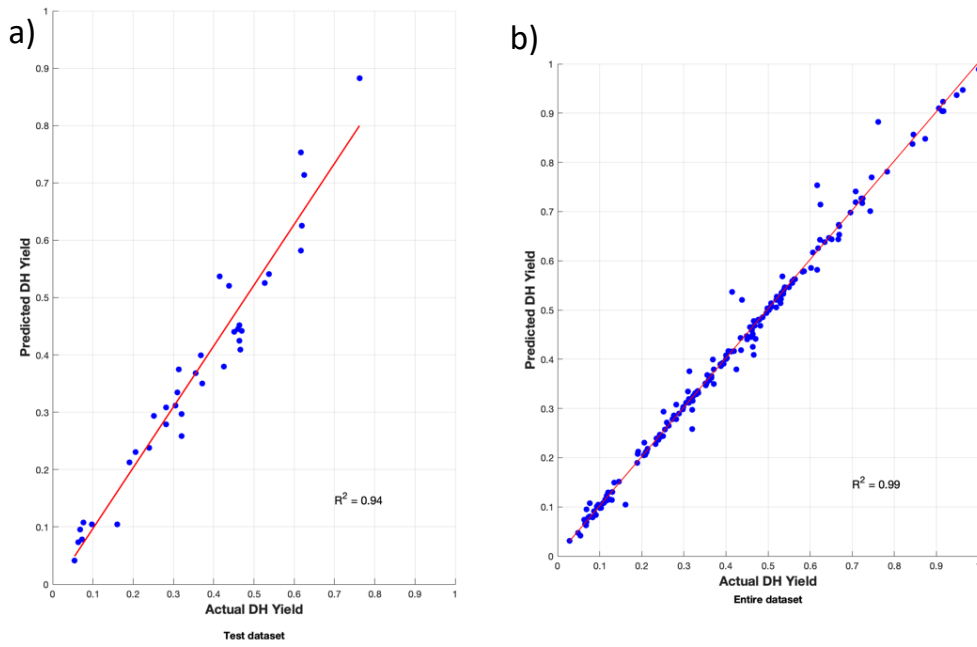


Figure 4. 7: Cross plot of Measured DH Yield and Predicted Yield using the GBR Model. The graph displays the results for both the test dataset (a) and the entire dataset (b).

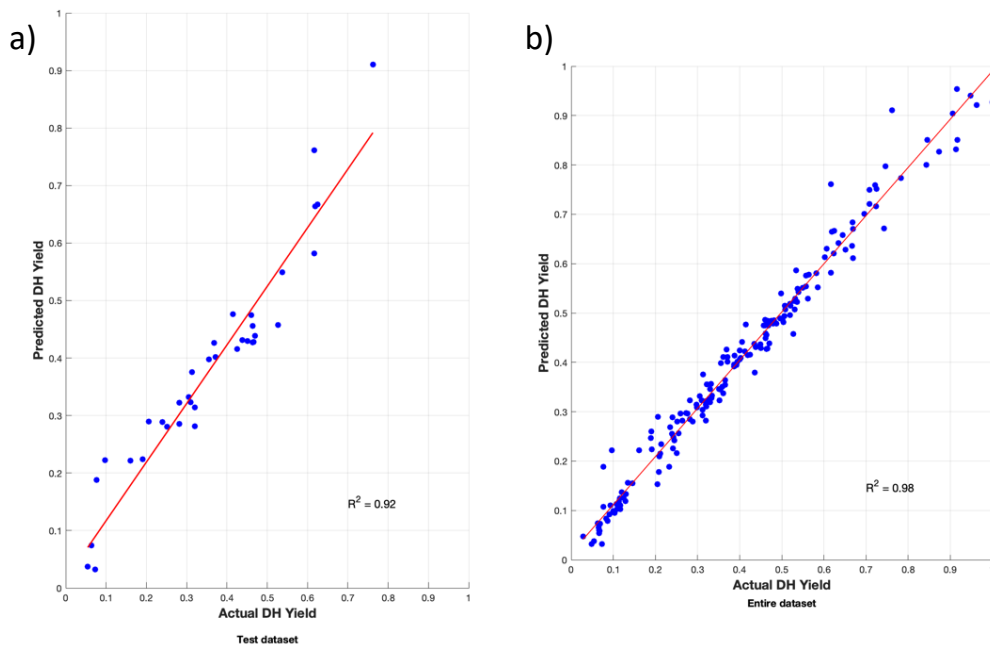


Figure 4. 8: Cross plot of Measured DH Yield and Predicted Yield using the XGBR Model. The graph displays the results for both the test dataset (a) and the entire dataset (b).

4.4.4 Comparison of Model Performance

The machine learning models demonstrate strong predictive capabilities, exhibiting R-squared values exceeding 0.8 for both the training and the unseen test data in predicting dehydrogenation yield, as detailed in Table 4.8. Notably, ensemble learning techniques—XGBR and GBR—exhibit exceptional training set fitting and overall performance, achieving R-squared values nearing 0.98 and 0.99, respectively, when tested across the dataset. Noteworthy is the comparability between the R-squared values of the training and test sets across all models, with the difference being even less than the low prediction error of the test set (i.e. RMSE) in all cases, showcasing robustness. In particular, the NuSVR model outperforms its training data (R-squared: 0.853) with the test set (R-squared: 0.893), emphasizing the models' reliability.

This demonstrates the chemometric models' possible ability to make accurate predictions and potential for generalizability. Moreover, by employing easily accessible features as demonstrated using the models, it suggests that researchers could identify catalysts with great potential for advancement without having to rely on traditional intricate and time-intensive experimentation.

Table 4. 8: Comparing the Performance of the ANN, NuSVR, XGBR and GBR Models

Model	R-squared (Training)	R-squared (Test)	R-squared (Entire dataset)	RMSE (Test)
ANN	0.908	0.82	0.87	0.086
NuSVR	0.853	0.89	0.88	0.065
XGBR	0.988	0.92	0.98	0.059
GBR	0.998	0.95	0.99	0.054

4.5 Model Interpretability

In this section, focus is on elucidating the chemometric models' prediction outcomes. The SHAP and permutation feature importance techniques are employed to elucidate the individual impact of each input feature on the final prediction outcomes of the model

4.5.1 Feature Partial Dependency

Figure 4.9 displays the partial dependence plots (PDPs) for both the ensemble learning and NuSVR models. These plots illustrate the impact of individual features on the model's predictions. Each plot corresponds to a specific feature, showcasing how altering that feature while holding others constant at their average values affects the model's prediction outcome. The y-axis represents partial dependence, showing the influence of the feature on the prediction outcome, while the x-axis displays the feature's values.

From the analysis, it's evident that Ni loading, Co loading, and Bi loading exhibit a positive influence on the prediction outcomes across all three models. However, there are nuanced differences between the models. For instance, the positive influence of Ni loading on the NuSVR model remains consistent across a range of values, whereas in the tree ensemble learning models, this influence diminishes beyond a loading greater than 5%.

Moreover, Zn, Mo, and Mn loading demonstrate a positive influence solely in the NuSVR model, indicating their impact on the prediction outcome specific to this model. Conversely, the Feed ratio doesn't seem to significantly affect the models' prediction outcomes. Additionally, while reaction temperature doesn't show any substantial influence in the ensemble learning techniques, the NuSVR model highlights a notably negative impact. This suggests that increasing the reaction temperature could potentially lead to lower dehydrogenation yield according to the NuSVR model's predictions.

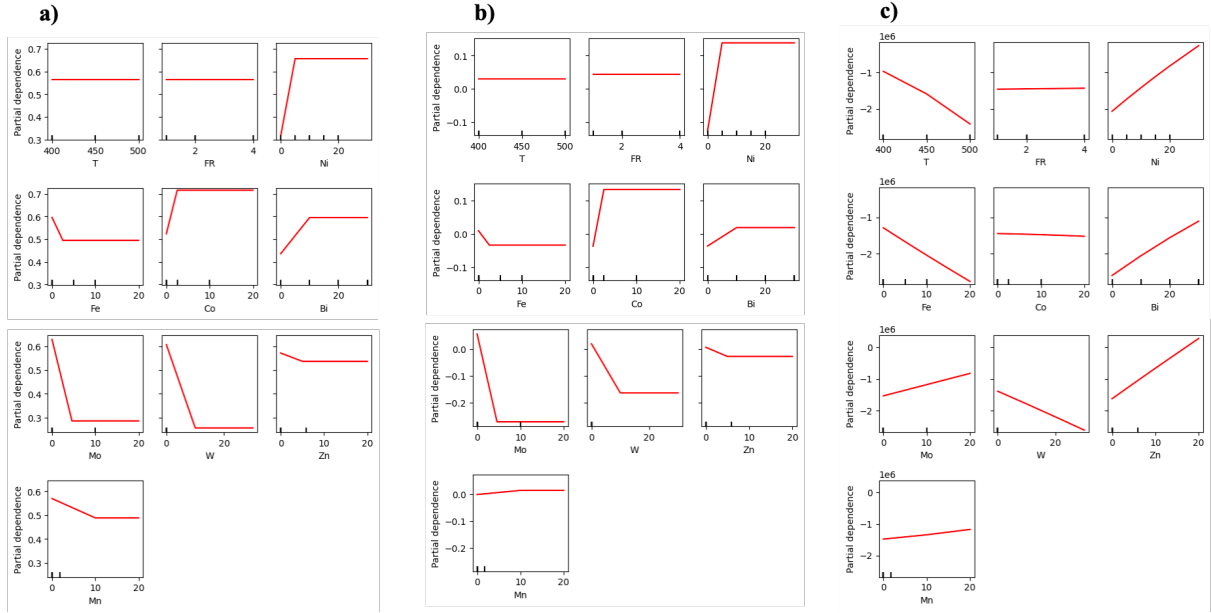


Figure 4. 9: Partial Dependence plots showcasing how Prediction of DH yield varies as each input feature is varied for XGBR model (a) GBR model (b) and NuSVR (c)

PDPs are indeed valuable for gaining insight into how individual features influence the prediction outcome of complex machine learning models. However, it is important to acknowledge a limitation arising from the technique utilized to generate the PDPs. When investigating the influence of one feature, all other features are held constant, which might not fully represent the intricate interactions within our system comprising ten input features. Independently varying one feature while keeping others fixed might not capture the true behaviour of that particular feature within the complex system accurately. This constraint can limit the comprehensive understanding of how a feature truly operates within the context of the broader set of interconnected features.

4.5.2 Local Interpretability

The ensemble tree learning models were analysed for local interpretability using the SHAP technique on the first instance in both models. Figure 4.10 illustrates the waterfall plots generated for this instance in each model. These plots break down the contribution

of each input variable to predict the dehydrogenation yield in-depth for the dataset's first instance. However, certain clarifications are necessary for a better understanding of how the waterfall plot relates to this study. Figure 4.10 shows that the input characteristics ranked in descending order from top to bottom on the y-axis according to how they affect the GBR and XGBR models' prediction for the first dataset's instance.

The SHAP values calculated, are shown on the red and blue arrows. These arrows represent the input variables influencing the models to make higher (red) and lower (blue) predictions until an almost precise prediction is reached. $f(x)$ denotes the model prediction, while $E[f(x)]$ signifies the model bias. In the plot, $f(x)$ equals the base value plus the sum of all SHAP values, indicated at the top of the y-axis as $f(x) = 0.855$ for GBR and 0.815 for XGBR, respectively. The bias appears at the x-axis, where the vertical discontinuous grey line intersects the x-axis, separating the blue and red arrows. Note that the base value remains constant for all instances, representing the dataset's average dehydrogenation yield. The plot's structure highlights the additive nature of positive and negative contributors and their role in determining the model prediction, $f(x)$.

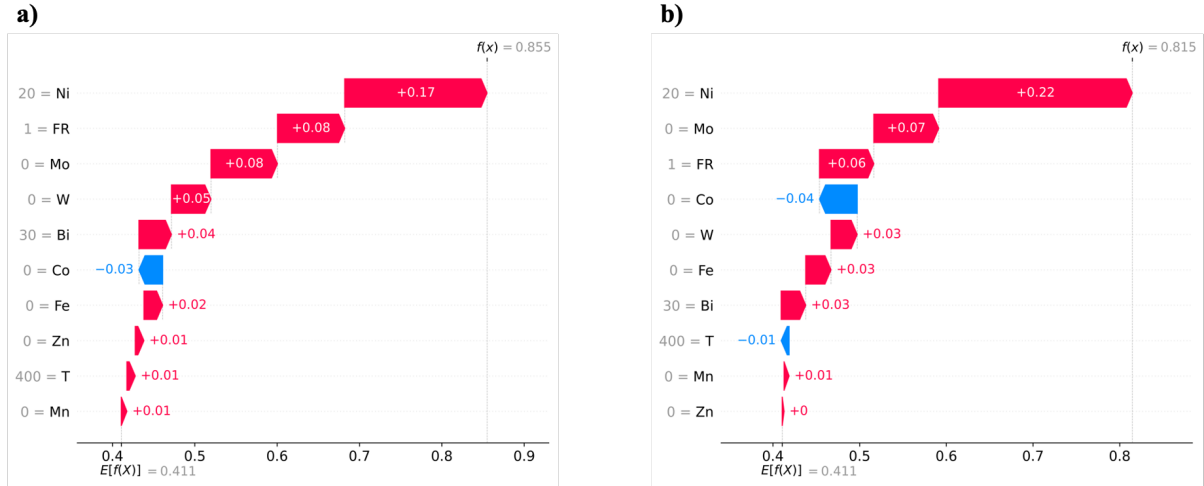


Figure 4. 10: Water fall plots showcasing the effect of all features on the dataset's first instance for the GBR (a) and XGBR (b) models

For the considered instance, comparing both models from Figure 4.10 reveals that Ni loading positively influences the prediction outcome and holds the highest influence in both models. Feed ratio and Molybdenum loading also positively impact the models' prediction. Conversely, Co loading exhibits negative influence in both models for the instance, while Mn loading, temperature, and Zn loading demonstrate minimal to no influence on the outcome using the models for this instance.

4.5.3 Global Interpretability

Bee swarm plots (refer to Figure 4.11) offer a more intricate and comprehensive visualization of SHAP values, enabling the determination of the relative importance of features. Moreover, they reveal the association of each feature with the predicted outcome. In Figure 4.11, the y-axis displays input features ranked by mean absolute SHAP values across the entire dataset, from highest at the top to lowest. Each instance in the dataset is represented by a point for every input feature, horizontally arranged based on their SHAP values. Vertical stacking indicates dense areas with identical SHAP values on the x-axis. It's essential to note that the colour bars correspond to the actual feature

values for each instance, not the SHAP values. A thorough examination of colour distribution along the x-axis for each feature provides valuable insights into the overall relationship between feature values and their SHAP values. The positioning of points on the x-axis illustrates the significant impact of each feature value on predicting dehydrogenation yield. The analysis reveals that the top two features that exert the greatest influence on the overall model prediction for all four models are Ni and Mo loading

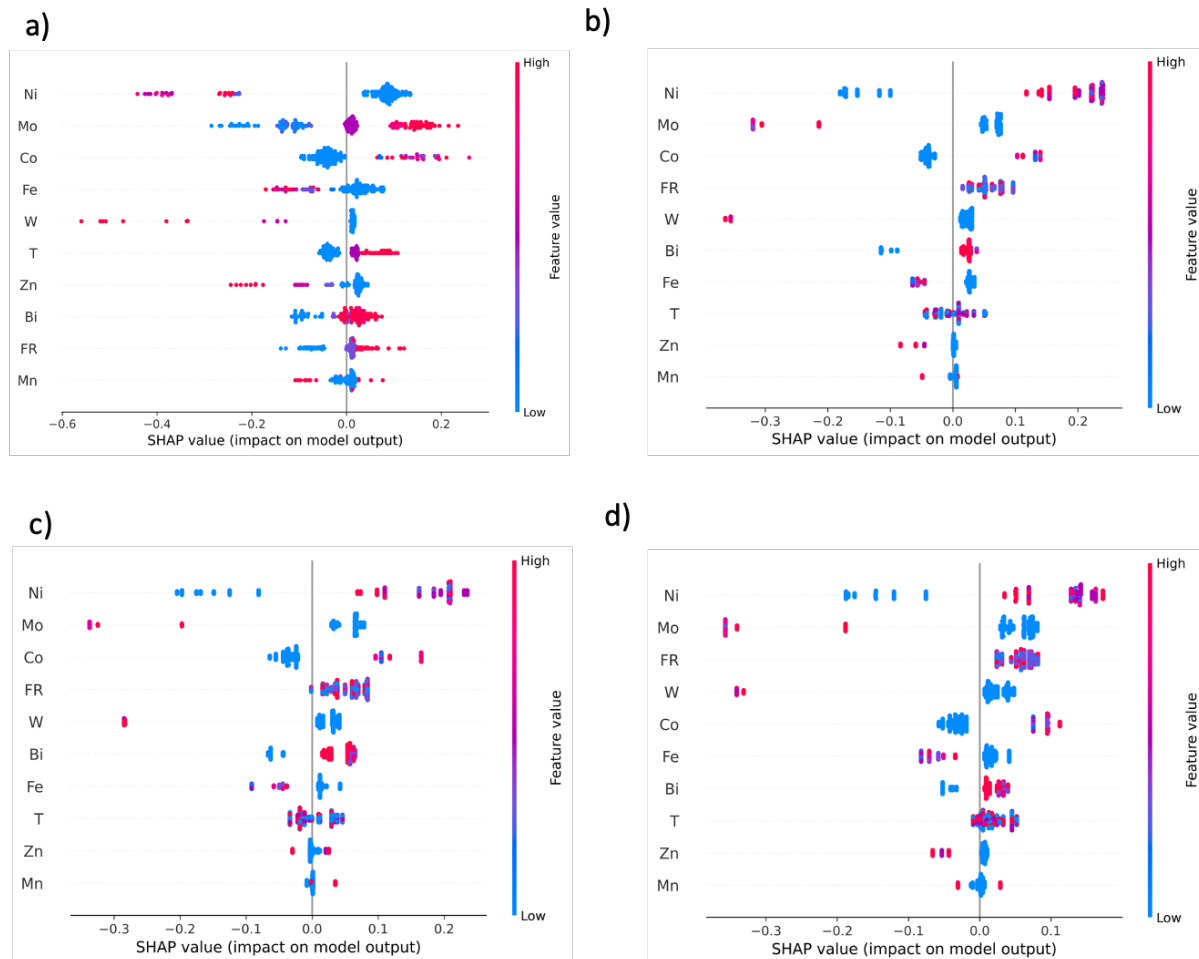


Figure 4. 11: Effects of all features on the overall model prediction outcome using SHAP analysis on the (a) ANN model, (b) XGBR model, (c) nusvr model, (d) GBR model

4.5.4 Feature Importance Analysis

Feature importance analysis was conducted to investigate which input features significantly influence the predicted yield. The result can guide future research on which parameters should be tuned to improve reaction yield. This was done using the permutation feature importance method on the developed models described earlier. This method randomly permutes the values of each feature using the test set and measures the resulting change in the model's performance. Features that cause a large drop in performance when permuted get a high importance score, while those that have little influence on the model's performance when permuted are ranked lower.

Figure 4.11 is a depiction of the outcome of the feature importance analysis. It shows that the amount of nickel (Ni) in the catalyst has the most influence of all the features on the yield of dehydrogenation products. It can also be deduced that zinc (Zn) and Manganese (Mn) have the least influence on the yield of dehydrogenation products of as shown on the feature importance test across all models. These observations are highly consistent with previous experimental studies conducted in our laboratory. Jermy et al. [37], [126] demonstrated that as the amount of Ni deposited on the gamma alumina support increased up to a saturation point of 30%, the selectivity to dehydrogenation products increased across different reaction temperatures.

Additionally, the findings by Tanimu and co-workers [186] are also in close agreement with these observations. Their study specifically investigated the effect of mixed oxides of Ni, Co, and Fe supported on gamma-alumina for the ODH of n-butane. They found that Ni exhibited remarkable selectivity towards dehydrogenation products, with the

highest dehydrogenation selectivity of 75% achieved when 20% Ni was loaded as the only active specie onto the catalyst support.

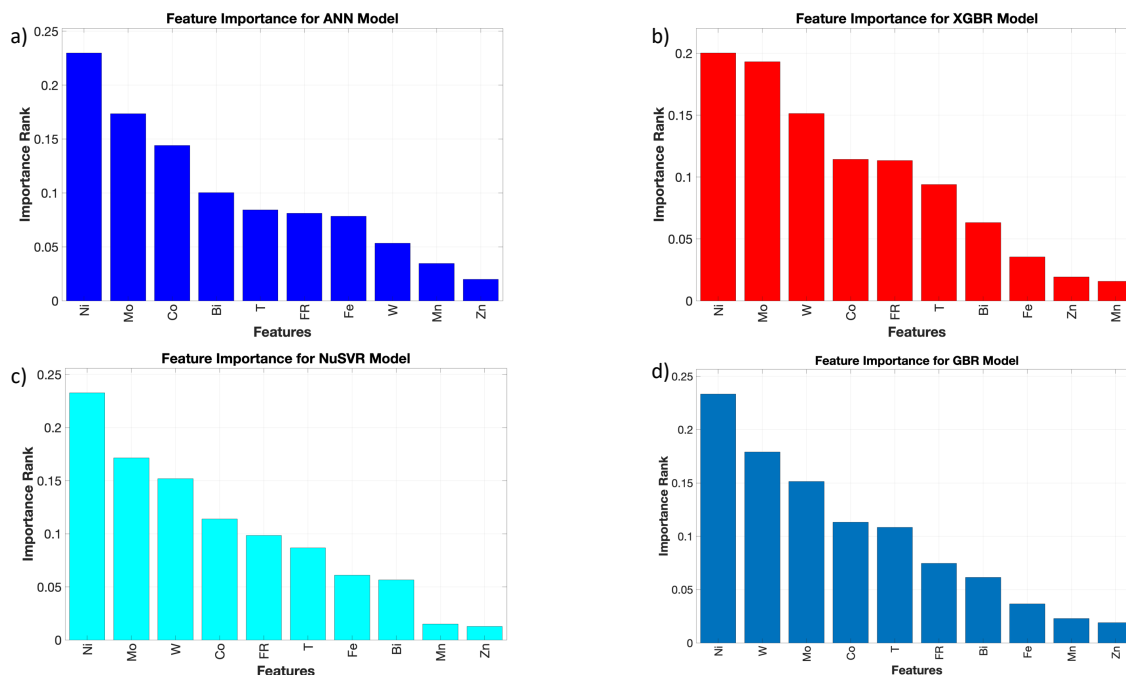


Figure 4. 12: Feature Importance Depiction Using Permutation Method on the (a) ANN model, (b) XGBR model, (c) NuSVR model, (d) GBR Model

4.6 Conclusions

This study employed four different ML algorithms to develop models for predicting the performance of mixed metal oxides catalysts for oxidative dehydrogenation of n-butane. The performance predictions obtained from the developed models were accurate, with R-squared values of 82%, 89%, 92%, and 94% achieved by the ANN, NuSVR, XGBR, and GBR models, respectively. Feature importance analysis was also conducted for the four developed ML models. The analysis revealed that presence of Ni in the catalyst has the greatest influence on the yield of dehydrogenation products. These findings demonstrate that reliable predictions of catalyst performance can be made even with simple and easily

accessible features, hence paving the way for the creation of more efficient catalyst design and discovery methods. It is evident that ML would play a great role in reaction and catalysis research in the coming years due to its unique ability to give insight into complex systems based on data, improved synergy between ML and experiments. Overall, this work underlines the importance of interdisciplinary research to tackle complex challenges in catalysis.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The investigation into the immobilization of bimetallic oxide species of Ni and Bi on a fibrous silica support (Ni-Bi/FS) for the oxidative dehydrogenation of n-butane to produce 1,3-Butadiene (BD) yielded promising results. Notably, the catalytic activity observed can be attributed to the high surface area characteristics of the FS support, facilitating enhanced interaction between the gas feed and the active sites of the FS-supported catalysts.

The varying metal loading ratios of Ni and Bi significantly influenced the distribution of the NiO active phase and the Bi_2SiO_5 phase on the catalyst surface. Characterization unveiled that the presence of the Bi_2SiO_5 phase improved selectivity towards BD by stabilizing the NiO phase, which in turn supplied the nucleophilic oxygen species activating the C-H bond.

The catalyst's performance evaluation revealed that the 20Ni-10Bi/FS catalyst, with moderate metal loading, showcased the most promising results, achieving an n-butane conversion of 40.1% and a BD selectivity of 50%. This catalyst demonstrated an optimal distribution of the NiO active phase and the Bi_2SiO_5 , ensuring improved catalytic activity while suppressing undesired reactions such as deep oxidation. The optimal operating

conditions were also determined to be 500 °C reaction temperature and O₂:n-C₄H₈ feed ratio of 1:1.

Additionally, this study employed four distinct chemometric models for predicting the performance of mixed metal oxides catalysts. These models exhibited strong predictive capabilities, with R-squared values based on unseen test data ranging from 82% to 94% for the ANN, NuSVR, XGBR, and GBR models, respectively. Feature importance analysis emphasized the significant influence of Ni presence on the yield of dehydrogenation products ODHB, highlighting its pivotal role in catalytic performance in ODHB. These findings demonstrate that reliable predictions of catalyst performance can be made even with simple and easily accessible features, hence paving the way for the creation of more efficient catalyst design and discovery methods. Overall, this work underlines the importance of interdisciplinary research to tackle complex challenges in catalysis.

5.2 Recommendation

Based on the findings presented in this work, the following recommendations are put forth for research in elucidating the effect of fibrous silica supported catalysts for ODHB and also the use of chemometrics for efficient catalyst design and discovery

- Other metal impregnation techniques should be investigated for the loading of metals on the support to check for possible improved active phase-support interaction and better dispersion of the active phase which could potentially lead to improved catalyst activity

- Continue detailed characterization to gain deeper understanding of the structure activity relationship of the catalysts, particularly at reaction conditions like the in situ Diffuse Reflectance Infrared Spectroscopy (DRIFTS)
- Conduct in depth studies to investigate the mechanism and kinetics of the reaction to further elucidate the role of the Bi_2SiO_5 and NiO phases in the ODHB
- Validate the chemometric models on a larger dataset to ensure their robustness and general applicability
- Generate catalyst component descriptors using techniques like atomistic scale simulations to develop chemometric models that can be used for extrapolative prediction of promising catalyst for ODHB.

APPENDICES

Appendix A

Table A. 1: Result from blank test (no catalyst) analysis for ODHB

Temp. (°C)	400	400	400	450	450	450	500	500	500
O ₂ :n-C ₄ Feed Ratio	1:1	2:1	4:1	1:1	2:1	4:1	1:1	2:1	4:1
n-C ₄ conv. (%) ±1.5	0.2	0.9	25.4	0.5	0.5	0.7	1.4	1.2	1.5
Selectivity (%) ±1.2									
DH	100.0	86.3	57.7	92.2	87.8	88.9	69.3	69.9	73.2
1-C ₄ ⁼	38.1	36.7	29.4	35.3	32.7	34.7	24.9	27.9	32.3
2-C ₄ H ₈	61.9	49.6	23.7	56.9	55.1	54.2	39.2	41.9	40.9
BD	0.0	0.0	4.6	0.0	0.0	0.0	5.3	0.0	0.0
OC	0.0	8.6	9.6	3.9	6.1	5.6	18.8	18.1	16.5
BD/DH	0.0	0.0	8.0	0.0	0.0	0.0	7.6	0.0	0.0
(1-C ₄ ⁼ +BD)/DH	38.1	42.5	58.9	38.3	37.2	39.1	43.5	40.0	44.1
BD/(1-C ₄ ⁼ +BD)	0.0	0.0	13.5	0.0	0.0	0.0	17.5	0.0	0.0
BD yield	0.0	0.0	1.2	0.0	0.0	0.0	0.1	0.0	0.0

DH = Dehydrogenation selectivity (selectivity of all C-4 olefines); BD = 1,3-butadiene; OC = Oxidative cracking selectivity; 1-C₄⁼ = 1-butene; 2-C₄H₈ = 2-butene.

Table A. 2: Result from re-run performance evaluation for 20Ni-10Bi/FS catalyst analysis for ODHB

Temp. (°C)	400	400	400	450	450	450	500	500	500
O ₂ :n-C ₄ Feed Ratio	1:1	2:1	4:1	1:1	2:1	4:1	1:1	2:1	4:1
n-C ₄ conv. (%) ±1.5	24.1	20.3	19.2	35.3	35.1	33.4	41.5	43.4	44.5
Selectivity (%) ±1.2									
DH	82.3	87.1	85.2	79.2	73.7	73.9	70.1	65.7	55.2
1-C ₄ ⁼	8.8	11.9	13.6	10.5	12.4	15.1	7.3	11.1	12.6
2-C ₄ H ₈	28.1	28.3	27.6	19.8	17.5	18.6	13.1	13.5	13.2
BD	45.3	46.9	43.9	48.9	43.8	40.2	49.7	41.0	29.4
OC	3.0	3.7	5.2	4.4	10.0	8.5	7.6	10.4	17.2
BD/DH	55.1	53.8	51.6	61.8	59.4	54.4	70.9	62.5	53.2
(1-C ₄ ⁼ +BD)/DH	65.8	67.5	67.6	75.0	76.2	74.8	81.3	79.4	76.1
BD/(1-C ₄ ⁼ +BD)	83.7	79.7	76.3	82.3	78.0	72.7	87.2	78.6	69.9
BD yield	10.9	9.5	8.4	17.3	15.4	13.5	20.6	17.8	13.1

DH = Dehydrogenation selectivity (selectivity of all C-4 olefines); BD = 1,3-butadiene; OC = Oxidative cracking selectivity; 1-C₄⁼ = 1-butene; 2-C₄H₈ = 2-butene.

Table A. 3: Result from performance analysis of 10Ni-10Bi/FS for ODHB

Temp. (°C)	400	400	400	450	450	450	500	500	500
O₂:n-C₄ Feed Ratio	1:1	2:1	4:1	1:1	2:1	4:1	1:1	2:1	4:1
n-C₄ conv. (%) ±1.5	11.4	11.3	11.1	22.1	22.3	21.7	32.1	31.6	29.6
Selectivity (%) ±1.2									
DH	94.0	92.7	92.1	86.7	86.3	85.3	75.6	75.6	74.5
1-C₄⁼	13.1	13.7	14.3	11.1	12.4	13.4	7.5	9.3	10.4
2-C₄H₈	41.7	41.0	41.1	25.6	25.7	26.7	14.5	15.8	18.0
BD	39.2	38.1	36.7	50.0	48.2	45.3	53.5	50.5	46.2
OC	1.6	2.5	3.0	3.2	3.5	4.4	6.5	6.9	8.4
BD/DH	41.7	41.1	39.8	57.6	55.8	53.0	70.8	66.8	62.0
(1-C₄⁼+BD)/DH	55.6	55.8	55.4	70.4	70.2	68.7	80.8	79.1	75.9
BD/(1-C₄⁼+BD)	75.0	73.6	71.9	81.8	79.5	77.2	87.7	84.4	81.7
BD yield	4.5	4.3	4.1	11.1	10.8	9.8	17.2	15.9	13.7

DH = Dehydrogenation selectivity (selectivity of all C-4 olefines); BD = 1,3-butadiene; OC = Oxidative cracking selectivity; 1-C₄⁼ = 1-butene; 2-C₄H₈ = 2-butene.

Table A. 4: Result from performance analysis of 15Ni-10Bi/FS for ODHB

Temp. (°C)	400	400	400	450	450	450	500	500	500
O₂:n-C₄ Feed Ratio	1:1	2:1	4:1	1:1	2:1	4:1	1:1	2:1	4:1
n-C₄ conv. (%) ±1.5	12.5	12.8	12.9	22.7	23.1	22.5	29.9	31.0	31.4
Selectivity (%) ±1.2									
DH	90.0	90.3	89.3	85.0	84.4	82.6	74.7	73.9	68.7
1-C₄⁼	12.2	12.5	12.6	9.9	10.7	11.2	6.6	8.4	8.9
2-C₄H₈	38.4	38.8	38.8	26.7	27.6	28.7	15.6	18.2	19.5
BD	39.4	39.1	38.0	48.4	46.1	42.8	52.5	47.4	40.3
OC	4.5	3.7	4.3	4.1	4.5	5.9	7.5	8.1	10.3
BD/DH	43.7	43.3	42.5	56.9	54.6	51.8	70.3	64.1	58.6
(1-C₄⁼+BD)/DH	57.3	57.1	56.6	68.6	67.3	65.3	79.2	75.4	71.7
BD/(1-C₄⁼+BD)	76.3	75.8	75.1	83.0	81.1	79.3	88.8	85.0	81.8
BD yield	4.9	5.0	4.9	11.0	10.6	9.6	15.7	14.7	12.6

DH = Dehydrogenation selectivity (selectivity of all C-4 olefines); BD = 1,3-butadiene; OC = Oxidative cracking selectivity; 1-C₄⁼ = 1-butene; 2-C₄H₈ = 2-butene.

Table A. 5: Result from performance analysis of 20Ni-20Bi/FS for ODHB

Temp. (°C)	400	400	400	450	450	450	500	500	500
O ₂ :n-C ₄ Feed Ratio	1:1	2:1	4:1	1:1	2:1	4:1	1:1	2:1	4:1
n-C ₄ conv. (%) ±1.5	12.0	11.8	11.1	21.6	20.7	18.8	28.9	27.4	24.7
Selectivity (%) ±1.2									
DH	94.3	92.2	90.5	86.8	85.8	83.3	75.2	74.4	70.3
1-C ₄ ⁼	12.7	13.9	14.0	10.5	11.6	11.9	7.4	9.2	9.9
2-C ₄ H ₈	41.8	41.6	42.1	28.3	29.6	31.1	17.2	20.0	22.0
BD	39.7	36.7	34.4	48.0	44.6	40.3	50.6	45.3	38.4
OC	1.1	2.7	3.9	3.3	4.3	6.3	7.5	8.7	12.1
BD/DH	42.1	39.8	38.0	55.3	52.0	48.4	67.2	60.9	54.6
(1-C ₄ ⁼ +BD)/DH	55.6	54.9	53.5	67.4	65.5	62.7	77.1	73.2	68.7
BD/(1-C ₄ ⁼ +BD)	75.7	72.6	71.0	82.0	79.4	77.2	87.2	83.2	79.5
BD yield	4.8	4.3	3.8	10.4	9.2	7.6	14.6	12.4	9.5

DH = Dehydrogenation selectivity (selectivity of all C-4 olefines); BD = 1,3-butadiene; OC = Oxidative cracking selectivity; 1-C₄⁼ = 1-butene; 2-C₄H₈ = 2-butene.

Table A. 6: Result from performance analysis of 20Ni-30Bi/FS for ODHB

Temp. (°C)	400	400	400	450	450	450	500	500	500
O ₂ :n-C ₄ Feed Ratio	1:1	2:1	4:1	1:1	2:1	4:1	1:1	2:1	4:1
n-C ₄ conv. (%) ±1.5	17.2	16.9	16.3	28.0	27.8	26.3	34.0	34.6	33.4
Selectivity (%) ±1.2									
DH	90.6	89.9	88.8	82.4	81.7	80.8	70.6	70.1	68.1
1-C ₄ ⁼	13.8	15.6	16.6	10.8	12.5	14.0	6.3	9.0	10.1
2-C ₄ H ₈	30.8	29.7	30.1	18.5	19.4	21.5	11.2	13.4	16.0
BD	46.1	44.7	42.1	53.1	49.7	45.3	53.0	47.7	42.0
OC	2.2	2.8	3.8	3.9	4.7	5.9	8.7	9.2	11.2
BD/DH	50.8	49.7	47.4	64.4	60.9	56.1	75.1	68.0	61.6
(1-C ₄ ⁼ +BD)/DH	66.0	67.0	66.1	77.5	76.2	73.4	84.1	80.8	76.5
BD/(1-C ₄ ⁼ +BD)	77.0	74.1	71.8	83.1	79.9	76.4	89.3	84.2	80.6
BD yield	7.9	7.5	6.8	14.9	13.8	11.9	18.0	16.5	14.0

DH = Dehydrogenation selectivity (selectivity of all C-4 olefines); BD = 1,3-butadiene; OC = Oxidative cracking selectivity; 1-C₄⁼ = 1-butene; 2-C₄H₈ = 2-butene.

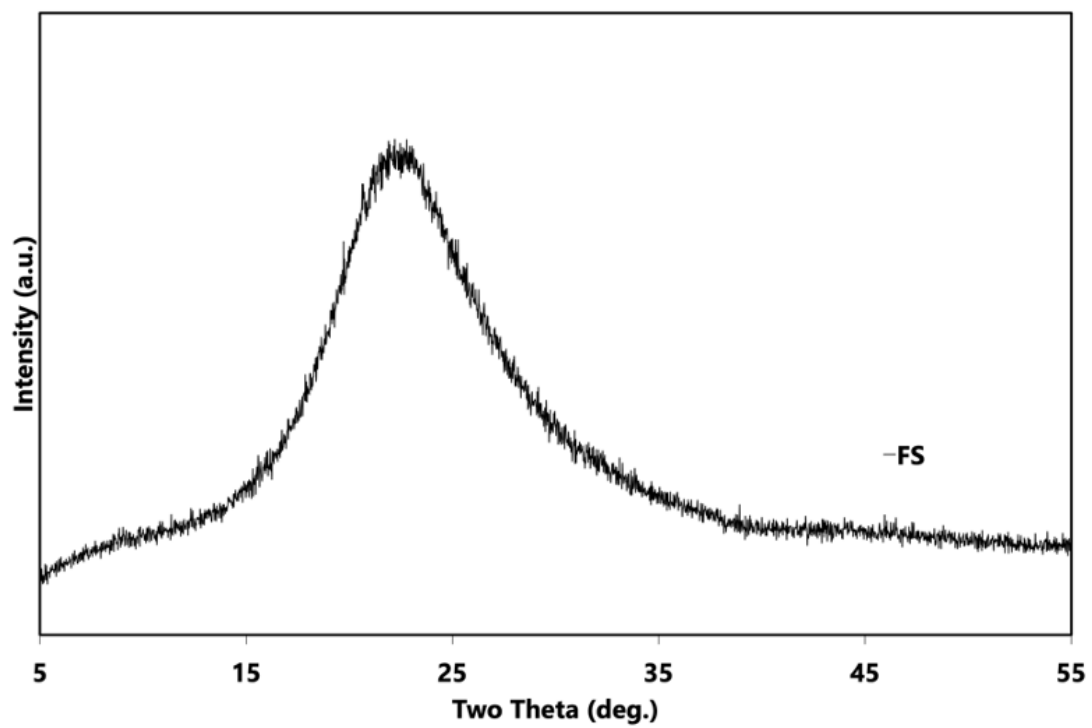


Figure A. 1: Fibrous silica XRD image showing the characteristic broad hump of silica appearing in the range of 16 to 24 degrees (2θ)

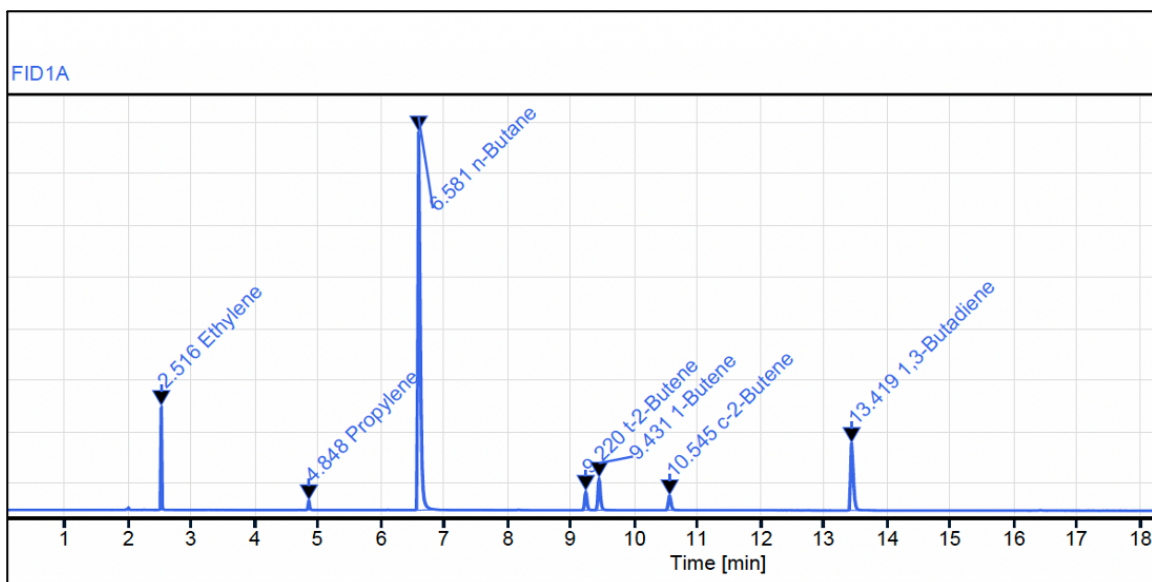


Figure A. 2: Sample chromatogram showing the FID peaks observed after analysing the product stream when the 20Ni-30Bi/FS catalyst was tested at 500 oC and O₂:n-C₄ feed ratio of 4:1

Table A. 7: Information about compounds identified in sample chromatogram shown in Figure A. 2

Compound Name	Retention time (min)	Peak area (%)	Retention factor
Ethylene	2.52	5.71	1893.88
Propylene	4.85	0.98	2759.94
n-Butane	6.58	66.93	3710.10
T-2-Butene	9.22	3.12	3485.65
1-Butene	9.43	5.76	3676.86
C-2-Butene	10.55	2.88	4028.48
1,3-Butadiene	13.42	13.39	3551.14

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Publications under Review/Preparation

1. Fibrous silica supported bimetallic Bi-Ni-O catalysts for oxidative dehydrogenation of n-butane to produce butadiene, **R. Lawal**, H. Alasiri, K. Negandra, G. Tanimu, Z. Qureshi.
2. Machine learning approaches for predicting the sooting tendency of petroleum fuels, **R. Lawal**, H. Alasiri, Abdulazeez Abdulraheem, Abdul Gani Abdul Jameel
3. Predicting the performance of mixed-metal oxides supported on Al₂O₃ for oxidative dehydrogenation of n-butane using artificial intelligence, **R. Lawal**, H. Alasiri¹, Abdullah Aitani, Abdulazeez Abdulraheem, Gazali Tanimu (Under Review)

Contribution to Symposia

1. Fibrous silica supported Ni/Bi oxide catalysts for oxidative dehydrogenation of n-butane; **R. Lawal**, H. Alasiri, K. Negandra, G. Tanimu, Z. Qureshi; presented at the 32nd Annual Saudi-Japan Symposium, Saudi Arabia, December 5th – 6th, 2023