

**OXIDATIVE CRACKING OF n-HEXANE TO LIGHT
OLEFINS OVER MgO/SrO MODIFIED VO_x/Al₂O₃
CATALYSTS**

BY

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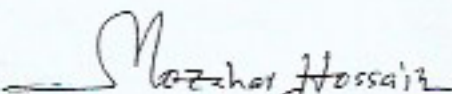
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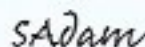
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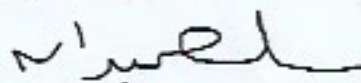
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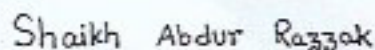
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[This work is dedicated to Almighty Allah]

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LIST OF ABBREVIATIONS

SC	:	Steam cracking
FCC	:	Fluid Catalytic Cracking
COC	:	Catalytic Oxidative Cracking
ODH	:	Oxidative Dehydrogenation
Olefins	:	ethylene, propylene and butenes
XRD	:	X-ray Diffraction
TPD	:	Temperature-Programmed Reduction
TPD	:	Temperature-Programmed Desorption

ABSTRACT

Full Name : Hussein Kehinde Amusa

Thesis Title : Oxidative Cracking Of n-Hexane to Light Olefins Over MgO/SrO
Modified VO_x/γAl₂O₃ Catalysts

Major Field : Chemical Engineering

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Catalytic oxidative cracking of alkanes is a viable alternative route to light olefins production. This study investigates new vanadium catalysts supported on MgO-γAl₂O₃ and SrO-γAl₂O₃ for the oxidative cracking of n-hexane to light olefins under an oxygen-free environment. In catalyst synthesis, different ratios of MgO-γAl₂O₃ and SrO-γAl₂O₃ were used to demonstrate the effect of MgO and SrO. The catalysts' composition, morphology, reducibility, and acidity were confirmed by relevant characterization techniques. NH₃-TPD analysis reveals a reduction in acidity with an increase in the amount of strontia and magnesia content. This reduction in acidity is the key to limiting excessive cracking products. The catalysts were evaluated in a CREC Fluidized Bed Riser Simulator at a reaction temperature range of 525 - 600 °C and from 10 to 25 sec. The modified catalysts display high performance due to balanced acidity and moderate VO_x-support interactions. Among the synthesized catalysts, VO_x/MgO-γAl₂O₃ 2:1 shows superior catalytic activity with 99.8 % n-hexane conversion and 96% light olefin selectivity. Similarly, VO_x/SrO-γAl₂O₃ 1:1 sample gives 84 % n-hexane conversion and 91% light olefins selectivity. The kinetic model developed for the best performing catalyst agrees with the experimental data. |

ملخص الرسالة

الاسم الكامل: حسين كيهينده اموسا

عنوان الرسالة: تكسير أكسدة η -هيكسان للأوليفينات الخفيفة فوق محفزات VO_x / Al_2O_3 المعدلة من MgO/SrO

التخصص: هندسة كيميائية

تاريخ الدرجة العلمية: أبريل ٢٠٢٠

التكسير التأكسدي الحفاز للألكانات هو طريق بديل لإنتاج الأوليفينات. تبحث هذه الدراسة في انتاج محفزات جديدة من الفاناديوم المدعمة على $MgO-\gamma Al_2O_3$ و $SrO-\gamma Al_2O_3$ للتكسير التأكسدي للهكسان إلى الأوليفينات الخفيفة في معزل من الأكسجين. في تحضير المحفز ، تم استخدام نسب مختلفة من $MgO-\gamma Al_2O_3$ و $SrO-\gamma Al_2O_3$ لدراسة تأثير MgO و SrO . تم دراسة نسب مكونات المحفزات ودراسة اشكالها وخواصها الحمضية من خلال عدة تقنيات. يكشف تحليل NH_3 -TPD عن انخفاض في الحموضة مع زيادة في كمية السترونشيم والمغنيسيوم . هذا الانخفاض في الحموضة هو اهم مؤثر للحد من منتجات التكسير المفرط. تم تقييم المحفز في CREC Fluidized Bed Riser Simulator في درجة حرارة تفاعل من ٥٢٥ - ٦٠٠ درجة مئوية ومن ١٠ إلى ٢٥ ثانية. تعرض المحفزات المعدلة أداءً عاليًا بسبب الحموضة المتوازنة ونسب VO_x المعتدلة. من بين المحفزات المركبة . يُظهر $VO_x / MgO-\gamma Al_2O_3$ بنسبه ٢ الى ١ نشاطًا تحفيزيًا فائقًا مع نسبه تحويل تجاوزت ٩٩,٨٪ من الهكسان . و ٩٦٪ انتقائية لانتاج الأولفين. وبالمثل ، فإن عينة $VO_x / SrO-\gamma Al_2O_3$ التي تحتوي على نسبه ١ الى ١ أعطت نسبه تحويل للهكسان حوالي ٨٤٪ و ٩١٪ انتقائية من الأولفين . تم تصميم نموذج لمحاكاة ديناميكا التفاعل والذي اعطى بدره نتائج رائعه في تماثله مع النتائج الاساسيه للتجربه المعملية

CHAPTER -1 INTRODUCTION

1.1 Background

Short chain olefinic compounds are the main basic chemicals for the petrochemical industry. Ethylene and propylene are used worldwide in the production of polymers, polyoxides, and important intermediate chemicals.[1]–[5]. The demand for these basic chemicals, particularly propylene, continues to rise over the years. This results from an increase in the human population, expansion of cities, and improvement in the quality of human life. Hence, an efficient production process of these raw materials is of paramount importance.

The commercialized processes available for the production of Olefins include steam-based naphtha cracking, fluid catalytic cracking, dehydrogenation, and methanol to alkenes [6]. Steam cracking uses light or heavy hydrocarbon feedstocks (Fig 1). These feedstocks are also called Naphtha or Gas oil. In principle, the process is simple; it involves a homogenous gas phase reaction at temperatures greater than 800 °C. At this high temperature, pyrolysis of the hydrocarbon feedstock with steam occurs via a free radical reaction. Feedstocks compositions and the level of pyrolysis severity largely determines the operating conditions in the cracking and quenching sections. By varying the pyrolysis severity conditions, the propylene to ethylene ratio can be tuned. Although steam cracking remains today's industrial method of producing light olefin, however, large CO₂ emissions accompanied this process. Additionally, steam cracking is an energy-intensive approach; takes about 70% of the total production cost [7]. Moreover, in the industry, plant operations frequently shut down for cleaning due to coke formation in the steam cracking Process [8]–[11].

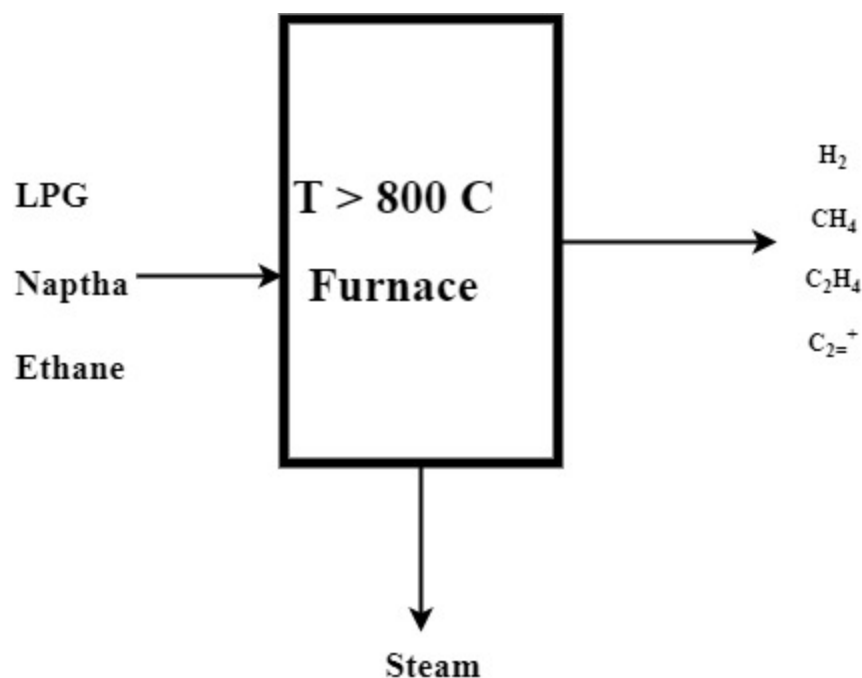
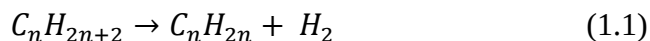


Figure 1: Steam cracking process

On the other hand, in the fluid catalytic cracking process coke is deliberately formed. This generated coke is sent to the regenerator and combusted in the boiler. Thus, the heat needed in the endothermic process is supplied from the combustion process. In this process, light olefins are produced as a side product in the refinery. More so, the endothermic cracking reaction involves high-energy demand. Moreover, the coke formed in this process causes catalyst deactivation. In addition, frequent catalyst regeneration can overcome the problem of catalyst deactivation through proper reactor design. Like steam cracking, fluid catalytic cracking also requires excessive heat due to the endothermic cracking reactions. Thus, the process is not economical for light olefin productions.

Dehydrogenation is the third commercialized process of light olefin production. It involves the reaction of light paraffin to the corresponding olefins. Typically, fixed bed reactors are used to perform this reaction. The general reaction is represented in equation 1.1. However, this process

is thermodynamically limited. Additionally, dehydrogenation also suffers excess heat demand because of the endothermic reaction and generates a lot of coke.



In the present time, a lot of research is being directed to develop an alternative process of light olefins production from relatively cheap feedstocks.

1.2 Catalytic Oxidative Cracking of Alkanes

Catalytic oxidative cracking of paraffin to light olefins has gained much recognition among several researchers. This process involves the cracking of paraffinic feedstock coupled with oxygen and/or using metal oxides catalyst systems. Two types of COC exist in the open literature; (1) gas-phase COC (Fig 2) and (2) gas-phase free COC called anaerobic COC developed by this research group (Fig 3).

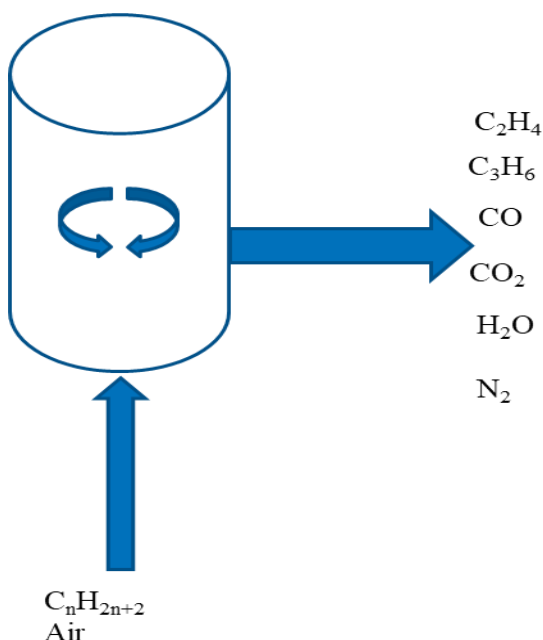


Figure 2: Gas-phase COC

The aerobic catalytic oxidative cracking (COC) process offers many opportunities; Firstly, oxygen present in the feed makes this process attractive in several ways: the operation is autothermal [11]. This leads to a low investment cost and effectively reduced CO_x emission. Secondly, the existence of oxygen as a reactant helps in avoiding the formation of coke during the reaction. Lastly, the use of catalysts causes the process to be conducted at relatively low temperatures [9,12,13]. Despite these benefits of the gas-phase oxidative cracking, the oxygen presence as a reactant is a major obstacle to the viability of this process. Under this process, unwanted CO_2 formation in the product is unavoidable.

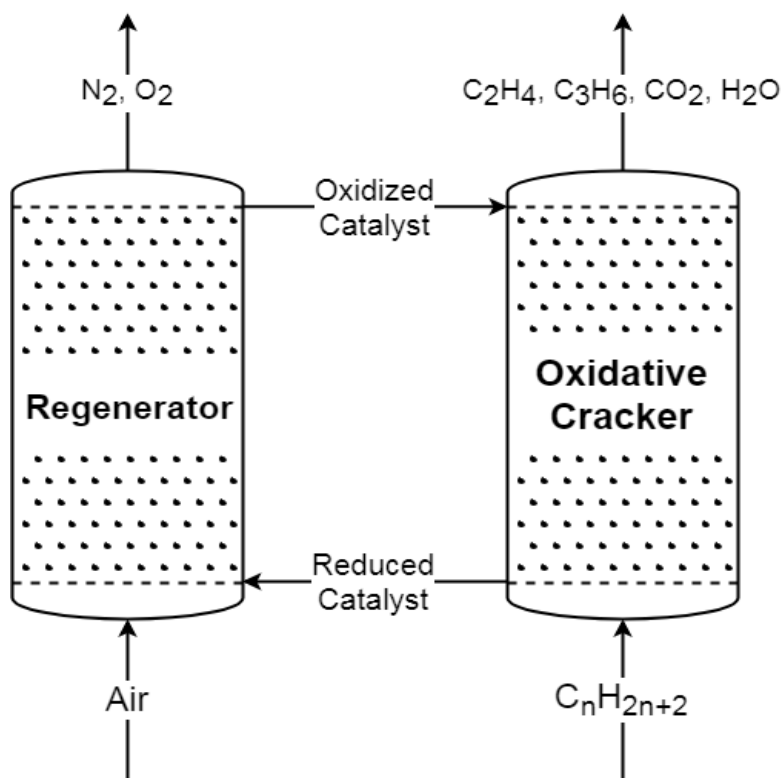


Figure 3: Gas-phase O_2 free COC process

To this end, our research group has developed a free molecular oxygen oxidative cracking for the conversion of paraffin to light olefins[16]–[18]. The novel anaerobic process consists of two stages: (1) cracking reaction using acidic support of a catalyst system, and (2) oxidative dehydrogenation using the lattice oxygen supplied by a metal oxide. This metal oxide also serves as the active species in the catalyst system. In this process, olefins are formed as the desired products due to oxidative cracking and oxidative dehydrogenation of alkane. This process also gives undesired carbon oxides formation due to complete combustion of the alkanes and olefins while methane is also formed as an undesired product as a result of excessive cracking of alkanes and olefins in this process.

The studies on COC catalysts were mostly performed in fixed bed reactors. However, these processes are limited by mass transfer and constrained by the formation of hot spots due to non-isothermal conditions in the reactor[19]. On the contrary, the fluidized-bed reactor is a promising alternative to fixed bed reactors, because it has excellent temperature control, and could overcome the challenge of mass transfer limitation [20]. Moreover, fluidized bed reactors allow the use of a small amount of catalyst which can be easily regenerated and reused [17], [21]–[23].

In this context, a structurally stable and highly active catalyst able to supply lattice oxygen and with a moderate acidity is required to make COC an alternative to the available processes of light olefins production. Various catalyst materials are being used in oxidative catalysis. Nevertheless, based on the literature survey, vanadium-based catalysts have been suggested to act as an appropriate catalyst in the oxidative conversion of alkanes[24]–[31]. This is because vanadium-based catalysts produce lattice oxygen required in the control of olefins selectivity. Several applications of vanadia based catalysts exist in the open literature, As an example, Elbadawi et al. [32] used $\text{VO}_x/\text{Ce-}\gamma\text{Al}_2\text{O}_3$ for the cracking of n-hexane to achieve 30 % n-hexane conversion and

60% olefin yield, In another study, the author reported 21% conversion and 85 % selectivity during the dehydrogenation of ethane to ethylene in an oxidative environment using $\text{VO}_x\text{-Nb/La } \gamma\text{Al}_2\text{O}_3$. Ayandiran et al. [7] demonstrated the effect of CaO in $\text{VO}_x/\text{CaO- } \gamma\text{Al}_2\text{O}_3$ for the oxidative conversion of propane to propylene. The catalyst shows excellent performance with 65% propane conversion and 85% selectivity to propylene. This is because the presence of CaO minimizes CO_x formation. More so, the addition of CaO to the vanadia catalyst ensured a balanced acidity which suppresses excessive cracking.

The behavior of supported vanadia catalysts largely is generally influenced by the content of the vanadium loadings, the surface structure of the vanadia species, method of preparation as well as the support system. Indeed, highly active and selective vanadium-based catalysts are obtained at moderate vanadium loadings and dispersions[33]. For example, Jeon et al. [34] revealed that the optimum amount of vanadium (6.7 to 11.3 mol %) leads to better activity in vanadium-doped zirconium oxide catalysts for propane dehydrogenation. Also, Al Ghamdi et al. [35] reported that balanced acidity (0.581 mmol NH_3/g) and appropriate vanadia surface structure at optimum vanadium loadings (i.e. 10 wt%) are important properties of vanadia based catalysts to achieve high olefin selectivity.

In addition, the acidity/basicity of the support affects the activity of the vanadium-based catalyst. This is due to the adsorption and desorption of the feed and product on different acid-base supports. It is known that acidic supports favors basic product desorption and reactant adsorption [36], [37]. Alumina properties such as robust mechanical strength, high hydrothermal stability, uniform pore size distribution, and high surface area make it efficient catalyst support in the oxidative conversion reactions. On the contrary, the acidic nature of alumina causes excessive cracking and coking reaction. Moreover, alumina strongly interacts with vanadium and thus result in the good

of vanadium [38]. Conversely, vanadium oxide doped on alumina shows a lower surface area compared to the alumina is mixed with a group II metal oxides such as MgO and SrO. Moreover, incorporation of MgO/SrO as a modifier leads to moderate acidity, which will maximize n-hexane conversion and gives higher olefins selectivity.

Keeping these in mind, this study aims to investigate the role of MgO and SrO on VO_x/MO ($\text{M} = \text{Mg, Sr}$)- $\gamma\text{Al}_2\text{O}_3$ catalysts with different ratios of the $\gamma\text{Al}_2\text{O}_3$ and the MO with n-hexane used as the feedstock to the oxidative cracking process.

Additionally, The metal-support interactions were studied by performing different characterization techniques on the synthesized catalysts. XRD and FTIR results show that analysis MgO, SrO, and $\gamma\text{-Al}_2\text{O}_3$ are present in the support material. Raman analysis confirms vanadia as the active component. The catalysts possess moderate acidity, better surface area, and balanced metal – support interactions. The catalytic oxidative aided n-hexane cracking to light olefins is carried out in a fluidized bed reaction condition in the CREC riser simulator. More insight into the CREC riser simulator procedure is available in the literature (2013) [39].

CHAPTER-2 LITERATURE REVIEW

2.1 Introduction

This chapter gives an overview of the several processes of light olefins production. Among the processes, catalytic oxidative cracking as a viable route is further discussed. Next, the chapter reports the different oxidative cracking catalysts, reactor types, and the kinetics of oxidative catalysis.

2.2 Light Olefins Production Processes

The classification of light olefin production processes can be categorized according to several ways: The process can be classified based on the current methods used in the industry, or the nature of components used as feedstock, or based on desired product distribution and according to the use of a catalyst.

The conventional processes used to produce light olefins in the industry are steam cracking (SC), fluid catalytic cracking (FCC), and dehydrogenation (DH)[7]. Surprisingly, major setbacks are observed in these processes. In the FCC process, coke is generated and combusted in the catalyst regenerator. The generated coke is used to produce the heat needed in the catalytic cracking unit, with the catalyst as an energy carrier. A major disadvantage of the FCC process is the cost associated with the endothermic cracking process [40].

Based on the nature of feedstock used, light olefins can be produced from shale gas, synthetic gas, alcohols, or light paraffin components (C_1 - C_5). Hirsu M et al, (2013) [41] wrote a review on the major production processes from synthesis gas. The review focused on the Fischer–Tropsch to olefins process (FTO). Several catalysts used in the Fischer–Tropsch process were analyzed and

compared. Among the different catalysts used: iron, cobalt, and zeolite-based catalyst; Iron-based catalysts are the most useful for FTO. More so, the catalyst leads to high CO conversion over a wide range of process operations. This is due to the ability of iron to resist contaminants present in the feedstock used. However, the Fischer–Tropsch process suffers from low selectivity of light olefins, when compared to other processes such as methanol to olefins. Besides the low selectivity drawback, economic and technical viability also limit the FTO process as an alternative to the light olefin production route.

Furthermore, the process can be categorized as either direct or indirect methods of producing light olefins. As an example, the oxidative coupling of methane (OCM) is a direct method of ethylene production while methanol to olefins (MTO) is an indirect production method. OCM is an active area of interest among several researchers, an extensive review is being written in this area [39]–[42]. However, developing a viable catalyst for this process remains a bottleneck among researchers[46].

In addition, olefin production processes can be divided based on the desired product distribution. In this regard, dehydrogenation is a method of producing both ethylene and propylene. Dehydrogenation of light hydrocarbons is an interesting process of light olefin production. However, the process is limited by thermodynamic constraints[47].

Lastly, the process can be classified as non-catalytic or catalytic processes. Catalytic processes involve thermal catalytic cracking, oxidative dehydrogenation of alkanes, and oxidative catalytic cracking. Although, some processes operate both as catalytic and non- catalytic processes such as pyrolysis and thermal cracking[48]–[50]. However, the rest of this work is focused on the catalytic oxidative cracking (COC) of alkanes to light olefins.

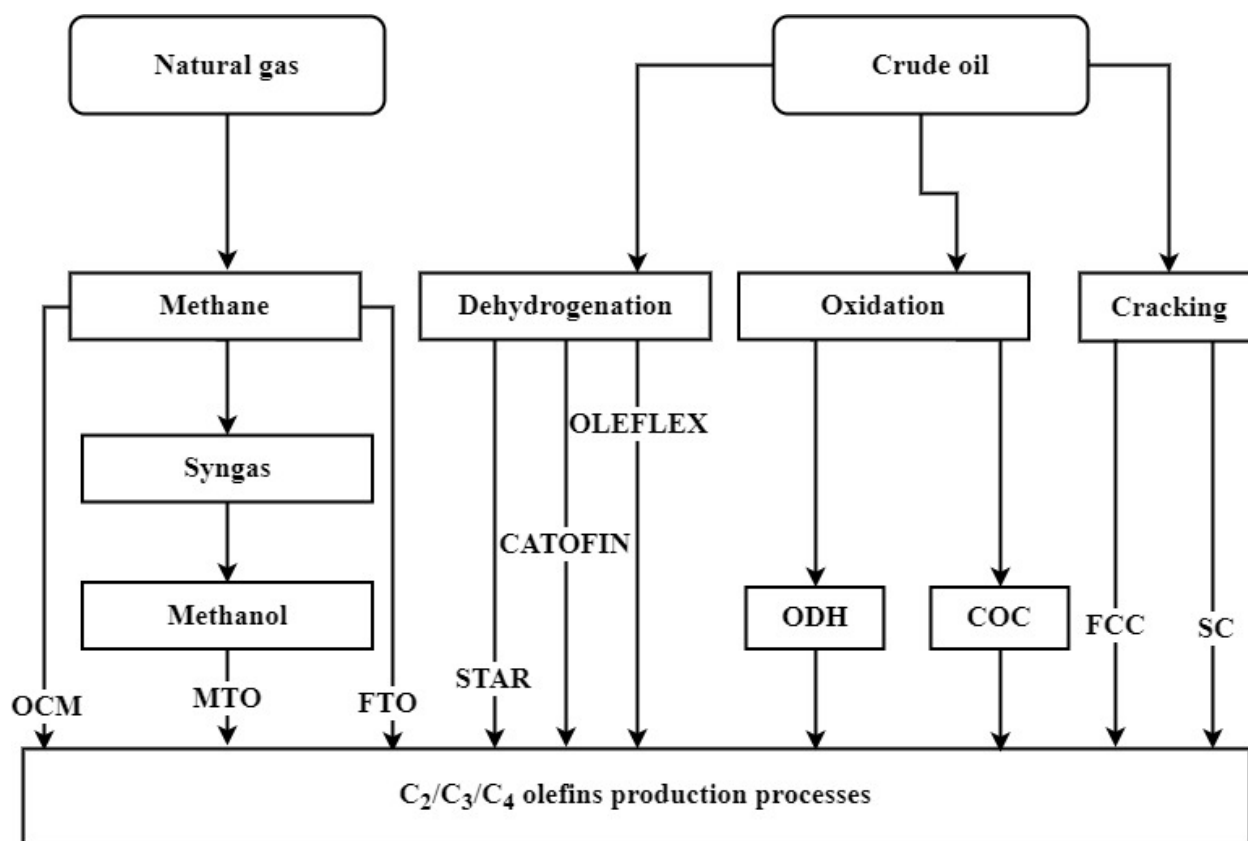


Figure 4: olefin production processes

2.3 Catalytic Oxidative Cracking of Alkanes

The oxidative conversion of paraffin with the aid of a catalyst to produce light olefins has been reported to be an efficient route for ethylene and propylene production with various alkanes used as feedstock model compounds[8], [39], [51]. Oxidative cracking proceeds via heterogeneous and homogeneous routes [13]. In this context, heterogeneous catalysis refers to the use of metal or metal oxide catalysts, while homogeneous catalysis refers to the influence of molecular oxygen or lattice oxygen in the reactive system. Thus, two types of catalytic oxidative cracking (COC) are distinguished in the literature: (1) Aerobic COC which involves the use of gas-phase oxygen, and (2) Anaerobic COC which uses the lattice oxygen of a metal oxide[35]. It should be noted, however, that the oxygen present in the feed constitutes major drawbacks to this process. These

include unwanted side reactions and potentially unsafe operation. On the other hand, the presence of a controlled amount of lattice oxygen ensures safe operation and favors selective production of olefins [23], [52]. It should be noted further that the use of an appropriate catalyst system helps to initiate cracking reactions at low temperatures as compared to thermal non-catalytic processes. Besides, a catalyst is required to produce a desired light olefins yield. Cracking reaction proceeds by catalyst initiation followed by gas phase thermal cracking [13]. In recent years, researchers have reported different catalyst systems for this process. Dudek et al. [53] reported the catalytic oxidative cracking of n-hexane using Perovskite oxides to achieve 49% conversion and 85% selectivity to light olefins at 750 °C. However, this process is limited due to the formation of hydrogen in the product. Narasimharao et al. [54], used nanosized gold supported $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ catalyst for the COC of propane to give 53% olefin selectivity and 46% conversion of propane at 550 °C. Also, AbdAlwadood et al. [55], applied $\text{VO}_x/\text{Ce-Al}_2\text{O}_3$ to investigate the kinetics of COC of n-hexane to olefins in the absence of gas-phase oxygen. They achieved a yield of 18% for light olefins at 550 °C. However, the use of highly acidic $\text{Ce-Al}_2\text{O}_3$ support leads to excessive cracking and the formation of unwanted CO_x products. More studies on the COC of n-hexane using V, Li, Bi, Mg, and Mo catalysts have been reported in the literature [8], [13], [56]. However, the commercialization of these catalysts systems is limited by excessive formation of CO_x .

It was reported that unwanted CO_x formation could be controlled with the aid of metal oxide catalysts, capable of producing the desired amount of lattice oxygen to limit the combustion of hydrocarbons and moderate catalyst support acidity[57], [58]. Among the metal oxides, vanadium oxide is particularly widely employed in oxidative cracking due to its ability to produce lattice oxygen for abstracting hydrogen from paraffin [58]–[60]. In addition to the active metal oxide, the catalyst system is loaded on a suitable support to provide the requisite dispersion and desired acid

sites responsible for the cracking reaction [61], [62]. Alumina support is the most common support utilized in this reaction as a result of its textural and structural properties[63]–[66]. However, excessive acidity in alumina-based catalysts causes excessive cracking to yield methane and CO_x products, thereby limiting the performance of this catalyst system [7], [66], [67].

Oxidative cracking catalysts varied from metal oxides catalysts and the noble metal catalysts. These different catalyst systems directly related to the catalyst cracking mechanism. Generally, metal oxides catalysts follow the surface initiation mechanism due to hydrogen abstraction of the paraffin, while in the noble metal oxide catalysts surface oxidation reaction proceeds thermal cracking. As far as metal oxide catalyst is concerned, different transition metal oxide catalysts (vanadium oxide, gallium oxide, molybdenum oxide, and zinc oxide), alkaline oxide (potassium oxide), alkaline earth oxide (magnesium oxides), rare earth oxide (lanthanum oxide, yttrium oxide) and noble metal oxide (iridium oxide, platinum oxide, gold-containing catalysts) are being reported in the literature. Boyadjian et al (2018) [13] reviewed the different catalyst systems used in catalytic oxidative cracking. However, the following section elaborates mainly on the vanadium-oxide based catalysts systems.

2.3.1 Vanadium-oxide Catalysts

This section mainly focuses on Vanadium-based catalysts. Several articles have been published on vanadium-based catalyst particularly, in the oxidative dehydrogenation reactions [59]–[76]. The studies of vanadium-based began about four decades ago.

Active site

Vanadium oxides exhibit strong activity in the oxidative reactions of hydrocarbons. The literature has established the dependence of vanadium-based catalyst active sites on the valence number of

vanadium, the carrier metal as well as the support surface area. Many researchers noted that polymeric V^{3+} and V^{4+} are the most active for oxidative conversion reactions[88]–[92]. Moreover, the amount of vanadium loading influences the activity of vanadium oxide species. Typically, VO_x loading greater than 10% weight leads to the formation of crystalline V_2O_5 specie. Crystalline V_2O_5 is non-selective and showed inactivity in oxidative catalysis [83]. Contrarily, the amorphous phase is more selective towards light olefins[94].

Catalyst deactivation

In the oxidative cracking of paraffin over lattice oxygen produced from vanadium oxide, catalytic deactivation occurs due to depletion of the lattice oxygen and coke formation. In other words, the catalyst needs to be regenerated by interaction with air (gas-phase oxygen). In this light, the use of effective supports and promoters can improve the performance of this catalyst.

Role of supports

Generally, the type of support used significantly affects the behavior of vanadium oxides catalysts. This directly influences the acidity/basicity of the catalyst. Vanadia is usually impregnated on supports such as Al_2O_3 , MgO , SiO_2 , ZrO_2 , USY, Ti-HMS, and MCM-41. It was concluded that γ/θ -alumina supports are the most suitable in this subject. [95]–[101]. Alumina is the most widely used support in vanadium-based catalysts. The structural and chemical properties of alumina make it efficient catalyst support in the oxidative conversion reactions. However, alumina acidity leads to excessive cracking which favors unwanted CH_4 formation. It is worthwhile that this acidity can be controlled by modification with the alkaline earth metals[100].

MgO has been reported as efficient support for VO_x . This is due to its alkaline nature. However, its use is limited as a result of its reduced mechanical strength and lower surface area. To improve

this support material. the combination of Al_2O_3 and MgO have been reported to enhance olefin yield in the partial oxidation of light alkanes[102].

Furthermore, several studies are on other supports materials including alpha-alumina, USZ, and NAY. Ajayi, B. P. et al [103] revealed that VO_x/USY catalyst is a highly selective and active catalyst for oxidative catalysis. This is due to its low acidity.

In addition, Sokolov et al reported that both Si/Al- base support enabled the enhancement of the catalyst activity and stability[104]. However, using strong basic sites as support in this catalyst leads to catalyst deactivation which in turn increased coke formation and reduces olefins selectivity.

Therefore, it is important to balance the acidity/basicity of the material used as support. One way to control this acidity is to incorporate alkaline earth metal oxides into the alumina matrix [100]. More so, the use of these basic supports as modifiers generate hydroxyl group on the support surface which leads to the formation of a well-dispersed catalyst. As a result, different alkaline earth metals have been used in oxidative catalysis to modify alumina support. For example, Ayandiran et al [7] demonstrated the effect of CaO in $\text{VO}_x/\text{CaO-}\gamma\text{Al}_2\text{O}_3$ for the oxidative dehydrogenation of propane to propylene. The catalyst shows excellent performance with 65% propane conversion and 85% selectivity to propylene. This is because the presence of CaO minimizes CO_x formation. More so, the addition of CaO to the vanadia catalyst ensured a balanced acidity which suppresses excessive cracking. In another study carried out by Bakare et al [61], three alkaline earth metals(CaO , MgO and BaO) were used to modify theta alumina supported vanadia catalysts. Although all the catalysts displayed excellent activity, $\text{VO}_x/\text{BaO-}\theta\text{-Al}_2\text{O}_3$ performed best.

Role of promoters

Different studies reported the use of different promoters to improve the catalyst activity of the vanadium-based catalyst. Ogonowski and Skrzynska reported that the yield of light olefins increased when CO₂ is added as a mild oxidant[105]–[107]. This is due to the use of CO₂ to form coke gasification, remove hydrogen by the reverse water- gas shift reaction, oxidize the strong vanadium reducing center, remove acid sites that form unwanted side reactions, However, the use of CO₂ depends mainly on the choice of the catalyst support. To achieve the best roles of CO₂ as a promoter on the catalyst, the support should maintain a balance between a strong base and weak base material.

Furthermore, MgO can also be used as a promoter to improve olefins selectivity and reduce coke formation[90]. This is because MgO suppresses coke formation due to its alkaline nature. Also, CaO has a modifier in the vanadium-based catalyst that has been demonstrated to result in the excellent oxygen-carrying capacity of the catalyst. These have a significant influence on olefin selectivity[108].

Catalyst preparation method

Typically, the method employed in the catalyst preparation influences the catalyst performance. Few studies have explained the behavior of the catalyst preparation method on oxidative catalysis. Meanwhile, catalyst systems show different activities due to the influence of the preparation method. The catalyst system used in OC is prepared by the sol-gel and impregnation (incipient wetness technique or excess solvent saturation impregnation technique) method. The incipient preparation method simply involves the diffusion of VO_x on a typical support material. In this technique, a certain mixture of vanadium oxide precursors and the support are prepared [64], [66].

This technique leads to different vanadium oxide surface species depending on the amount of VO_x loading. Generally, four different vanadyl species are observed (Figure 4); (1) below the monolayer, isolated VO_x species exists, (2) intermediate polymeric VO_x occur, (3) hybrid of isolated and polymeric vanadyl species are present and (4) V_2O_5 species occur above the surface coverage [109]–[112]. On the contrary, the excessive solvent impregnation method uses an organic vanadium precursor such as vanadyl acetyl acetate in an excess amount of ethanol or toluene. In this method, more quantities of VO_x can be incorporated on the support material [21]–[23]. A higher percent weight of VO_x species on the support may result in high dispersion of 3D VO_x species. In addition, in the impregnation preparation method, the catalysts are usually calcined at high temperatures. In this regard, the possibility of mixed oxides may accompany the support oxide. Hence, the catalyst synthesis should be subjected to minimal thermal treatment.

On the other hand, in the sol-gel method, the active metal is incorporated on the support. This avoids losses in the catalyst surface area due to calcination at high temperatures caused by the impregnation method [113], [114]. Thus, the sol-gel catalyst preparation method tends to have a high surface area and higher activity compared to the same catalyst prepared by the impregnation method.

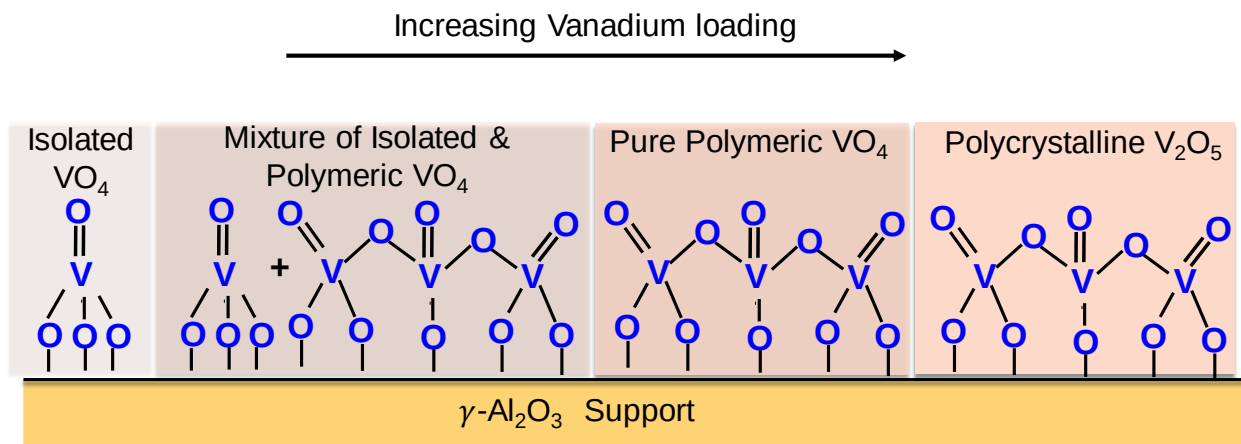


Figure 5: VOx surface structure

2.4 Catalytic Oxidative Cracking Reactors

While extensive studies are on catalysts development, limited studies exist in reactor design and optimum reactors development to ensure the viability of the catalytic oxidative cracking in light olefins production. The literature mainly provides extensive work on a fixed bed reactor. However, the use of a fixed bed reactor has the challenges of hot spot formation due to non – uniform reactor temperature, mass transfer limitation, and rapid catalyst deactivation due to catalyst damage. According to Boyadjian et al, the optimized reactor system is of paramount importance in enhancing olefins yields in the COC of alkanes. Based on efforts from the literature, fluidized bed and membrane reactors are promising reactors in the oxidative catalysis reaction. Fluidized bed reactors possess several important advantages such as; uniform temperature operation, avoidance of mass transfer limitation, constant residence time distribution, and a small amount of catalyst requirement. Fluidized bed reactors offer an alternative to the threat of catalyst deactivation and damages due to the consequences of hot spot encountered in fixed bed reactors.

In addition, fluidized bed reactors allow easy regeneration of catalysts, especially in a specific type of fluidized bed reactor- called the CRER riser simulator. In this reactor, catalysts are transported

from the oxidative cracking section where catalyst reduction occurs due to the release of lattice oxygen in the cracking reaction to the regenerator section where catalysts re-oxidation occur. Hence, the implementation of this technology is an important consideration at an industrial scale.

Furthermore, in fluidized bed and membrane reactors, low oxygen partial pressure in the reactor could be attained when performing COC under aerobic conditions. Consequently, undesired combustion reactions could be suppressed[115], [116]. This will be significantly improved the yield of light olefins.

In addition, limited studies are on fluidized bed membrane reactor. As an example, the fluidized bed membrane reactor has been used in the oxidative catalysis of ethane to Ethylene; in this reactor type, the author investigates the influence of reaction time and temperature [117]. Thus, the fluidized bed membrane reactor performs better and improves the yield of ethylene.

2.5 Summary of Oxidative Cracking Catalysts

Table 1 (below) presents the catalysts used for catalytic oxidative cracking of several alkanes. The best catalyst, however, should be thermally stable at the desired reaction conditions, suppress coking due to the influence of promoter and/or completely prevent coking using high boiling solvents (additives) and minimize total thermal gas-phase oxidation.

Table 1: Previous works on the catalytic oxidative cracking catalyst

Catalyst	Temp (C)	Conversion (%)	Selectivity (%)	P/E ratio	Yield (%)	Rf
Hexane						
Na ₂ WO ₄ /CaMnO ₃	725	49	85	0.7	36	[53]
Na ₂ WO ₄ /SrMnO ₃	725	53	82	NR	NR	[53]
VO _x / Ce-Al ₂ O ₃	550	30	60	0.4	NR	[14]
Li/MgO	700	64	67	NR	NR	[8]
MoO ₃ -Li/MgO	575	38.51	60	NR	23.9	[8]
Li/MgO	575	28	60	NR	17	[8]
Plasma- Li/MgO	600	55.0	64.0	NR	35.2	[118]
BiOCl	600	50.7	38.4	0.4	52	[119]
LaOCl	600	38.3	22	0.6	NR	[119]
SmOCl	600	27.4	32.8	0.7	NR	[119]
CoN/ Al ₂ O ₃	600	76.7	48.7	0.36	37.3	[120]
BiOCl	650	20.0	21.0	1.33	4.2	[121]
Butane						
Li/Cl/Dy/Mg	600	20.1	97.1	1.83	16.0	[122]
Mg-ZSM-5	650	83.8	40.5	NR	0.67	[123]
Propane						
Au/La ₂ O ₃	550	46	53	NR	NR	[124]

Au/SO_4^{2-} $/Ce_{0.5}/Zr_{0.5}O_{02}$	650	62	68	NR	42.2	[125]
Phosphate La_2O_3 $/ZSM-5$	650	NR	60	NR	NR	[126]

2.6 Kinetic Modelling

Few studies deal with the kinetics of oxidative cracking of n-hexane to light olefins [32]. It was reported that oxidative cracking of n-hexane proceeds via three steps: (1) Cracking, (2) Oxidative dehydrogenation, and (3) catalyst deactivation. Interestingly, the model agrees with the experimental data. This indicates that oxidative cracking reactions follow the three steps above for the chosen catalyst ($VO_x/Ce-Al_2O_3$).

Generally, oxidative catalysis kinetic studies are model based on the Mars-Van Krevelen and Langmuir-Hinshelwood mechanisms. Mar-Van Krevlen mechanism assumes that some products escape the catalyst's surface with a component of the catalyst's lattice oxygen[127]. Therefore, it was suggested by[128] to suggest two surface species (Θ and λ) for catalyst reducibility. Consequently, this results in data correlation when the Mar-Van Krevlen mechanism is used in oxidative catalysis.

Regarding the second mechanism, it assumes that the alkane feed and oxygen species are both adsorbed on the catalyst surface[129]. This mechanism has been applied for several oxidative dehydrogenation reactions with good data fittings. For example, [130] applied the mechanism during the synthesis of propene from propane. The author employed nonlinear regression to determine the kinetic parameters. This mechanism agreed well with the experimental data.

2.7 Research Gaps

Based on the numerous studies outlined in the literature review, a vanadium-oxide based catalyst is an appropriate matrix for the catalytic oxidative cracking of alkanes. In this system of catalyst, vanadium oxide is the active species. This is largely attributed to its high activity and selectivity towards partial oxidation from its lattice oxygen. Additionally, vanadium oxide possesses redox property which enables it to undergo simultaneous re-oxidation and reduction over many repeated cycles.

Furthermore, gamma-alumina is widely used for the oxidative cracking of light paraffin. This is because gamma-alumina has a high BET surface area, large pore size volume, uniform size distribution, robust mechanical strength, and high hydrothermal stability. However, due to the high acidic nature of alumina, which caused excessive cracking to unwanted side products. It is usually modified with the oxide of group II elements. Among the alkaline earth metal oxides, MgO and SrO are potential good additive due to their basic nature, ability to reduce coke formation, and increased selectivity towards desired light olefins. In this light, the incorporation of VO_x on these support materials will pose several advantages in the study of catalytic oxidative cracking of light paraffin.

Lastly, the studies of COC catalysts are mostly performed in fixed bed reactors. However, this reactor inherently imposes mass transfer limitation and the constraint of a hot spot due to a non-isothermal temperature in the reactor. On the contrary, the fluidized-bed reactor is a promising alternative to a fixed bed reactor, since the fluidized bed reactor operates in an isothermal temperature and can overcome the challenge of mass transfer limitation. Above all, fluidized bed reactors require the use of a small amount of catalyst, which can be regenerated with ease.

Therefore, this study aims to evaluate the roles of two fluidizable catalysts ($\text{VO}_x/\text{MgO-}\gamma\text{Al}_2\text{O}_3$ and $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$) for the oxidative conversion of n-hexane.

2.8 Conclusions

The following important conclusions are outlined after the exploration of the literature.

1. The catalytic oxidative cracking of alkanes is an emerging process for light olefins production.
2. The anaerobic catalytic oxidative cracking enables better tuning of olefin selectivity and overcome the challenges of oxygen used in the feed-in aerobic catalytic oxidative cracking of alkanes.
3. VO_x has been proved as a suitable active species due to its redox property and affinity towards partial oxidation.
4. The use of MgO and SrO to modify the Al_2O_3 support will not only balance the acidity of the support but also minimize coke formation.
5. Fluidized-bed reactors will suppress the issue of mass transfer limitations and increase alkane conversion.

CHAPTER – 3 OBJECTIVES

This study mainly involves the development of highly active and stable catalyst(s) suitable for fluidized bed oxidative cracking of n-hexane under gas-phase oxygen-free conditions. Further to its catalytic role, the developed catalysts supposed to act as a source of lattice oxygen. In this regard, MgO and SrO modified $\text{VO}_x/\gamma\text{Al}_2\text{O}_3$ have been investigated. The following are the specific objectives of this work:

- i. To study the effects of MgO and SrO on the activity, oxygen-carrying capacity, and stability of the $\text{VO}_x/\text{MgO-}\gamma\text{Al}_2\text{O}_3$ and $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ catalysts.
- ii. To investigate the variation of $\text{MgO}/\gamma\text{Al}_2\text{O}_3$ and $\text{SrO}/\gamma\text{Al}_2\text{O}_3$ ratios on the catalyst performances.
- iii. To elucidate the metal-support interaction by various physicochemical characterizations.
- iv. To develop the phenomenological based kinetics model(s) representing the fluidized conversion of n-hexane over $\text{VO}_x/\text{SrO-}\gamma\text{-Al}_2\text{O}_3$ catalysts.

CHAPTER – 4 MATERIALS AND METHODS

This chapter describes the materials and method used in the synthesis of a vanadium oxide supported on Al/Mg and Al/Sr mixed oxide catalysts. More so, we report the characterization techniques used to investigate catalysts' behavior. Finally, we outlined the catalyst evaluation procedure in a fluidized bed riser simulator.

4.1 Catalyst Synthesis

4.1.1 Chemicals

- i. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as alumina precursor obtained from Sigma-Aldrich
- ii. $\text{Sr}(\text{NO}_3)_2$ as strontia precursor obtained from Sigma-Aldrich
- iii. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as magnesia precursor obtained from Sigma-Aldrich
- iv. $(\text{NH}_4)_2\text{CO}_3$ as hydrolyzer obtained from Fisher limited
- v. $\text{C}_{10}\text{H}_{14}\text{O}_5\text{V}$ as vanadium precursor obtained from Sigma-Aldrich

4.1.2 Mixed $\text{SrO}-\gamma\text{Al}_2\text{O}_3$

The SrO modified $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts were prepared with varying ratios of the mixed supports. To prepare the $\text{VO}_x/\text{SrO}-\gamma\text{-Al}_2\text{O}_3$ catalysts, pure $\gamma\text{-Al}_2\text{O}_3$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were placed in 250 mL of deionized water and the mixture was allowed to stand at 60 °C with stirring for about 45 minutes. Then, an equivalent amount of a solution of $(\text{NH}_4)_2\text{CO}_3$ (~0.4 M) was added to the mixture dropwise until a white gel was formed, indicating the presence of alumina and modified alumina. The mixture was aged in an oven at 60 °C for 48 hours and was centrifuged to remove the water. The resulting product was calcined in a furnace at 500 °C for 10 hours using

three operating modes. Following the same procedure, three supports SrO- γ -Al₂O₃ supports were prepared in the ratio 0:1, 1:1 and 2:1

4.1.3 Mixed MgO- γ Al₂O₃

The MgO modified VO_x/MgO- γ Al₂O₃ catalysts were prepared with Mg/Al ratios of 1:1, 1:2, and 2:1. To prepare the catalyst, an appropriate amount of Al (NO₃)₃·9H₂O and MgCl₂·6H₂O were placed in 250 mL of deionized water, and the mixture was allowed to stand at 60 °C with stirring for about 45 minutes. Then, an equivalent amount of a solution of (NH₄)₂CO₃ (~0.4 M) was added to the mixture dropwise until a white gel was formed, indicating the presence of mixed oxides of Al/Mg. The mixture was aged in an oven at 60 °C for 48 hours and was centrifuged to remove the water. The resulting product was calcined in a furnace at 500 °C for 10 hours using three operating modes.

4.1.4 Active site Preparation

The metal oxide catalyst was prepared using the excessive solvent impregnation method. In this approach, an excess amount of ethanol is added to a beaker containing prepared supports. Subsequently, an equivalent amount of 10 wt % (~0.781g) of vanadium acetylacetonate was added as the vanadium precursor to the mixture and stirred thoroughly for 24 hours at 60 °C. Then, the mixture was dried on the stirrer and the resulting product was calcined at 500 °C for 4 hours.

For ease of samples identification, the following nomenclatures were used:

Table 2: SrO catalyst synthesis nomenclature

Catalyst	SrO/ γ-Al₂O₃	Wt. % of V	Nomenclature
VO _x / γ -Al ₂ O ₃	0:1	10	V1
VO _x /SrO- γ -Al ₂ O ₃	1:1	10	S1
VO _x /SrO- γ -Al ₂ O ₃	2:1	10	S2

Table 3: MgO modified catalyst synthesis nomenclature

Catalyst	MgO/ γ-Al₂O₃	Wt. % of V	Nomenclature
VO _x /MgO- γ -Al ₂ O ₃	1:1	10	V2
VO _x /MgO- γ -Al ₂ O ₃	1:2	10	V3
VO _x /MgO- γ -Al ₂ O ₃	2:1	10	V4

4.2 Catalyst Characterization

4.2.1 X-Ray Diffraction (XRD)

XRD has numerous applications. Among these applications are:

- i. Identification of compounds
- ii. Identification of different phases in a compound
- iii. Crystallite size

iv. Study of phase equilibrium etc.

In this work, XRD was used to determine the crystallinity properties of the $\text{VO}_x/\text{MO-Al}_2\text{O}_3$ samples using a rigaku MiniFlex II benchtop. The equipment operates with the following parameters: wavelength = 0.15406 nm, 20 mA, 40 kV and a scan rate of 2 degrees scan per minute for the range of 2θ between 10-90 degrees and increment of 0.02

4.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is used to find out the type of functional groups on the support. The as-synthesized catalysts FTIR was carried using a Nicolet 6700 Thermo Fisher Scientific instruments. The analysis uses 3 mg of a catalyst sample thoroughly mixed with 0.4 g of standard KBr. Further, the infrared band of the catalysts was recorded between 400 to 4000 cm^{-1} .

4. 2.3 Scanning Electron Microscope (SEM)

The catalysts' morphology and compositions were studied using a field-emission scanning electron microscope. For the analysis, each sample was coated with gold before FE-SEM imaging and an accelerating voltage of 30 kV was used for the quantitative analysis.

4. 2.4 X-Ray Fluorescence (XRF)

X-Ray Fluorescence Spectrometer (XRF) was used to determine the elemental compositions of the prepared catalysts. A Brucker Tornado M4 micro -ED XRF spectroscopy equipment was used to analyze the elemental compositions of the samples. The equipment operates alongside with high-performance XFlash detector for the analyses.

4.2.5 Laser Raman Spectroscopy

This study uses Raman spectroscopy to investigate the nature of the VO_x present on the catalysts. The analysis was done in the range of 0 – 1200 cm⁻¹.

4.2.6 Temperature Programmed Desorption (TPD)

Temperature Programmed Desorption (TPD) analysis typically uses ammonia to determine the acidity of a catalyst. This present study uses METTLER TOLEDO equipment. Before the analysis, about 10 – 15mg of the catalyst was loaded to the analyzer. Following this, the sample was then cooled to 100 °C temperature from 600 °C. Subsequently, an NH₃/He gas mixture (5% NH₃/He) at a rate of 50 ml/min was passed to bring the sample to saturation. Helium was allowed then to flow at 100 °C at 50 cm³/min to remove any gas-phase ammonia in the system and unadsorbed ammonia trapped in the catalyst bed. Finally, the ammonia was desorbed by raising the temperature to 600 °C at 10 °C/min. Thermal conductivity was used to record the ammonia concentration of the effluent gas.

4.2.7 Pyridine FTIR

In this study, pyridine FTIR was further to determine the nature of the acid sites and acidity. That is, this analysis can be used to investigate the catalysts Lewis or Bronsted concentration. In this technique, pyridine was used as a probe molecule. Typically, a catalyst sample of 400 mg was first dried in nitrogen flow for 2 hrs at 500 °C and subsequently was cooled to 150 °C. Then, the sample was maintained at 150 °C while passing pyridine under nitrogen flow. Following this, pyridine was adsorbed for 1 hr. Then, nitrogen flow at 150 °C was passed to remove any loosely adsorbed pyridine. Subsequently, the was placed in a DRIFTS. Finally, FTIR spectra were measured at 25 °

C using a Nicolet 6700 Thermo Fisher Scientific instruments operating at 90 scans and 3 cm⁻¹ resolutions.

4.2.8 Temperature Program Reduction

The temperature program reduction program was used to study the reducibility and reduction temperature of the synthesized samples. An AutoChemII 2920 equipment was used to perform the TPR. Typically, 0.1 g of the samples were loaded in a U – tube quartz glass using wool as the catalyst bed. The tube was inserted into a retaining chamber. Before the actual TPR program, the samples were first pretreated under argon flow for 3 hours to remove any volatile material. After pretreatment, the temperature was cooled to ambient. Then 10 % H₂ in Argon flow was passed with a flow rate of 50 ml/min at a heating rate of 10 C/min. A thermal conductivity detector was used to measure the H₂ concentration during the analysis.

4.2.9 Nitrogen Adsorption Analyses

The catalysts' specific surface area and the desorption branch pore size distribution of the pure support and doped samples were analyzed using a Micromeritics model ASAP 2010 analyzer. To obtain a clean surface, 0.2g of the sample was first degassed at 350 C for 3 hrs. Following this, Nitrogen adsorption was conducted at 77 K in the range of 10⁻⁶ to 1 pressure value.

4.3 Catalyst Evaluation

4.3.1 The CREC Riser Simulator

The CREC riser simulator was used to determine the stability and activity of the synthesized VO_x/MgO-Al₂O₃ catalyst. Figure 6 (below) shows the schematic of the CREC riser simulator. The reactor is a bench-scale(53cm³) reactor that modeled the ones used in the industry. Basically, the

reactor consists of the upper and lower reactors sections, impeller, valves, temperature controllers, transducers, and vacuum boxes. The vacuum box is attached to the reactor where the product is subsequently transferred to the GC for analysis[131].

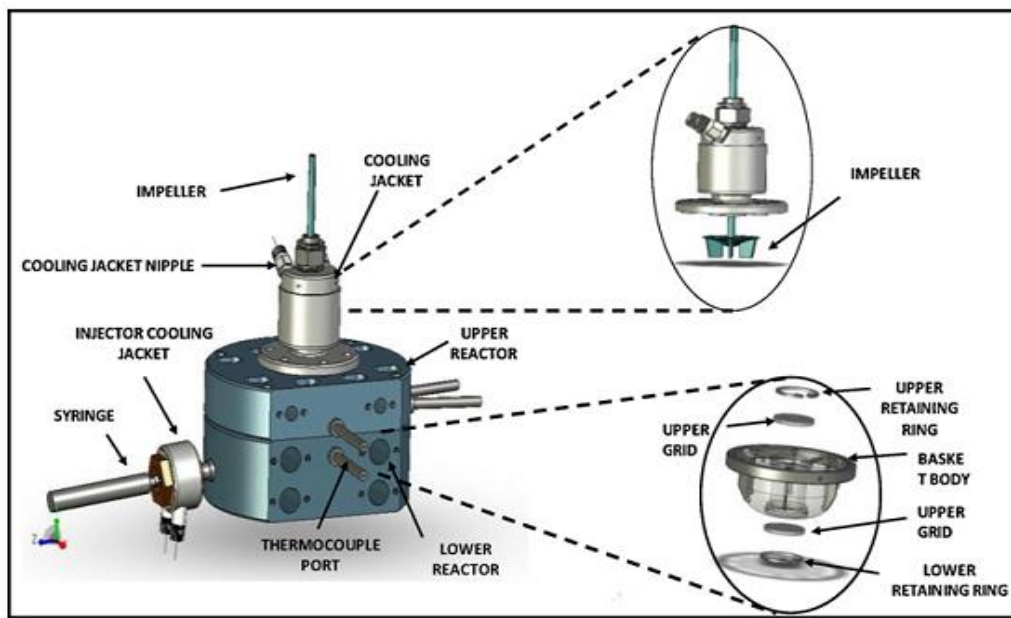


Figure 6: The CREC Riser simulator

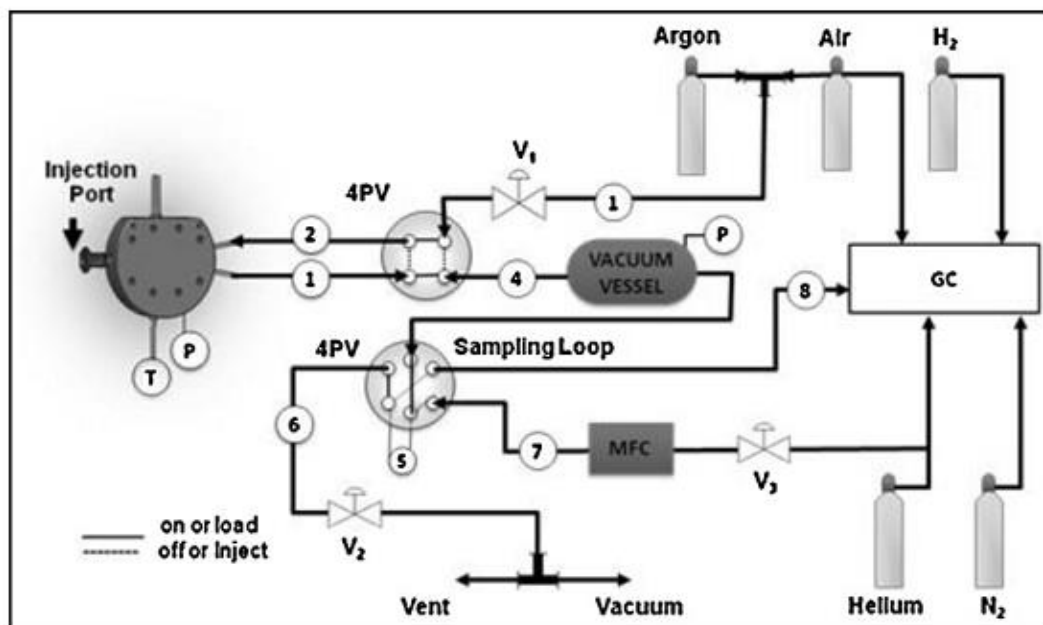


Figure 7: Schematic diagram of the CREC riser simulator in operation

4.3.2 Catalytic Oxidative Cracking of n-hexane

The oxidative conversion of n-hexane cracking was performed in a fluidized bed CREC Riser Simulator. More information about the CREC reactor fluidized bed can be found in the works of our research team [132]. The CREC Riser Reactor Simulator body 3D diagram is as shown in Fig. 7, while Figure 8 provides a schematic diagram for the experimental set-up of the CREC Riser Simulator including the GC analysis.

n-hexane oxidative cracking experiments were performed with a constant amount of catalyst (0.425g). Before the actual cracking of n-hexane, a leak test was performed on the reactor to confirm the presence of any leak. Subsequently, the reactor was slowly taken to the set temperature and Argon gas was continuously passed to the system. Thereafter, the vacuum pump was started until it reaches 20.7 kPa (3.75 psi) after achieving the desired temperature. At this stage, the impeller was operated to prepare the catalyst for fluidization. After this, pure n-hexane feed was pumped into the reactor with the aid of a tightly fitted syringe. Then, the reaction was allowed for the desired period. Subsequently, the insulation valve that connects the reactor and the vacuum box opens automatically after the reaction is completed. All the product gases enter the vacuum box, which then is analyzed by the FID and TCD detector of an online Agilent 7890 GC. Thermal experiments were also performed to decide if some non-catalytic thermal cracking at the operating conditions would occur or not. Ultimately, the catalysts' activity was measured using a GC. The catalytic activity is using equations 4.1 and 4.2 and 4.3.

$$X_{C_6H_{14}}(\%) = \frac{\sum_j z_j n_j}{6n_6 + \sum_j z_j n_j} \times 100 \quad (4.1)$$

$$S_j(\%) = \frac{z_j n_j}{\sum_j z_j n_j} \times 100 \quad (4.2)$$

$$Yield = X_{C_6H_{14}} \times S_{olefins} \times 100 \quad (4.3)$$

Where $X_{C_6H_{14}}$ (%) is n-hexane conversion, n_6 means moles of unconverted n-hexane, the atoms of carbon is represented by the letter z_j , and n_j is the number of carbons of component j.

CHAPTER – 5 CATALYST CHARACTERIZATION AND EVALUATION

The chapter consists of two sections- Role of MgO and role of SrO in $\text{VO}_x/\text{MO}-\gamma\text{-Al}_2\text{O}_3$ (M=Mg or Sr) catalysts. Each section reports the results of the prepared catalysts' characterization and activity in a fluidized bed reactor. The activity of the catalysts was studied by varying temperature and reaction time. Following this, the best catalyst was evaluated for kinetic studies.

5.1 Role of MgO

This section mainly investigates the role of MgO on $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ in the oxidative cracking of n-hexane to produce light olefins at low reaction temperatures. It mainly focuses on the catalytic behavior of the $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ catalyst.

5.2 Catalyst Characterization

5.2.1 X-ray diffraction

XRD patterns of the prepared catalysts are presented in Fig 8. As depicted in the figure, peaks at 37° , 45° , and 67° represent $\gamma\text{Al}_2\text{O}_3$ phase [7]. VO_x peaks were not detected in the samples. This is either due to a well-formed vanadia in the amorphous phase in the samples or the formation of unnoticeable VO_x peaks due to its size [51]. The peaks at 2θ angles of 42° and 61° may be attributed to MgO [133]. Increasing MgO content in the supports reduces the peak intensity of $\text{VO}_x/\text{Al}_2\text{O}_3$. Thus, it is proposed that the incorporation of MgO in the samples leads to a well-dispersed amorphous phase in the samples. This well dispersed amorphous phase observed is due to the influence of the more basic MgO which creates a hydroxyl group on the support. This

observation is an important criterion for oxidative cracking catalysts performance. However, for the catalyst sample without MgO, the XRD pattern displays no well-formed amorphous phase. Consequently, this leads to reduced oxygen-carrying capacity and therefore the catalyst activity is reduced due to enhancing active site agglomeration[134].

Moreover, other phases such as AlV_2O_9 and MgV_2O_6 were not detected in any of the catalysts. Therefore, we propose that the active vanadia species and support material possess moderate interaction that leads to mixing at high temperatures.

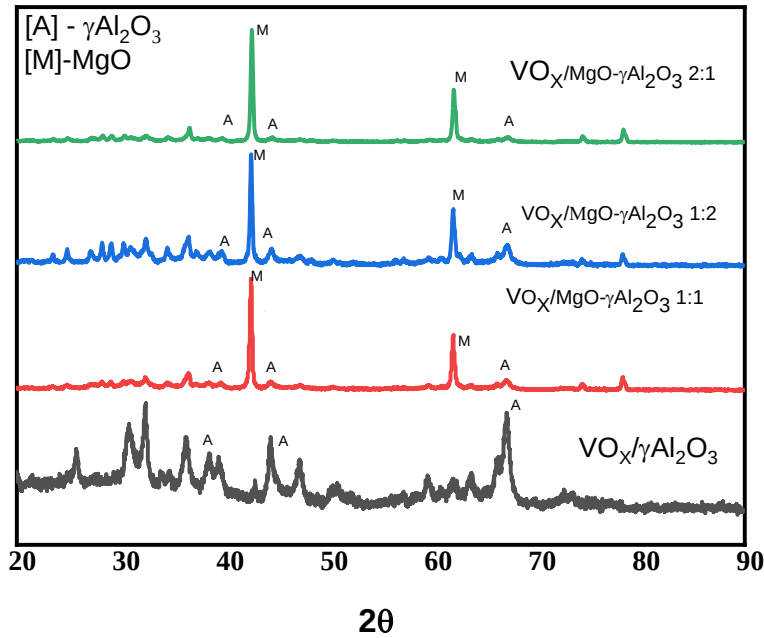


Figure 8: XRD patterns of the prepared catalyst.

Furthermore, the mean crystallite sizes of the samples were calculated using Scherrer's formula (equation 5.1) and presented in Table 4.

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (5.1)$$

In this expression, D represents the crystallite size, k is the Scherrer's constant taken as 0.9, λ is the wavelength of the x-ray radiation (0.15406 nm for $\text{CuK}\alpha$), β is the full width of half-maximum (FWHM) intensity expressed in radians, θ is the diffraction (Bragg) angle.

Table 4: Mean crystallite size

Catalyst	Mean Crystallite size D_m (nm)
$\text{VO}_x/\gamma\text{Al}_2\text{O}_3$	8.22
$\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:2	10.0
$\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:1	11.4
$\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 2:1	13.4

5.2.2 FTIR

Fig. 9 represents the FTIR analysis of the catalysts under study. $\gamma\text{Al}_2\text{O}_3$ peaks appeared at 3464 cm^{-1} , 1629 cm^{-1} and 821 cm^{-1} as shown in the figure[72]. The peaks of MgO appeared at 864 cm^{-1} , 1058 cm^{-1} , and 1466 cm^{-1} . More so, the peaks around 1630 cm^{-1} and 3400 cm^{-1} are due to the stretching mode of H-O-H and the OH bending vibration of water[133].

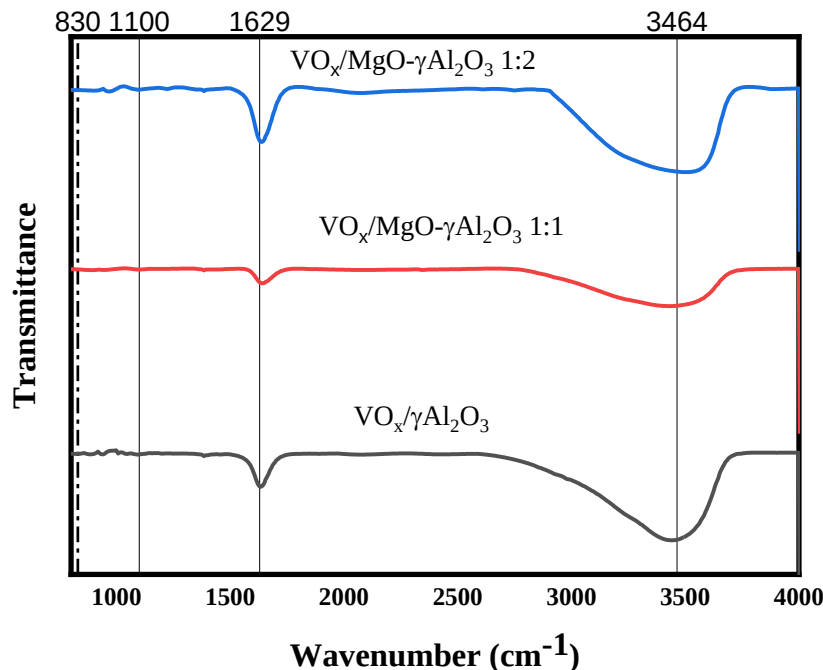


Figure 9: FTIR spectra of the catalyst samples.

5.2.3 Raman Spectra

Fig. 10 shows the Raman spectra of the prepared catalysts. The band at 888 is attributed to V-O-V stretching in the polyvanadate species. The band at 984 is the stretching of V=O in the polyvanadate vanadia species[135]. The peaks observed from 20 cm⁻¹ to 600 cm⁻¹ peaks in the range are ascribed to the vibration of bulk VO_x[21]. Furthermore, MgO peaks are not observed in the selected Raman region. This observation agrees with the XRD result that as the MgO content is increased, VO_x/γAl₂O₃ peaks become reduced indicating the formation of well-dispersed amorphous between the active metal and the support. Similarly observation has been reported in the literature[91], [136].

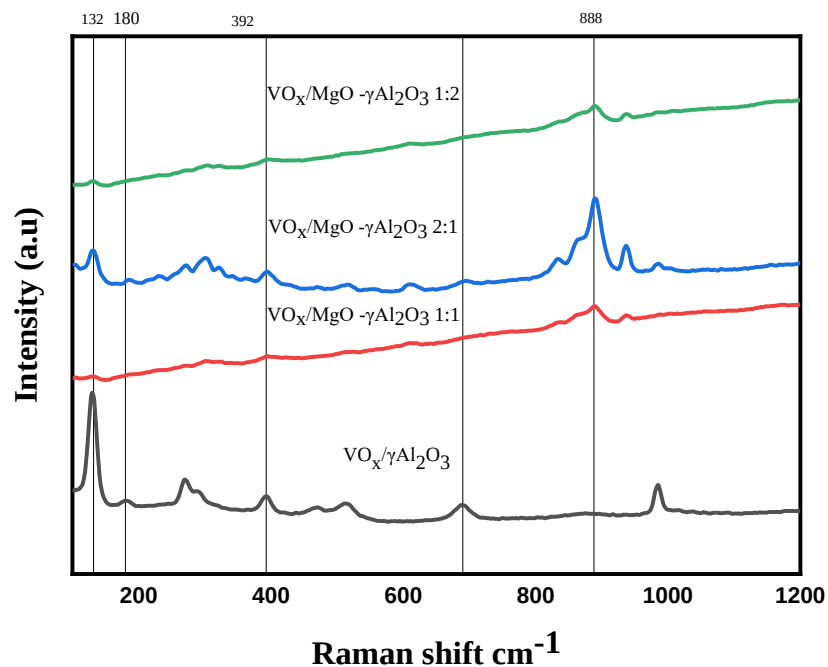


Figure 10: Raman spectra

5.2.4 XRF Analysis

The result of XRF analyses shows that the elemental percentages observed were appropriate with the expected in the samples with a slight deviation. Table 5 shows the weight percent aluminum, magnesium, and vanadium elemental analysis as obtained from XRF.

Table 5: Catalyst elemental analysis

Sample	Al (%)	Mg (%)	V (%)
γ -Al ₂ O ₃	99.83	nil	Nil
V ₂ O ₅ /γ-Al ₂ O ₃	64.75	nil	34.99
V ₂ O ₅ /MgO /γ-Al ₂ O ₃ 1:1	37.78	34.98	27.00
V ₂ O ₅ /MgO /γ-Al ₂ O ₃ 1:2	44.42	21.52	34.02

V ₂ O ₅ /MgO / γ -Al ₂ O ₃ 2:1	27.69	47.08	24.98
MgO	nil	94.19	Nil

5.2.5 SEM-EDX analysis

Fig 11a depicts the SEM morphology of the as synthesized γ -Al₂O₃. This figure shows the uniform particle size distribution of the pure γ -Al₂O₃ which is an important property of γ -Al₂O₃. Fig 11b shows the morphology of VO_x/MgO- γ -Al₂O₃1:2. The rod-like shape indicates the presence of VO_x nanocrystallites which is largely dispersed on the support. This well-dispersed phase of VO_x nanocrystallite confirms the XRD pattern observed above. Increasing the MgO content makes the VO_x dispersed phase more obvious as shown for VO_x/MgO- γ -Al₂O₃ 1:1 and VO_x/MgO- γ -Al₂O₃ 2:1. Samples.

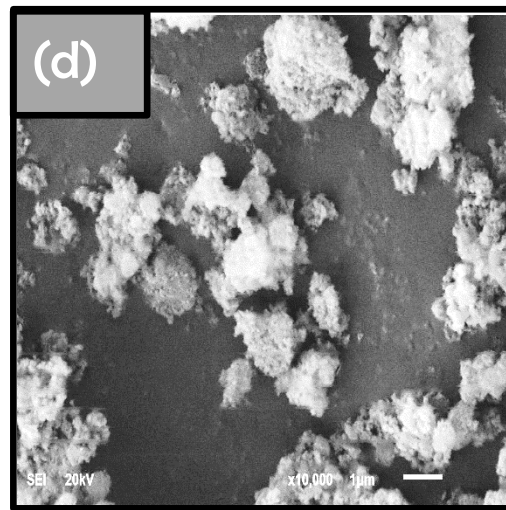
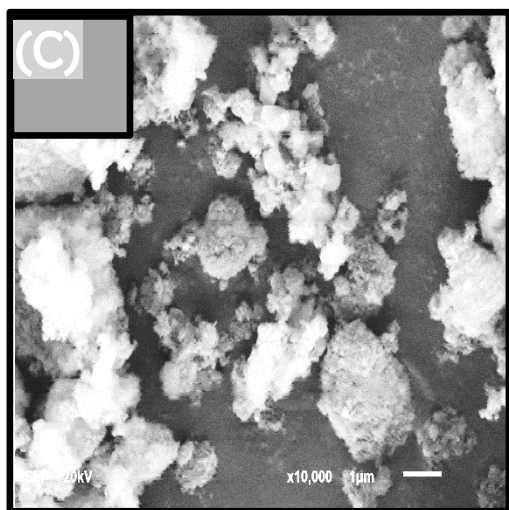
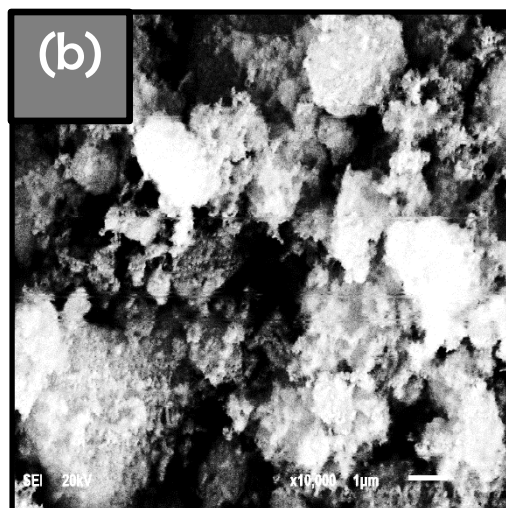
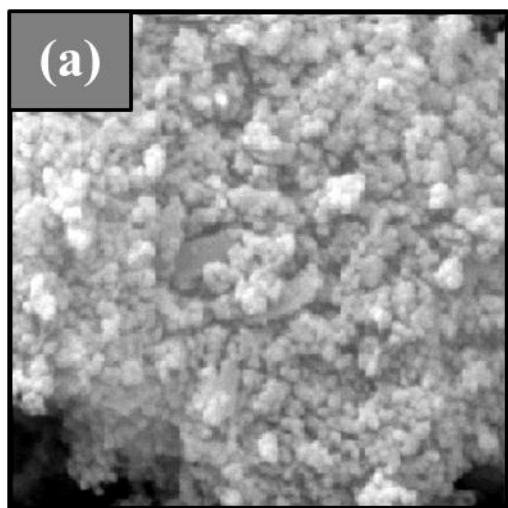


Figure 11: SEM images of $2\ \mu\text{m}$ (a) $\gamma\text{Al}_2\text{O}_3$ (b) $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:2 (c) $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:1, and (d) $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 2:1

5.2.6 Nitrogen Adsorption

The textural characteristics of the catalysts are presented based on N_2 sorption analyses. Table 6 shows the results of the N_2 sorption analyses of the synthesized samples. The BET surface area of pure $\gamma\text{Al}_2\text{O}_3$ is $74 \text{ m}^2/\text{g}$, which is in the range expected for gamma-alumina ($50\text{-}300 \text{ m}^2/\text{g}$). However, after the impregnation of VO_x , the BET surface area of the sample decreases sharply to $60 \text{ m}^2/\text{g}$. Consequently, it can be inferred that the impregnation of vanadium species on the support obstructs the pores of the support[51]. For pure MgO , the BET surface area was found to be $5 \text{ m}^2/\text{g}$ with 70% occupying the external area which is the area important for the oxidative cracking reactions. Likewise, high values of the supported catalysts' external surface area compared to the micropores' surface area connote that the active sites of the catalysts are exposed to readily adsorb the feed during the reaction. Therefore, one can predict that the catalyst surface area is directly related to its activity, higher support surface area would lead to excessive cracking causing unwanted cracked components. On the other hand, MgO 's poor surface area may result in lower conversions of n-hexane[30]. Thus, a balanced support surface area is required for optimum catalyst activity.

Table 6 also shows the average pore sizes of the synthesized catalysts determined from the BJH adsorption and desorption values. These values are in the range of 18 to 44 nm, indicating that the samples are in the mesoporous range (2-50 nm). The surface densities of the supported vanadium catalyst were calculated based on the expression of Khodakov et al. [137].

$$\text{surface density} = \frac{\text{VO}_x \text{ wt}(\%) \times 6.023 \times 10^{23}}{\text{Vanadium molecular weight} \times 100 \times S_{\text{BET}}} \quad (5)$$

High surface density values above $8.8 \text{ V}/\text{nm}^2$ confirm the Raman analysis results, indicating the absence of monovanadate species. The calculated surface density values of $\text{VO}_x/\gamma\text{Al}_2\text{O}_3$,

VO_x/MgO- γ -Al₂O₃ 1:2, VO_x/MgO- γ -Al₂O₃ 1:1 and VO_x/MgO- γ -Al₂O₃ 2:1 are 19.7, 21.1, 23.6, and 35.5 V/nm², respectively. This further elucidates the X-ray diffraction patterns reported above that VO_x crystallites are present in small amounts.

Table 6: Nitrogen sorption analysis

Catalyst	S_{BET}	S_{EXT}	S_{micro}	V_p[*]	D_p^{**}	Surface density (V/nm²)
	[m²/g]	[m²/g]	[m²/g]	[cm³/g]	(nm)	
γ -Al ₂ O ₃	74	64	10	0.48	25.1	Nil
VO _x / γ -Al ₂ O ₃	60	51	9	0.41	26.9	19.7
VO _x / MgO- γ -Al ₂ O ₃ 1:2	56	50	6	0.22	18.9	21.1
VO _x / MgO- γ -Al ₂ O ₃ 1:1	50	40	10	0.27	25.0	23.6
VO _x / MgO- γ -Al ₂ O ₃ 2:1	33	29	4	0.18	24.1	35.8
MgO	5	3.5	1.5	0.02	43.7	Nil

*single point pore volume calculated from the adsorption isotherm

** average pore diameter calculated from the average of the BJH adsorption and desorption data

5.2.7 Acidity and Metal – Support Interaction

The acidity of the catalyst was determined based on the NH_3 -TPD analysis. This analysis also reveals the kind of metal – support interactions in the catalyst system. The use of ammonia in the TPD analyses was due to its special features such as strong basicity and small molecular size. Moreover, ammonia is an excellent candidate in the analysis of acidity and acid strengths over several temperature ranges. Table 7 shows the total acidities of the prepared catalysts. Bare $\gamma\text{Al}_2\text{O}_3$ shows a total acidity of 0.728 mmol/g. This acidity increases when the active component VO_x nano crystallite was dispersed on the $\gamma\text{Al}_2\text{O}_3$ to a value of 0.98 mmol/g. On the contrary, the acidities of the mixed oxide supported system decrease depending on the mixed oxide support ratio on the catalyst system. This is because of MgO's basic nature which leads to a decrease in acidity. The total acidities of 0.47 mmol/g, 0.04 mmol/g, and 0.036 mmol/g were revealed for the $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:2, $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:1 and $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 2:1 respectively. It appears that $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:2 shows a moderate acidity which is due to the low amount of MgO on the system.

Table 7: Catalysts total acidities

Catalyst	Total acidity (mmol/g)
$\gamma\text{Al}_2\text{O}_3$	0.7279
$\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:2	0.470
$\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:1	0.040
$\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 2:1	0.036

5.2.8 Pyridine FTIR

To further determine the nature of the acid sites and acidity, pyridine FTIR was used to investigate the catalysts Lewis or Brønsted concentration. Fig 12 shows the pyridine FTIR spectra of the as-synthesized catalysts. Generally, the bands at 1448 cm^{-1} are ascribed to the Lewis sites while the band at 1540 cm^{-1} are assigned to the Brønsted acid sites. In this figure, the Lewis acid sites are dominant in the MgO modified supported catalysts. This is an important factor that improves vanadium supported catalyst activity.

Furthermore, Table 8 shows Lewis to the Brønsted ratio of the synthesized catalyst. In this table, $\text{VO}_x/\gamma\text{Al}_2\text{O}_3$ shows that Brønsted acid sites dominate over the Lewis acid concentration in the samples. This is due to the influence of VO_x on the bare alumina which means surface Lewis acid sites are being blocked by the adsorbed pyridine. This observation is in accordance with the surface area analysis above. Conversely, the addition of MgO on the catalyst leads to more pyridine been adsorbed on the Lewis surface acid sites. Consequently, high Lewis to Brønsted acid concentration was obtained in the MgO modified samples. Contrarily, the Brønsted acid site dominates in the $\text{VO}_x/\gamma\text{Al}_2\text{O}_3$ which is due to the effect of VO_x on the bare alumina. This observation agrees with the NH_3 -TPD analysis(above) that acidity increases when VO_x is doped on bare alumina.

Therefore, it can be concluded that the presence of alumina and magnesia result in pyridine being absorbed on the Lewis acid sites, on the other hand, vanadia favors pyridine absorbance on the Brønsted acid sites. Thus, the $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 2:1 sample possessed a high Lewis/Brønsted acid concentration of 46.76 compared to $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:1 and $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:2 which gave Lewis/Brønsted acid concentration of 17.53 and 20.32 respectively.

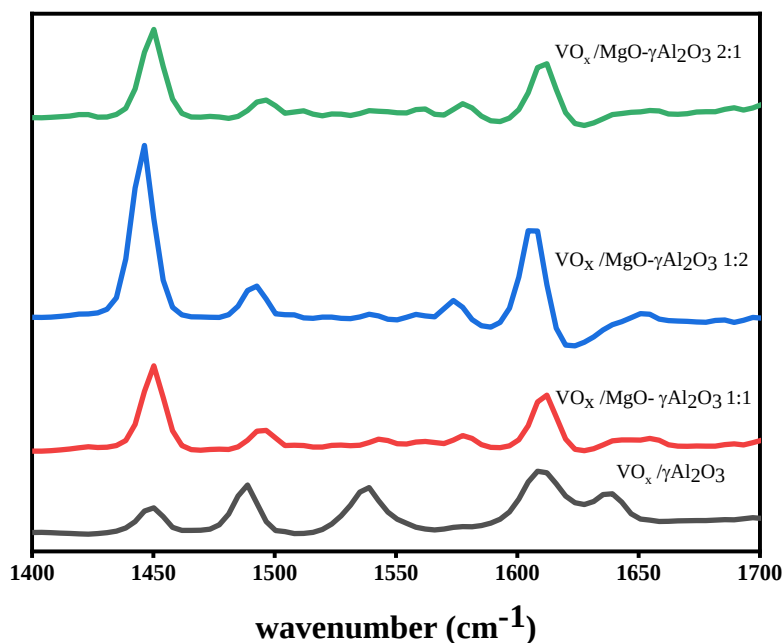


Figure 12: pyridine FTIR spectra

Table 8: Catalysts pyridine FTIR acidities

Catalyst	Lewis/Brønsted ratio
VO _x /γAl ₂ O ₃	0.342
VO _x /MgO- γAl ₂ O ₃ 1:2	17.530
VO _x /MgO- γAl ₂ O ₃ 1:1	20.318
VO _x /MgO- γAl ₂ O ₃ 2:1	46.759

5.2.9 Reducibility

Temperature programmed reduction analysis is an important tool used for the characterization of gas-phase free oxidative cracking catalysts. In this study, H₂-TPR was conducted to investigate the reducibility of the prepared catalysts. As shown in Figure 13, the samples have a reduction peak

at a single temperature. This single peak confirms the Raman analysis above of the vanadia phase mainly in the polvanadates regions [138].

The peak at 592 °C for the $\text{VO}_x/\text{MgO-}\gamma\text{Al}_2\text{O}_3$ 1:2 sample implies a moderate interaction between the support and the active vanadium species. We proposed that the strength of the metal support interaction increases as the MgO content of the samples is increased. Consequently, this shifts the reduction temperature towards lower temperatures in the other samples. The main reduction peak of $\text{VO}_x/\text{MgO-}\gamma\text{Al}_2\text{O}_3$ 1:1 is at 585 °C. This phenomenon agrees with the observed XRD pattern, where the peak intensity decreases as MgO content is increased. A further shift in the reduction peak to lower temperature when the MgO content is increased is also noticed[66].

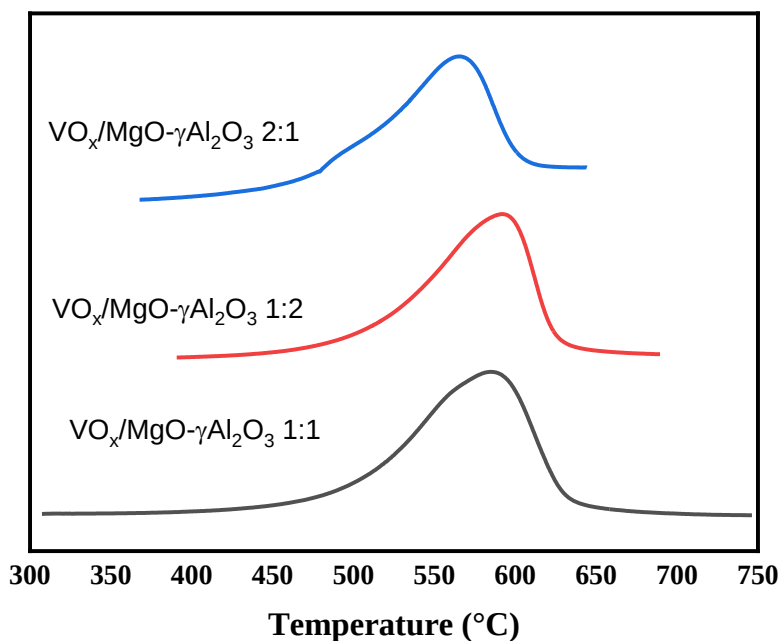


Figure 8: TPR profile of $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ catalysts.

Furthermore, the TPR analysis result was also used to determine the extent to which the catalyst is being reduced. This is generally expressed as the ratio of the exposed reducible VO_x to the actual VO_x content in the catalysts. The quantity of hydrogen consumed is used to correlate the exposed

reducible VO_x during the TPR analyses by taking the area under the reduction peak using numerical integration. The details of the calculation of the degree of reduction are available in the publications of Hossain and co-workers[32], [36], [139]. Table 9 shows the quantity of the probe molecule used and the percent vanadia reduced.

Table 9: Reducibility of the catalysts.

Catalysts	Peak Temperature (°C)	H₂ consumed (mmol/g)	% Reduction
$\text{VO}_x/\text{MgO} - \gamma\text{Al}_2\text{O}_3$ 2:1	565	0.969	58.12
$\text{VO}_x/\text{MgO} - \gamma\text{Al}_2\text{O}_3$ 1:1	585	1.413	84.80
$\text{VO}_x/\text{MgO} - \gamma\text{Al}_2\text{O}_3$ 1:2	592	1.681	99.26

From Table 9 above, one can observe that the degree of catalyst reduction which is related to the oxygen-carrying capacities of the catalysts suggests that the addition of magnesia to the support result in excellent oxygen storage capacity of the catalyst. This is important to suppress the extent of thermal gas-phase oxidation during the oxidative cracking reaction.

5.3 Catalyst Evaluation

5.3.1 Effect of Temperature

Figures 13 – 15 illustrate the effect of temperature on the as-prepared catalysts between 525 °C and 600 °C at a step of 25 degrees. In all the three catalysts, n-hexane conversion increases with temperature which is due to the presence of crystalline VO_x detected by the Raman analysis. This crystalline VO_x has been reported to enhance alkane conversion during oxidative catalysis[7]. This observed increase in conversion with temperature is mainly because lattice oxygen becomes activated at high temperatures. Similarly, olefin selectivity increases with reaction temperature.

This performance is attributed to the moderate metal support interactions in the catalysts. In addition, the presence of polyvanadates in the synthesized catalysts confirmed by Raman spectra analysis implies that these catalysts are easily reducible. These reducible vanadium species are key to enhanced olefin selectivity. Conversely, CO_x selectivity decreases during the fluidized bed reactions which indicate reduce coke formation due to the influence of MgO. In all these samples lower CO_x selectivities were obtained at the high reaction temperature of 25s with 1.4 % for VO_x/MgO- γ -Al₂O₃ 2:1, 0.8% for VO_x/MgO- γ -Al₂O₃ 1:1 and 3.25% for VO_x/MgO- γ -Al₂O₃ 1:2. Among the tested catalysts, it appeared that VO_x/MgO- γ -Al₂O₃ 1:2 performs best among the synthesized catalysts, giving the highest n-hexane conversion and olefin selectivity. This superior performance can be ascribed to its moderate acid level of the catalyst and intermediate mixed support active metal interactions[7], [19]. Therefore, optimum MgO content is required to achieve optimum catalytic activity. Consequently, the effect of reaction time would be demonstrated over VO_x/MgO- γ -Al₂O₃ 1:2 sample.

Overall, MgO in the samples increased olefin selectivity and decreased CO_x selectivity. This is because the introduction of MgO causes lower catalysts' total acidities, moreover, it also reduces the Brønsted acidities as indicated by the Pyridine FTIR analysis. This reduced Brønsted acidity inhibits excessive cracking during the oxidative cracking reactions. The literature also supports this MgO effect[136].

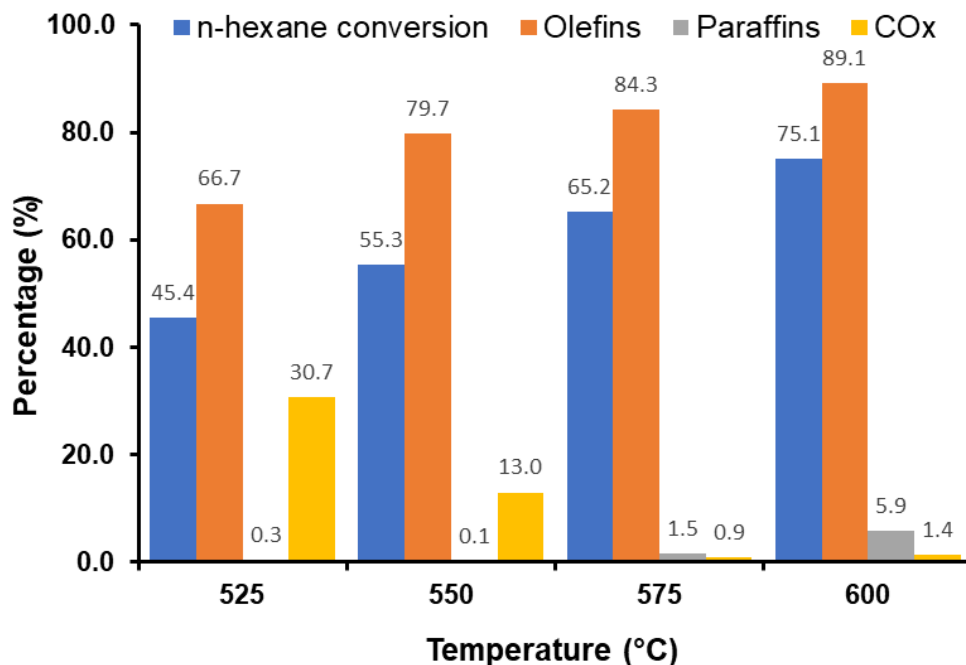


Figure 13: Effect of temperature on n-hexane conversion for $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 2:1 at reaction conditions of $t = 25$ sec, feed = 0.2 mL hexane, and weight of catalyst $z = 0.425$ g.

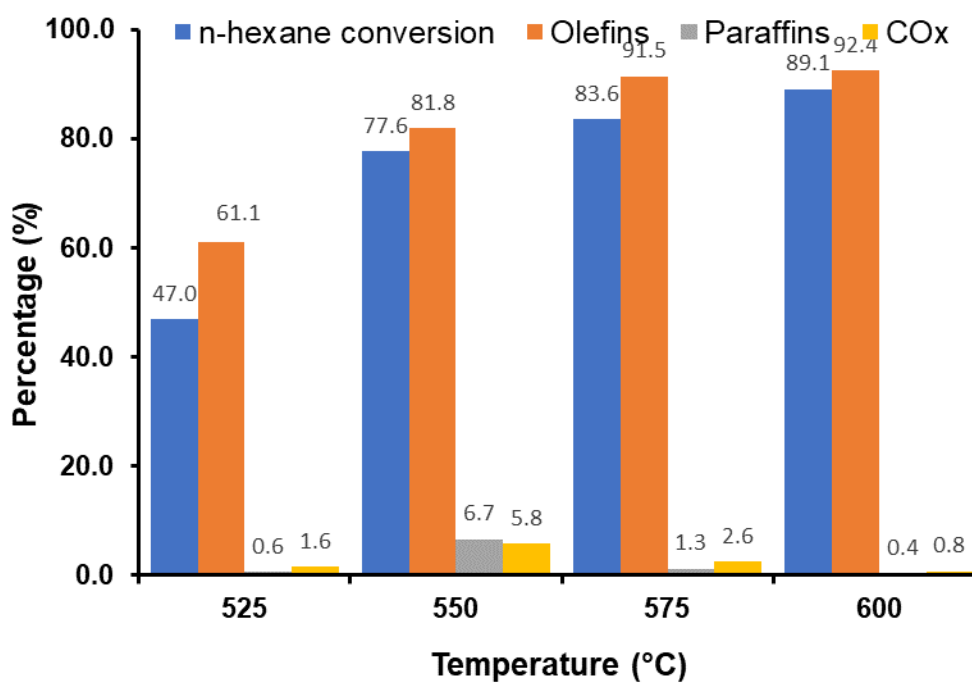


Figure 14: Effect of temperature on n-hexane conversion for $\text{VO}_x/\text{MgO-}\gamma\text{Al}_2\text{O}_3$ 1: 1 at reaction conditions of $t = 25$ sec, feed= 0.2 mL hexane, and weight of catalyst $z = 0.425$ g.

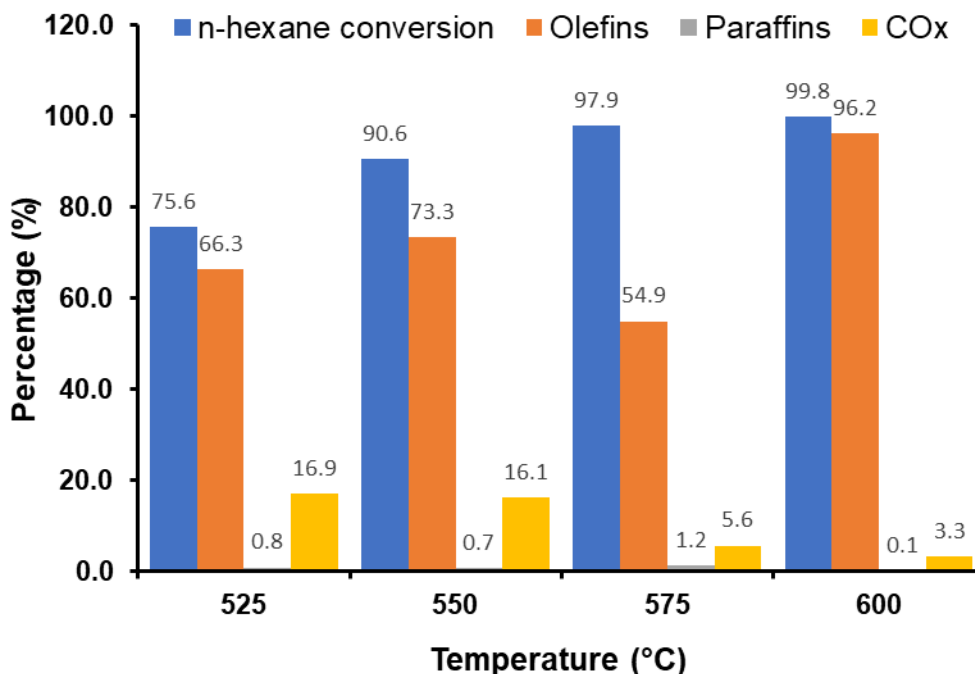


Figure 15: Effect of temperature on n-hexane conversion for $\text{VO}_x/\text{MgO-}\gamma\text{Al}_2\text{O}_3$ 1:2 at reaction conditions of $t = 25$ sec, feed= 0.2 mL hexane, and weight of catalyst $z = 0.425$ g.

5.3.2 Effect of reaction time

Further, to study the influence of reaction time, the experiments were performed at a reaction time of 10, 15, 20, and 25 s. It is observed that n-hexane conversion increases with time over the investigated contact times. However, Olefin selectivity increases with reaction time from a low of 31.35% at 10s and reaches a maximum of 96.17% at 25s. On the other hand, the carbon oxides selectivity decreases over the reaction periods. These observed increased in olefins selectivity and decrease in carbon oxides selectivity implied the controlled release of lattice oxygen and subsurface lattice oxygen which were continuously depleted during the experiments. Moreover,

the above observation suggests that olefins are the main reaction product while carbon oxides occur due to total oxidation of the feed and olefin product[32]. The observed behavior of the $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:2 sample during the oxidative cracking of n-hexane to light olefins indicates that both the oxidation and cracking reactions are influenced by both the catalyst reducibility and the acidity. Hence, this result is due to the moderate acidity of the $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:2 and excellent oxygen-carrying capacity revealed by the TPD and TPR analyses respectively[7].

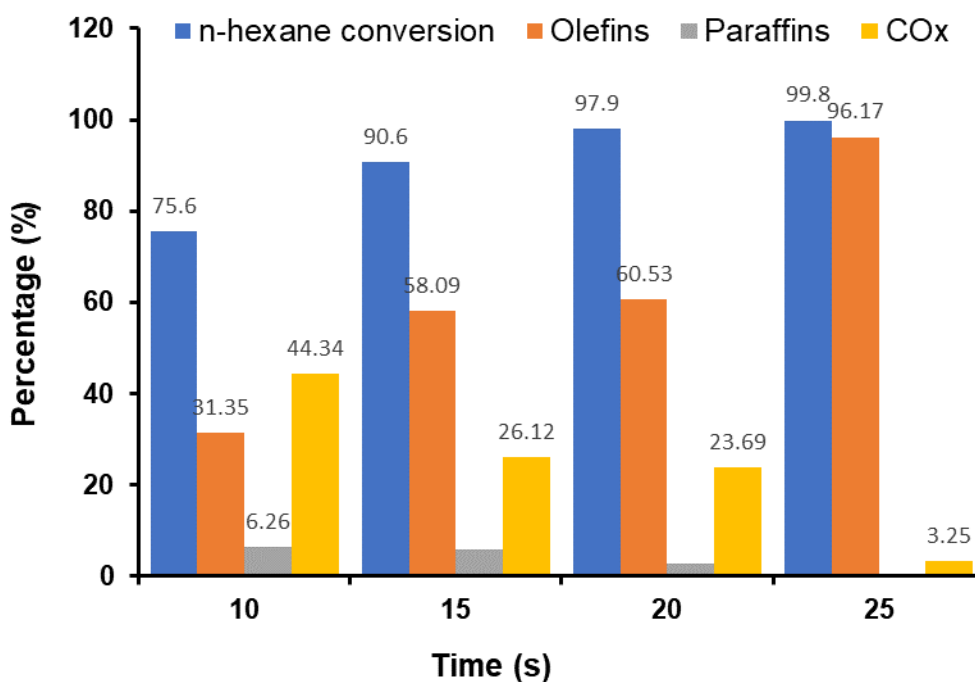


Figure 16: Effect of time on n-hexane conversion for $\text{VO}_x/\text{MgO} - \gamma\text{Al}_2\text{O}_3$ 1:2 at reaction conditions of temperature = 600 °C, feed= 0.2 mL hexane, and weight of catalyst z= 0.425g.

5.4 Conclusion

A novel fluidizable $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ catalysts were synthesized with varying ratios of $\text{MgO}/\gamma\text{Al}_2\text{O}_3$ for the oxidative cracking of n-hexane. All the catalysts show an increase in n-hexane conversion with temperature. This performance is due to moderate acidities and a controlled amount of lattice oxygen. Among the three samples studied, $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:2 displayed superior performance (i.e. 75.6 - 99.8% n-hexane conversion and 31.35% to 96.17 % light olefin selectivity) due to its moderate acidity which inhibits excessive cracking of hydrocarbons and deep oxidation to CO_x . The selectivity of light olefins reached 96 % at 600 °C and 25s contact time.

5.5 Role of SrO

This section aims to investigate the effect of SrO on a novel $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ catalyst with different ratios of the $\gamma\text{Al}_2\text{O}_3$ and SrO using n-hexane as a model compound feedstock to the oxidative cracking process.

5.6 Catalyst Characterization

5.6.1 XRD Pattern

Fig 17 illustrates the XRD patterns of the prepared catalysts (SrO , $\text{VO}_x/\gamma\text{Al}_2\text{O}_3$, $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ 1:1, and $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ 2:1). The major SrO peaks appear at 2θ angles of 25° , 30.3° , and 42° [140]. The other peaks at 50.5° , 59° , 71° , 82° also correspond to crystalline SrO peaks. The peaks at 2θ angles of 37° , 45° , and 67° are ascribed to $\gamma\text{Al}_2\text{O}_3$ [141]. Furthermore, SrO in the samples reduces the crystalline phase in the samples, as indicated by the results in Figure 17. Diffraction peaks due to VO_x are not distinguishable in the XRD patterns of the samples. This is due to the presence of VO_x as a well-dispersed amorphous phase and/or the formation of very small VO_x nanoparticles [142]. The formation of highly dispersed VO_x phases is likely due to the presence of amorphous polymeric vanadia species at intermediate monolayer surface coverage. Additionally, the absence of AlV_2O_9 and SrV_2O_6 in the prepared catalysts indicates that reactions between vanadium and the support $\text{SrO-}\gamma\text{Al}_2\text{O}_3$ do not occur during the treatment at high temperature.

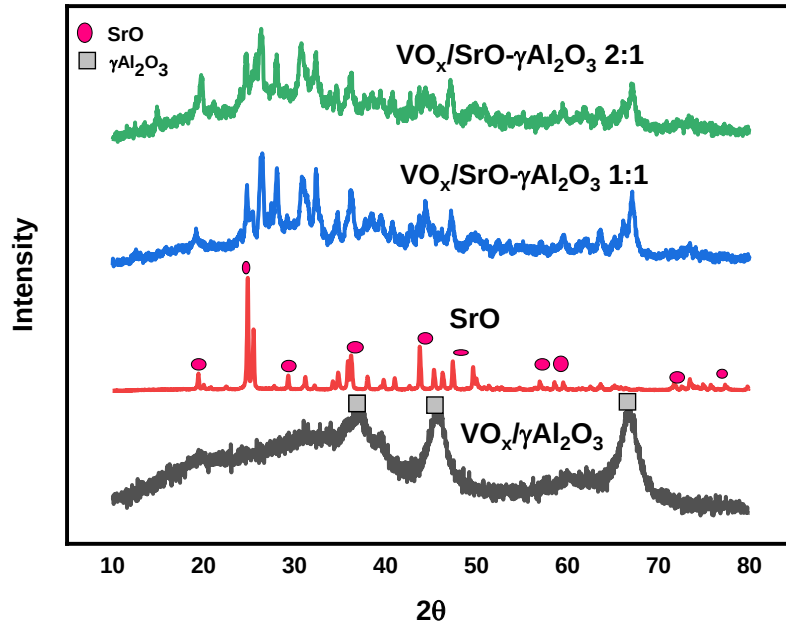


Figure 17: XRD patterns of $\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ catalysts.

Furthermore, the mean crystallite size of the samples was calculated using Scherrer's formula (equation 8) and presented in Table 10.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (8)$$

where: D is the mean crystallite size, k is the Scherrer's constant (0.9), λ is the wavelength of the x-ray radiation (0.15406 nm for $\text{CuK}\alpha$), β is the full width of half-maximum (FWHM) intensity expressed in radians, θ is the diffraction (Bragg) angle.

Table 10: Mean crystallite size

Catalyst	Mean Crystallite size D_m (nm)
$VO_x/\gamma Al_2O_3$	8.22
$VO_x/SrO-\gamma Al_2O_3$ 1:1	3.85
$VO_x/SrO-\gamma Al_2O_3$ 2:1	9.09

5.6.2 FTIR Analysis

FTIR analysis was performed to further investigate the type of support present in the prepared catalyst. Figure 18 shows the FTIR spectra of the catalyst samples. SrO peaks appear at 3749 cm^{-1} , 2990 cm^{-1} , 2386 cm^{-1} , 1456 cm^{-1} , 1116 cm^{-1} , and 858 cm^{-1} . The peaks around 1630 cm^{-1} are attributed to the H-O-H stretching and the OH bending vibration of water[143]. The absence of VO_x peaks confirms the XRD results, indicating the well-formed dispersed amorphous vanadia phase and/or undetected small crystalline vanadia species. The strong band around the 880 cm^{-1} in the $VO_x/SrO-\gamma Al_2O_3$ 1:1 confirms the presence of γAl_2O_3 . The effect of γAl_2O_3 is also observed as a shift in the peaks towards higher wavenumbers around 880 cm^{-1} , and 2927 cm^{-1} in the $VO_x/SrO-\gamma Al_2O_3$ 2:1 sample.

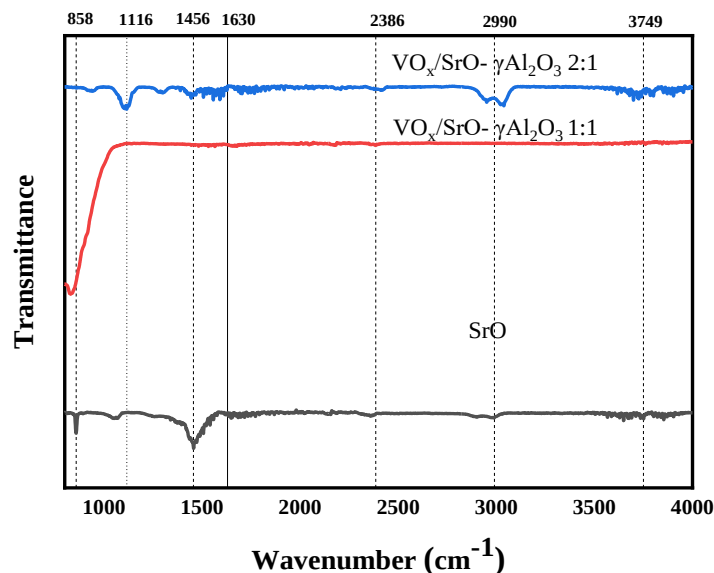


Figure 18: FTIR spectra of the $\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ catalysts.

5.6.3 Raman Analysis

Fig 19 shows the Raman spectra of the prepared catalysts. The figure shows the presence of polyvanadate and bulk crystals of VO_x nanoparticles for all samples. The nonexistence of bands beyond 1033 cm^{-1} indicates the absence of isolated monovanadate species in the samples. This is due to the high vanadia content (10wt %) in the samples. The band at 888 cm^{-1} is attributed to the V-O-V stretching of the surface polyvanadate species. In addition, the band at 984 cm^{-1} is due to the stretching vibration of surface $\text{V}=\text{O}$ in the polyvanadate species[35]. This observation corroborates the XRD patterns above that the vanadia species in the samples are highly dispersed amorphous polymeric moieties. Further, the peaks observed from 180 cm^{-1} to 600 cm^{-1} are due to the vibration of bulk VO_x [21]. The peaks at 132 cm^{-1} are attributed to the presence of V_6O_{13} [144]. The alumina support does not produce Raman peaks due to the ionic nature of the Al-O bond. This is consistent with previous work published in the literature[145].

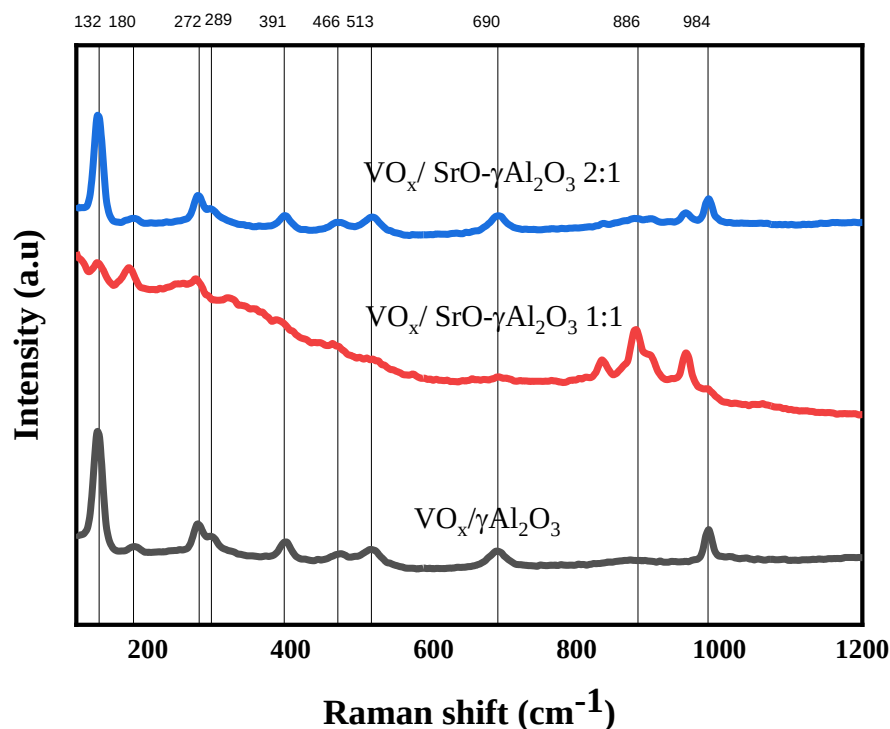


Figure 19: Raman spectra of VO_x/SrO- γ Al₂O₃ catalysts.

Table 11: Raman peaks of the VO_x/SrO- γ Al₂O₃ catalysts.

Bands (cm ⁻¹)	VO _x Phase	VO _x surface structure
180 to 600	bulk VO _x vibration	Crystalline
888	V-O-V stretching	polyvanadate
984	V=O	Polyvanadate

5.6.4 SEM-EDX Analysis

The SEM image of SrO shown in Figure 20a indicates a morphology which represents a “quasi” zero-dimensional small sphere particles [146]. EDX results indicate the presence of only strontium and oxygen. Figure 20b and Figure 20c show the SEM images of the 1:1 VO_x/SrO- γ Al₂O₃ 1:1 and VO_x/SrO- γ Al₂O₃ 2:1 respectively. The images show the formation of aggregates due to the addition of vanadia to the samples. This is due to the existence of vanadia as several different

phases, as revealed by Raman spectra described earlier. More so, the SEM image (Figure 20d) shows that $\text{VO}_x/\gamma\text{Al}_2\text{O}_3$ has a highly mesoporous structure owing to the catalyst synthesis method used in this work.

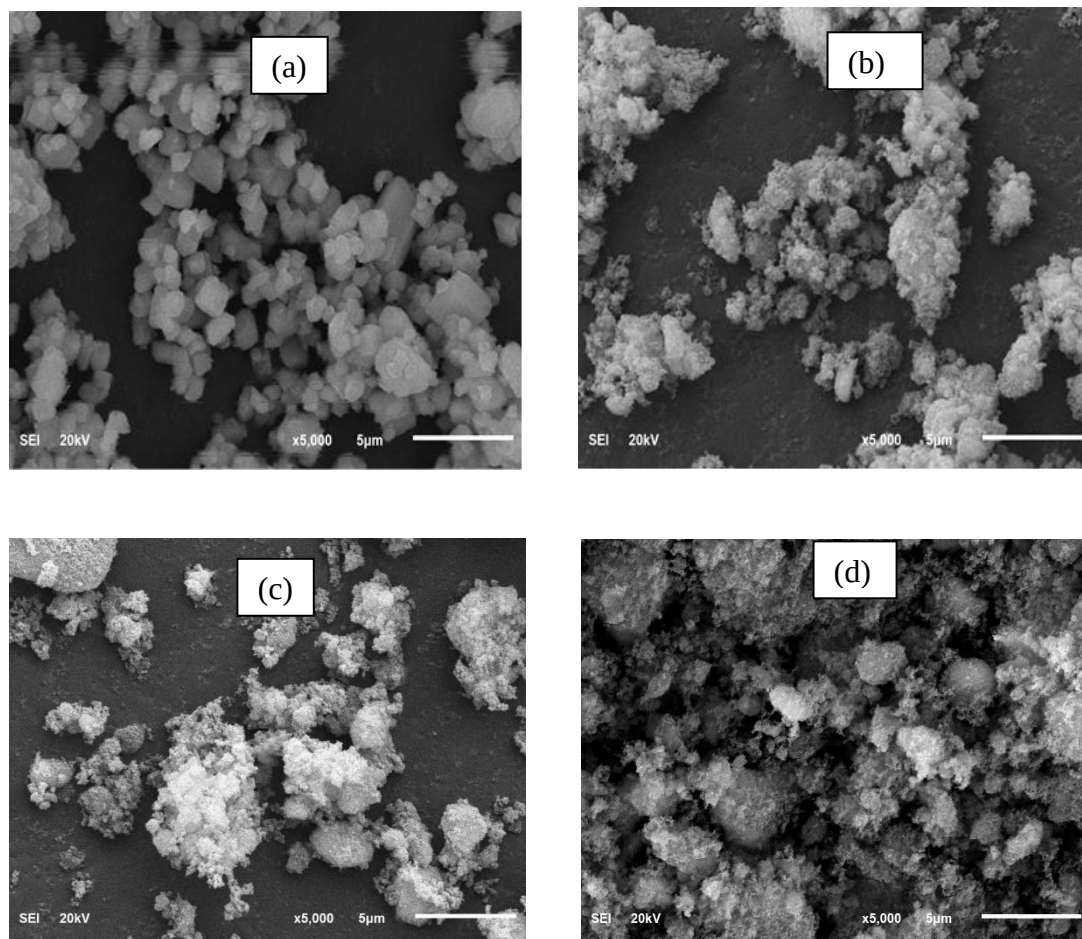


Figure 20: SEM images of a) SrO b) $\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ 1:1 c) $\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ 2:1, and d) $\text{VO}_x/\gamma\text{Al}_2\text{O}_3$.

5.6.5 Nitrogen Adsorption

The textural characteristics of the catalysts are presented based on N_2 sorption analyses. Table 12 shows the results of the N_2 sorption analyses of the synthesized samples. The BET surface area of pure $\gamma\text{Al}_2\text{O}_3$ is $74 \text{ m}^2/\text{g}$, which is in the range expected for gamma-alumina ($50\text{-}300 \text{ m}^2/\text{g}$).

However, after the impregnation of VO_x, the BET surface area of the sample decreases sharply to 60 m²/g. This decrease in the surface area can be attributed to the blockage of the pores of the support by the vanadia species. On the other hand, the BET surface areas of pure SrO was found to be 80 m²/g. Thus, it can be concluded that the higher surface area of SrO increases the surface area of strontia modified samples which enhances the catalytic activity of the samples. This is due to the clustering of this mixed support as indicated by the SEM images of the strontia modified catalysts. One can also observe the high values of the catalysts' external surface area compared to the micropores' surface area. These high values connote that the active sites of the catalysts are exposed to readily adsorb the feed during the reaction, which indicates better catalytic behavior.

Table 1212 also shows other properties of the catalysts. The average pore size was determined from the BJH adsorption and desorption values. These values are in the range of 10 to 28 nm, indicating that the samples are in the mesoporous range (2-50 nm). The surface densities of the supported vanadia catalyst were calculated based on the expression of Khodakov et al. [147].

$$\text{surface density} = \frac{\text{VO}_x \text{ wt}(\%) \times 6.023 \times 10^{23}}{\text{Vanadium molecular weight} \times 100 \times S_{\text{BET}}}$$

High surface density values above 8.8 V/nm² confirm the results obtained from the Raman spectra, indicating the absence of monovanadate species below the theoretical monolayer coverage. The calculated surface density values of VO_x/γAl₂O₃, VO_x/γSrO-Al₂O₃ 2:1, and VO_x/γAl₂O₃ 1:1 are 19.7, 16.9, and 15.6 V/nm², respectively. Therefore, it appears that the surface vanadia species are mainly present as polyvanadate and small crystallites of VO_x nanoparticles. Besides, the reduced XRD crystallite sizes of the catalysts compared to the catalysts' pore diameter further confirm that the amorphous nature of the catalysts. Peaks due to these VO_x nanoparticles crystallites are present in the X-ray diffraction patterns, as reported above.

Table 12: N₂ sorption analysis BET surface area and pore volume of the catalysts.

Catalyst	S _{BET} [m ² /g]	S _{EXT} [m ² /g]	S _{micro} [m ² /g]	V _p [*] [cm ³ /g]	D _p ^{**} (nm)	Surface density (V/nm ²)
γAl ₂ O ₃	74	64	10	0.48	25.1	-
VO _x /γAl ₂ O ₃	60	51	9	0.41	27.5	19.7
VO _x / SrO- γAl ₂ O ₃ 1:1	76	70	6	0.36	10.0	15.6
VO _x / SrO-γAl ₂ O ₃ 2:1	70	63	7	0.35	17.3	16.9
SrO	80	71	9	0.21	14.9	-

*single point pore volume calculated from the adsorption isotherm

** average pore diameter calculated from the average of the BJH adsorption and desorption data

5.6.6 Reducibility

Temperature programmed reduction analysis is an important tool used for the characterization of gas-phase free oxidative cracking catalysts. In this study, H₂-TPR was used to investigate the reducibility of a vanadium oxide supported on SrO modified gamma-alumina. As shown in Figure 21, the samples have a reduction peak at a single high temperature. This single reduction peak temperature may be attributed to the presence of polyvanadate vanadia species in the samples[148]. This behavior confirms the XRD and Raman analyses results above of highly polymeric amorphous species. The profile also shows the vanadia species with a single oxidation state in the catalyst samples. The oxidation state of the vanadia species is a characteristic of the catalyst preparation method, calcination temperature used, type of support employed, and the active species[55].

The peak at 521 °C for the VO_x/γAl₂O₃ sample implies a strong interaction between the support and the active vanadia species. We proposed that the strength of the metal support interaction

increases as the SrO content of the samples is increased. Consequently, this shifts the reduction temperature towards higher temperatures. The main reduction peak of $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ 1:1 is at 578 °C. This observation is consistent with the observed XRD pattern, where the peak intensity decreases as SrO content is increased. Furthermore, the shift in the reduction peak to higher temperatures when the SrO content is increased may also be attributed to the ability of strontium to inhibit the release of oxygen[149]. Moreover, the strontium modified samples have minor shoulders. The $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ 1:1 sample shows two shoulders at 525 °C and 650 °C. The slight increase in the reduction peak temperature of $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ 1:1 compared to that of $\text{VO}_x/\gamma\text{Al}_2\text{O}_3$ suggest a moderate metal-support interaction in the $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ 1:1 sample.

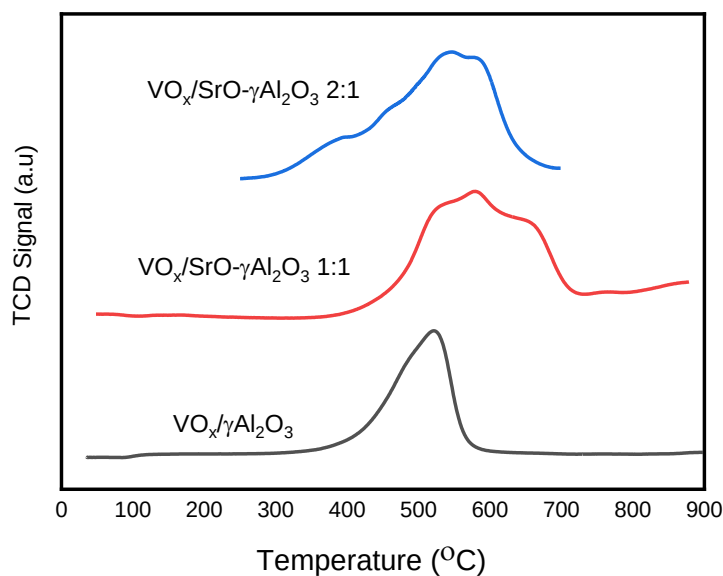


Figure 21: TPR profile of $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ catalysts.

Furthermore, the result from TPR analysis was also used to determine the degree of catalyst reduction. The degree of reduction of the catalysts is defined as the ratio of the exposed reducible VO_x to the actual VO_x content in the catalysts. The exposed reducible VO_x nanoparticle can be determined from the amount of hydrogen used during the TPR analyses by taking the area under the reduction peak using numerical integration. The details of the calculation of the degree of

reduction are available in the publications of Hossain and co-workers[36], [139]. Table 13 shows the quantity of the probe molecule used and the percent vanadia reduced.

shows the amount of hydrogen consumed in the reduction and the percent reduction.

Table 13: Reducibility of the catalysts.

Catalysts	Peak Temperature °C	H₂ consumed (mmol/g)	% Reduction
VO _x /γAl ₂ O ₃	521	0.633	99.18
VO _x /SrO-γAl ₂ O ₃ 1:1	578	0.260	73.66
VO _x /SrO-γAl ₂ O ₃ 2:1	570	0.095	29.11

Reduction kinetics

Generally, the reducibility of metal oxides in TPR analysis consists of several steps. One of these steps controls the rate of reaction. The rate of reaction depends on either the diffusion of the reducing agent, surface reaction, or product desorption. In this work, the assumption made in the work of Elbadawi [150] follows, since the TPR analysis was carried out under the same conditions. Thus, the overall reaction rate is a function of bulk reducible metal oxide and the gas phase compositions expressed as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)(P_{H_2}P_{H_2O}) \quad (5.1)$$

Where α , the degree of catalysts reduction is also referred to as the progress of the reaction. This parameter is expressed as:

$$\alpha = \frac{\Delta n_t}{\Delta n_{total}} \quad (5.2)$$

Δn_t : The number of moles of hydrogen consumed at time t(min)

Δn_{total} : The total number of moles of hydrogen consumed.

The partial pressure of the components H₂ and H₂O.

(P_{H₂} P_{H₂O}) are considered constant as a result of the constant feed flow rate during the TPR analysis.

Thus, equation 5.1 reduces to

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (5.3)$$

k(T) is the reaction rate constant expressed in terms of the Arrhenius equation:

$$k(T) = k_o \exp \left[\frac{-E_A}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \right] \quad (5.4)$$

Where E_A is the energy of activation, R is the ideal gas constant and T_m is called the centering temperature. The parameter T_m is used to minimize the cross-correlation between the parameters.

It should be noted that

$f(\alpha)$ is a function of the applied model used in the estimation of the kinetics parameters. Several models have been developed to determine the degree of catalysts reduction function[139], [151]. Avrami-Erofeev model is a typical model employed in the reduction and oxidation of supported oxides. In this study, the model assumed the nucleation and growth mechanisms. This mechanism consists of the following steps:

- i. H₂ dissociation
- ii. V-O_x bond is broken, and V atoms and H₂O are produced

- iii. V atoms diffuse away from reaction Centre (nucleation)
- iv. V atoms cluster together (growth)
- v. The formed clusters form crystallites.

In principle, Avrami-Erofeev model is expressed as:

$$f(\alpha) = n(1 - \alpha)(-\ln[1 - \alpha])^{n-1/n} \quad (5.5)$$

n is the Avrami exponent which suggests the reduction mechanism of crystal dimension growth.

Table 14 shows the variant of the Avrami-Erofeev model

Table 14: Variants of Avrami-Erofeev model

n takes	Model	Expression
n	Avrami-Erofeev	$f(\alpha) = n(1 - \alpha)(-\ln[1 - \alpha])^{n-1/n}$
1	Random nucleation	$f(\alpha) = (1 - \alpha)$
2	2D Avrami-Erofeev	$(\alpha) = 2(1 - \alpha)(-\ln[1 - \alpha])^{1/2}$
3	3D Avrami-Erofeev	$f(\alpha) = 3(1 - \alpha)(-\ln[1 - \alpha])^{2/3}$

In this work, n takes the value of 2 and according to the work of Hossain et al [152] and the Avrami-Erofeev reduced to the random nucleation model given by:

$$f(\alpha) = 2(1 - \alpha)(-\ln[1 - \alpha])^{1/2} \quad (5.6)$$

Hence, equation 3 becomes

$$\frac{d\alpha}{dt} = 2k_o \text{Exp}(1 - \alpha)(-\ln[1 - \alpha])^{1/2} \quad (5.7)$$

Since the heating heat relates the independent variables time and temperature via the relation:

$$T = T_0 + \beta t \quad (5.8)$$

Differentiating

$$dT = \beta dt$$

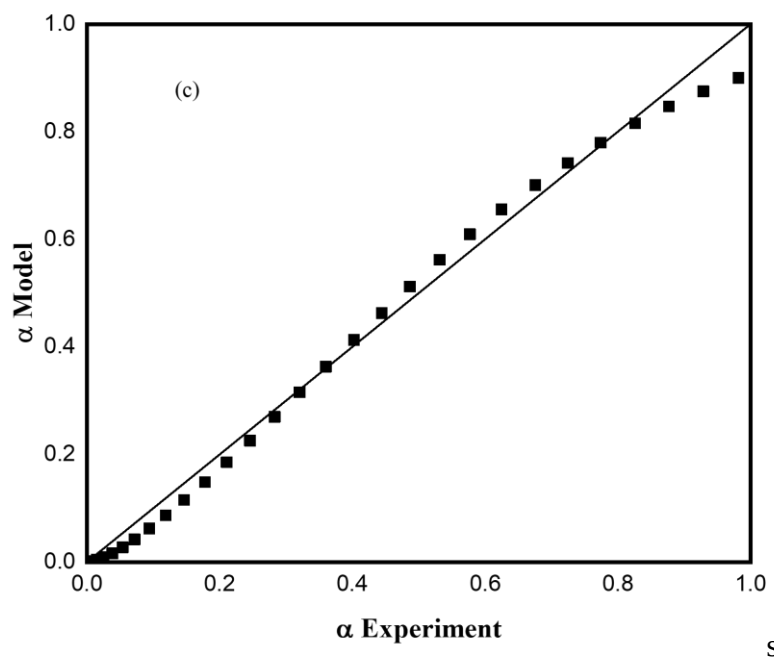
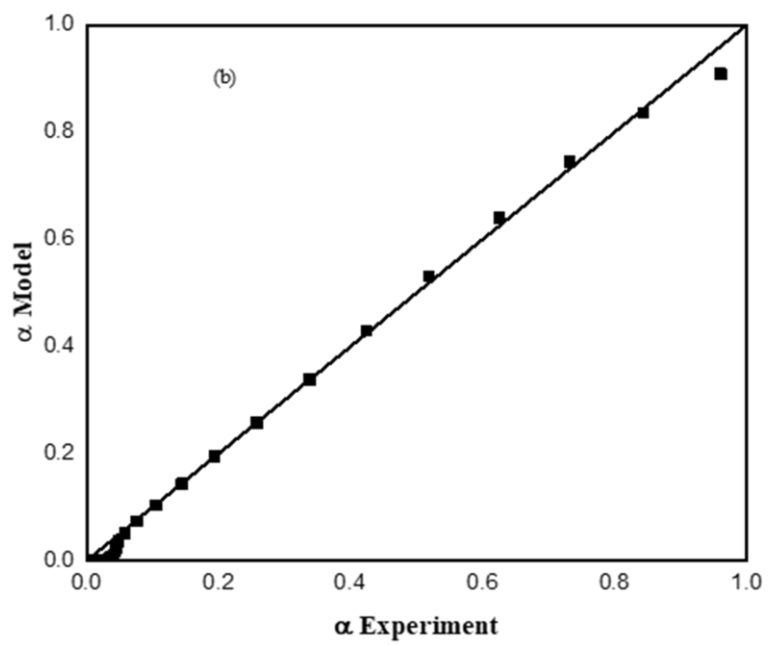
And equation (5.8) can be written as:

$$\frac{d\alpha}{dT} = 2 \frac{k_o}{\beta} \text{Exp} \left[\frac{-E_A}{R} \left(\frac{1}{T_0 + \beta t} - \frac{1}{T_m} \right) \right] (1 - \alpha)(-\ln[1 - \alpha])^{1/2} \quad (5.9)$$

The MATLAB lsqcurvefit function is used to determine the kinetics parameters. This command minimizes the sum of the squares of error between the model and the experimental data.

Table 15: Reduction of kinetics parameter values

Catalyst	k_o	E_A (Kj/mol)	R^2	SSE
V ₂ O ₅ /γ-I ₂ O ₃	7.8	2.3399	0.8804	0.1495
V ₂ O ₅ /SrO-γ-I ₂ O ₃ 1:1	0.48	3.63	0.9952	0.0104
V ₂ O ₅ /SrO-γ-I ₂ O ₃ 2:1	0.5	5.2029	0.9920	0.0232



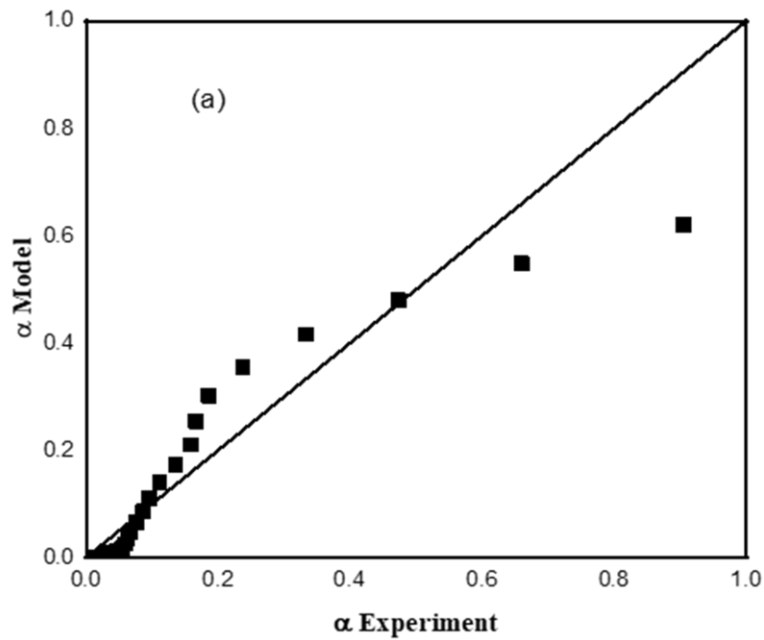


Figure 22: Parity plot of the experimentally determined degree of reduction and values predicted by the model for a) $\text{V}_2\text{O}_5/\gamma\text{Al}_2\text{O}_3$, (b) $\text{V}_2\text{O}_5/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ 1:1 and (c) $\text{V}_2\text{O}_5/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ 2:1

The MATLAB lsqcurvefit function is used to determine the kinetics parameters. This command minimizes the sum of the squares of error between the model and the experimental data.

Table 16: Kinetic parameters and statistical data for the catalyst reduction.

Catalyst	k_o	E_A (Kj/mol)	R^2	SSE
$V_2O_5/\gamma Al_2O_3$	7.8	2.340	0.880	0.150
$V_2O_5/SrO-\gamma Al_2O_3$ 1:1	0.48	3.630	0.995	0.0104
$V_2O_5/SrO-\gamma Al_2O_3$ 2:1	0.5	5.202	0.992	0.0232

Table 16 shows the reduction of kinetic parameter values of the synthesized catalysts. The activation energies obtained gave a high correlation coefficient (R^2) in the range of 0.88 – 0.99 and the minimum sum of the square of error. These represent a good correlation between the model data and the experimental data.

$V_2O_5/\gamma Al_2O_3$ gave the minimum activation energy. This results from the catalyst high reducibility obtained and thus the high amount of hydrogen consumed during the TPR experiment. It is observed that the addition of strontium oxide decreases the catalyst degree of reduction which indicates the ability of strontium oxide to resist oxygen release. This is an important factor for catalyst activity to control oxygen release during the oxidative cracking reaction. The decrease in

catalyst reduction as the amount of strontium oxide is increased. This agrees with the observation of the XRD and FTIR analyses reported above.

5.6.7 Acidity Analysis

Temperature programmed desorption (TPD) is an important tool used for the characterization of supported vanadia catalysts. TPD is used to determine the total acidity, acid sites as well as the metal-support interaction of the support and the active vanadium oxide. In TPD analyses, ammonia is used as the probe molecule due to its strong basicity. The NH_3 -TPD can determine the total acidity, which is the sum of the weak and strong acid sites.[153]. However, this method cannot differentiate between Lewis and Bronsted acid sites, it only gives the total acidity. The total acidities of the synthesized catalysts determined using NH_3 -TPD are presented in Table 17. Pure alumina possesses the highest total acidity of 0.728 mmol/g. Moreover, the addition of VO_x nanoparticle to the pure alumina slightly increased the total acidity to 0.99 mmol/g as a result of the strong interaction of the active VO_x nanoparticle with bare alumina. This increased in acidity when VO_x nanoparticle is added to bare alumina agreed with the work of Sameer et al. (2014)[77]. It is also observed that the addition of SrO to the catalysts further decreases the total acidity. This observation is due to the basic nature of SrO support. One can infer that the $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ 1:1 displays moderate acidity. This moderate acidity is important to achieve a high activity in oxidative cracking reactions. On the contrary, the $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ 2:1 low acidity value is not very effective for this type of reaction. However, according to literature, supported vanadia catalyst low acidity is an effective criterion in the partial oxidation of hydrocarbons to hydrogen[154]–[156]. This is an interesting area to be investigated in future research.

Table 17: The total acidity of Catalysts.

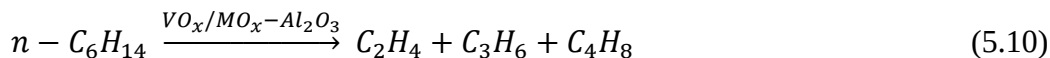
Catalyst	Total acidity (mmol/g)
$\gamma\text{Al}_2\text{O}_3$	0.7279
$\text{VO}_x/\gamma\text{Al}_2\text{O}_3$	0.9850
$\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ 1:1	0.5612
$\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ 2:1	0.030

5.7 Catalytic oxidative cracking of n-hexane in CREC Riser simulation.

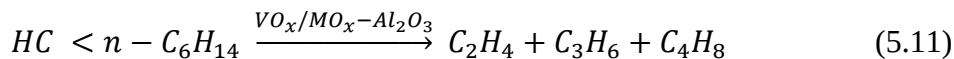
In the actual catalyst evaluation, the reaction temperature was selected between 525 to 600 °C at reaction conditions $t = 25$ sec, feed= 0.2 ml hexane, and weight of catalyst = 0.425g. Before the next temperature runs, the catalyst was regenerated by passing airflow at 600 °C while the impeller is constantly being rotated. This is to achieve the twin effect of the reactor of both cracking and regenerator (Figure 1 above). That is, the catalyst was continuously reduced by the feed injection, while it was re-oxidized by flowing air. The data analysis of the product of the several reactions consists mainly of light olefins (ethylene, propylene, and Butenes), paraffin (light alkanes), and carbon oxides (CO and CO₂). It is worthwhile to mention that herein the reaction products are mainly assigned as olefins to mean ethylene, propylene, and Butenes, paraffin represents ethane to pentane, and carbon oxides mean CO and CO₂. Possible reaction routes during the oxidative conversion of n-hexane are proposed thus:

Desired reactions

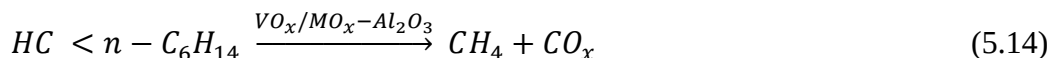
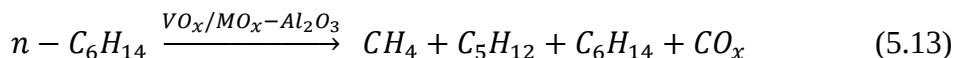
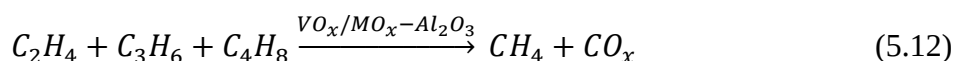
n-hexane cracking and ODH



light paraffins (C₂-C₅) ODH



Undesired reactions



5.7.1 Effects of Reaction Temperature

The selected reaction temperatures of 525 °C to 600 °C are in the range of the catalyst's reduction temperature based on the TPR analysis above. Figures 23-25 show the reactivity of the catalyst while the temperature is varied. The reactivity of different catalysts samples varies with the temperature between the selected reaction temperatures of 525 °C to 600 °C. These figures show n-hexane conversion and the selectivity to olefins, paraffin, and CO_x in the oxidative cracking of n-hexane under an oxygen-free environment. It can be observed that the different catalyst formulations show different reactivity during the oxidative conversion reactions. However, in general, n-hexane conversion tends to increase with temperature for all three tested catalysts. This behavior can be ascribed to the presence of bulk VO_x on the support as revealed by the Raman analysis above. For the VO_x/γAl₂O₃ catalyst, n-hexane conversion increase with

temperature(68.6% to 85.8%) between the temperature range of 525 °C to 600 °C and slightly drop 600 °C. This observation is partially due to the increase in the n-hexane molecule's average kinetic energy and the abundant VO_x lattice oxygen over the temperature of 525 °C to 600 °C[61]. On the other hand, the decrease in conversion at a higher temperature may be ascribed to the loss in lattice oxygen, which limit the reduced VO_x activity. For the samples with SrO modified γ -Al₂O₃, conversion initially increases with temperature and remains almost stable at higher temperatures 525 °C and 600 °C. This is due to the ability of strontia to maintain the degree of catalysts' reducibility in the samples.

Regarding olefin selectivities, the VO_x/ γ -Al₂O₃ shows a linear decrease in selectivity(23.9% to 8.7 %) with temperature. This observation is due to the depleting lattice oxygen in the catalyst as the reaction progressed. We proposed that as the reaction progresses, the desired olefin is being converted to the undesired CO_x product. CO_x formation is mainly due to the partial and total oxidation of the feed and the more reactive light olefin products. More so, the γ -Al₂O₃ acidic nature as revealed from the TPD analysis leads to excessive cracking which favors the intermediate paraffin products particularly, at higher temperatures. On the contrary, the VO_x/SrO- γ -Al₂O₃1:1 and VO_x/SrO- γ -Al₂O₃ 2:1(81% to 91%) show an increase in olefin selectivities at reaction temperatures of 525 °C and 550 °C. This behavior is due to their lower binding energy at these temperatures due to the controlled release of lattice oxygen. This controlled oxygen release results from the catalyst's moderate acidity. However, at higher reactions temperature, loosely adsorbed oxygen released during the regeneration steps contribute to the available lattice oxygen. This further promotes oxidation to undesired CO_x formation.

The performance of supported vanadium catalysts depends on the surface structure of vanadia species present on the catalysts. This, in turn, depends on the surface densities of the catalysts[157],

[158]. According to Table 11 in section 5.1.3 the $\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ 1:1 gives the lowest value which is close to the theoretical monolayer region at which polyvanadate species start to evolve. It was reported that vanadia catalysts perform best in this region[159]. More so, the XRD crystallite size in the range of 3.75 nm and the Raman spectroscopy data shows mainly amorphous polyvanadate vanadia species which is responsible for the high selectivity towards the desired olefin.

In this study, CO_x formation is mainly due to the partial and total oxidation of the feed. Also, intermediate paraffin is produced due to the cracking of the n-hexane feed caused by the acidic supports. As gas-phase oxygen is absent, the partial oxidation of the feed and intermediate paraffin to CO_x results from the release of lattice oxygen and subsurface oxygen from the active component of VO_x . These two types of oxygen consequently lead to the total oxidation of the feed and further re-oxidation of the more reactive olefins to carbon oxides. Furthermore, Al-Ghamdi and De Lasa[39] have reported that another type of more reactive oxygen is present on the surfaces of the catalysts. This non-selective oxygen may originate from the surface and the bulk of the catalysts or as weakly adsorbed oxygen released during the regeneration steps. The weakly adsorbed oxygen causes total oxidation, which promotes CO_x formation. Other studies[160]–[165] have reported different forms of active oxygen surface species (e.g., O_2^- and O^- from electrophilic lattices and O^{2-} oxygen from nucleophilic lattices). Besides, Kung and Anderson [166] also reported that the site and number of lattice oxygen on the catalyst surface are two key factors towards the selectivity of oxidative reaction catalysts.

Based on the above findings, it is important to optimize the amount of oxygen, and the operating temperature to apply our catalyst in a fully fluidized condition in the industry. The $\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ 1:1 sample appears to be the most selective catalyst. This is attributed to its large BET surface area due to the influence of SrO on the mixed support. Moreover, the catalyst possesses

balanced acidity needed to curtail over cracking during the oxidative catalysis reaction. In addition, XRD and TPR analyses show the catalyst's reduced crystallite size and moderate oxygen release ability. Thus, these lead to minimum combustion of the feed and olefin product. Moreover, the 550 °C temperature represents the optimum temperature of this work.

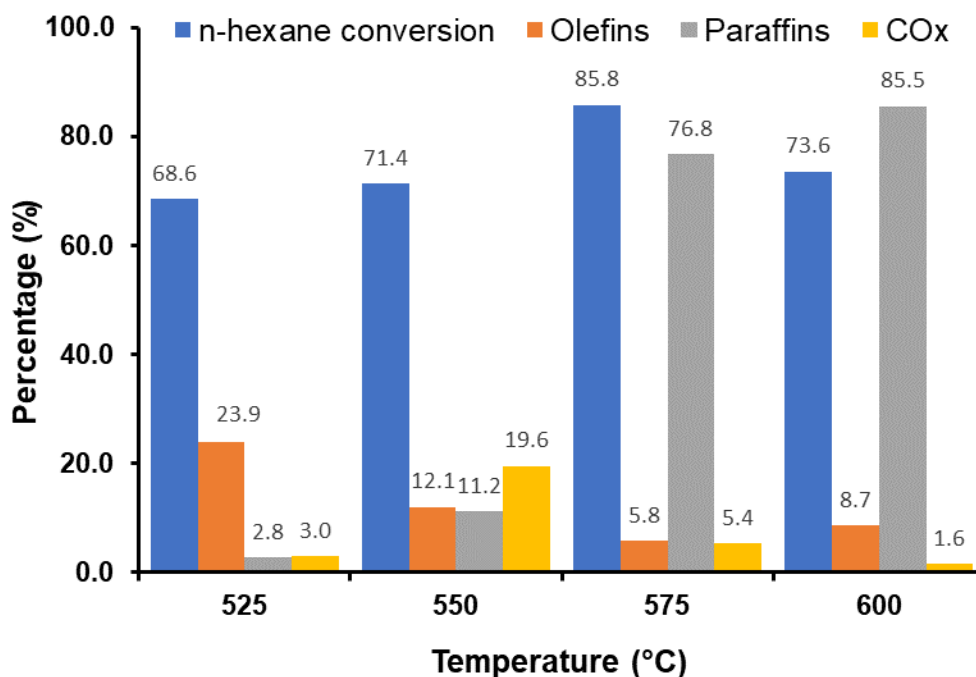


Figure 23: Effect of temperature on n-hexane conversion for $\text{VO}_x/\gamma\text{Al}_2\text{O}_3$ at reaction conditions of $t = 25$ sec, feed = 0.2 mL hexane, and weight of catalyst $z = 0.425$ g.

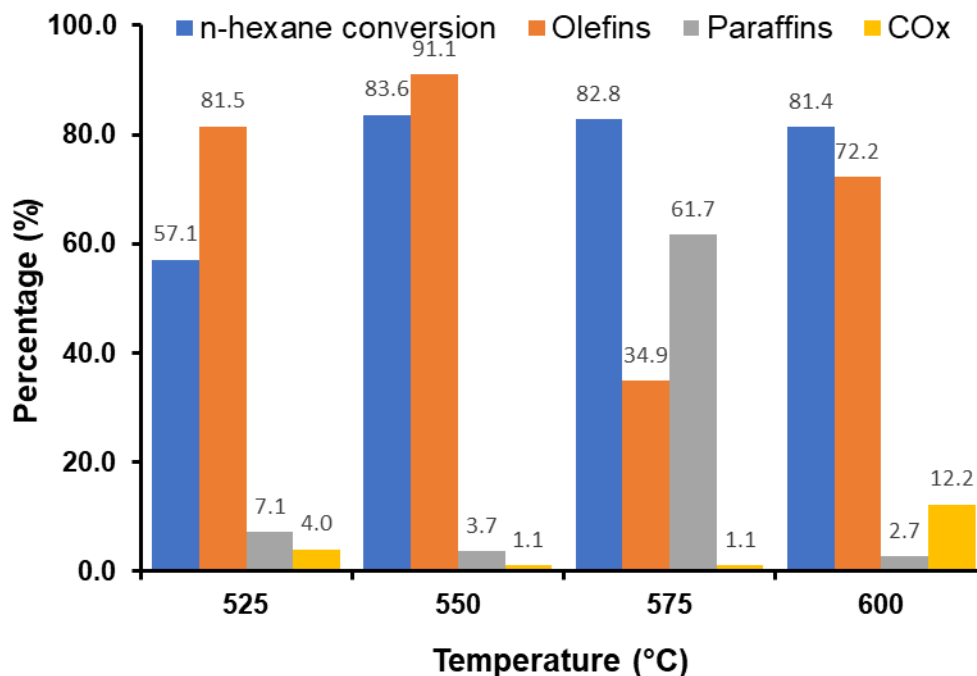


Figure 24: Effect of temperature on n-hexane conversion for $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ 1:1 at reactions conditions of $t = 25$ sec, feed = 0.2 mL hexane, and weight of catalyst $z = 0.425$ g.

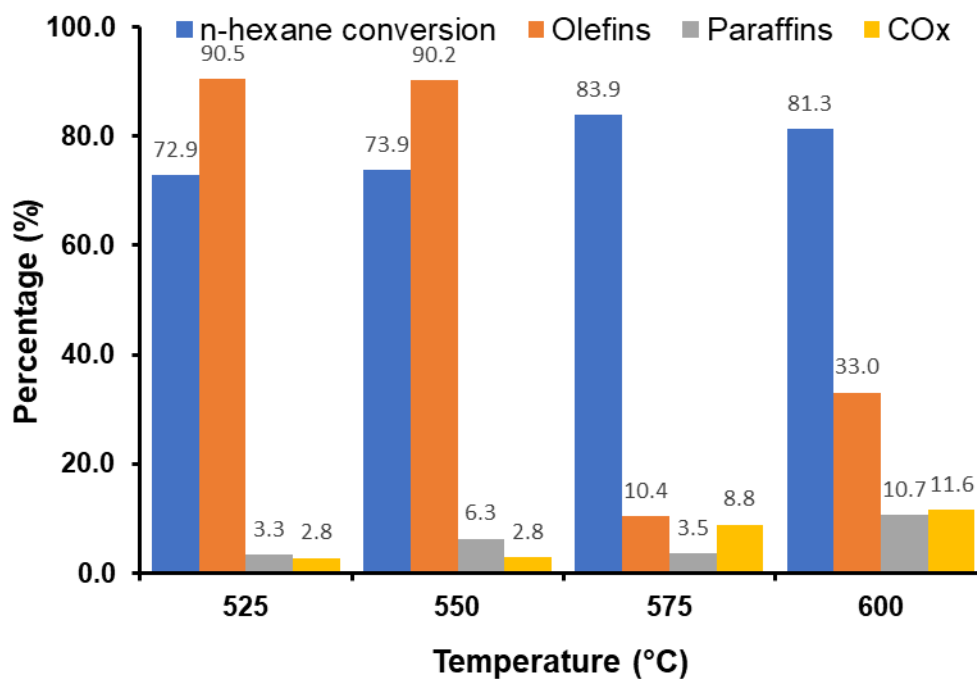


Figure 25: Effect of temperature on n-hexane conversion for $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ 2:1 at reactions conditions of $t = 25$ sec, feed = 0.2 mL hexane, and weight of catalyst $z = 0.425$ g.

5.7.2 *Effect of reaction time*

The effect of the reaction time was also studied on the best catalyst using reaction times of $t = 10$, 15, 20, and 25 sec, at a reaction temperature of 550 °C. It is observed that n-hexane conversion increases with increasing reaction time at the selected temperature of 550 °C as shown in Fig 26. The observed increase in conversion with time is attributed to the mesoporosity coupled with the balanced acidity of the catalyst. Since the average pore diameter is 10 nm (Table 3). This implied that the feed n-hexane is completely trapped within the pores of the catalyst. Consequently, more contact time is required to cause the release of the binding lattice oxygen. Hence, n-hexane conversion is favored at moderately high reaction time.

The figure also examined the effect of the contact time on the selectivity of the desired olefin intermediate paraffin and undesired CO_x products at a constant temperature of 550 °C. The catalyst sample shows high activity over the entire tested reaction time range (Figure 26). The selectivity of olefins increases slightly from 10 to 20 s and then decreases with reaction time at 25 sec. On the contrary, Cox selectivity decreases from 10 to 20 sec and then increases at 25 sec. The decrease in olefin selectivity and the rise in the selectivity of carbon dioxide at higher reaction time is mainly due to the successive oxidation of olefin and the deep oxidation of n-hexane and/or paraffin to carbon dioxide. In this study, the selectivity to paraffin is the results of the cracking step during the oxidative conversion of n-hexane under aerobic conditions. It is evident that this paraffin also contributes to the formation of olefins and coke through oxidative dehydrogenation route and combustion.

In summary, the observation above indicates that optimum reaction time favors higher olefin selectivity and inhibit deep oxidation of the feed and products paraffin and olefin to carbon oxides.

On the other hand, higher contact time favors n-hexane conversion. The observed increase in conversion with time is attributed to the mesoporosity of the catalyst as seen in the N₂ sorption analysis above. Besides, a well-dispersed amorphous phase mainly in the polymeric region can be attributed to the increase in olefin selectivity. Moreover, the decrease in CO_x selectivity to a minimum at 20 sec may be ascribed to the limited amount of lattice oxygen available during the oxidative catalysis reaction. Conversely, CO_x formation at 25 sec is due to the re-oxidation of the catalyst at longer contact time making up for the depleting lattice oxygen on the catalyst surface during the regeneration step of the experiment. This trend concurs with the results of the previous research work(Elbadawi et al., 2016b [36]).

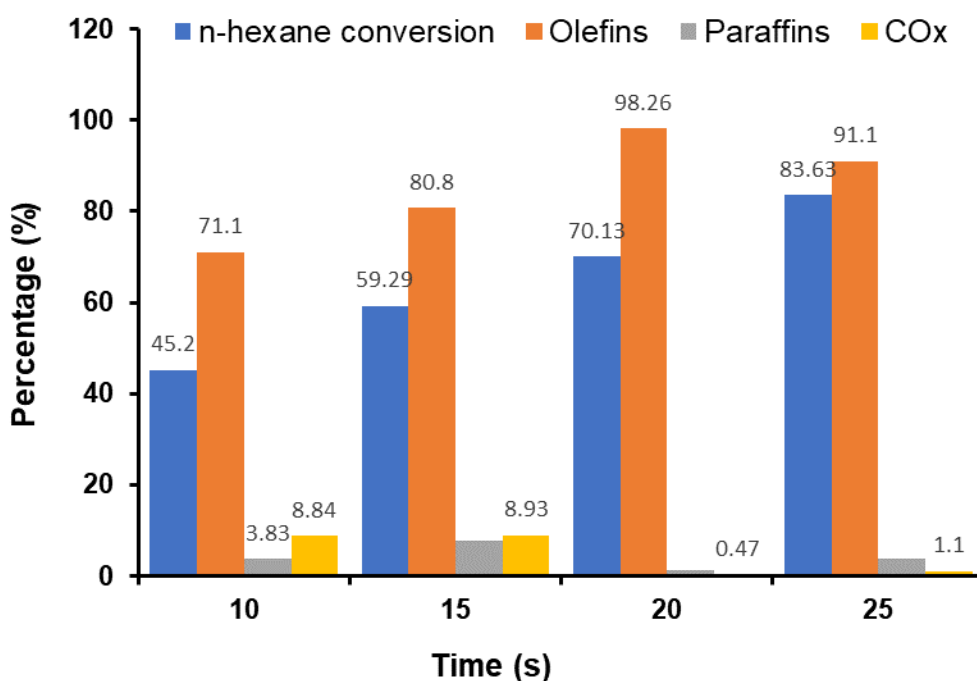


Figure 26: Effect of the reaction time on n-hexane conversion with VO_x/SrO-γAl₂O₃ 1:1, at reactions conditions of T = 550 °C, feed= 0.2 mL hexane, and weight of catalyst z = 0.425g).

Now, we will compare the yield and selectivity of olefins based on these contributions with the studies published in the literature. VO_x/SrO-γAl₂O₃ and VO_x/MgO-γAl₂O₃ show superior

performance compared to similar catalysts (Table 19) used for the oxidative conversion aided light olefins. Furthermore, $\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$ displays strong activity due to the presence of strontia, which inhibits the release of an excessive amount of lattice oxygen during the ODH of light paraffin to the desired olefin products.

Table 18: Comparison of the present studies with other catalysts published in the literature.

Catalysts	Temp (C)	n-hexane Conversion (%)	Olefins Selectivity (%)	CO_x Selectivity (%)	Olefins Yield (%)	Rf
$\text{VO}_x/\text{SrO-}\gamma\text{Al}_2\text{O}_3$	550	84	91	1.1	76.4	Present study
$\text{VO}_x/\text{MgO-}\gamma\text{Al}_2\text{O}_3$	600	99.8	96	3.2	95.8	Present study
$\text{Na}_2\text{WO}_4/\text{CaMnO}_3$	725	49	85	1.7	41.65	[53]
$\text{Na}_2\text{WO}_4/\text{SrMnO}_3$	725	53	82	0.4	43.46	[53]
$\text{VO}_x/\text{Ce-}\gamma\text{Al}_2\text{O}_3$	550	30	60	30	18.00	[36]
Plasma-Li/MgO	600	55	64	19	29.70	[167]
Li/MgO	575	28	60	30	16.8	[168]

5.8 Conclusions

Following are the major findings of the present study:

1. The excessive solvent impregnation method is a viable technique to synthesize $\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ catalysts with the desired properties for the oxidative conversion of n-hexane.
2. The newly prepared $\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ catalysts display moderate acidity, good surface area (up to $76 \text{ m}^2/\text{g}$), and moderate metal–support interactions. XRD and FTIR confirmed the presence of SrO and $\gamma\text{Al}_2\text{O}_3$ in the support material, while Raman analysis confirmed the presence of the VO_x active phase.
3. The VO_x species were mainly observed in the amorphous phase with a very small crystalline VO_x phase. NH_3 -TPD showed a reduction in acidity as the amount of strontia is increased in the sample.
4. The new $\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ having SrO/ $\gamma\text{Al}_2\text{O}_3$ ratio of 1:1 catalyst performed remarkably in n-hexane conversion (84%) to light olefins (selectivity = 91%) at 25 sec and 550°C .
5. Finally, the presence of SrO controlled the amount of lattice oxygen readily released during the performance evaluation of the catalyst in fluidized bed CREC riser simulator. Above all, the catalyst is active and stable over many repeated redox processes.

CHAPTER – 6 KINETIC MODELLING

6.1 Introduction

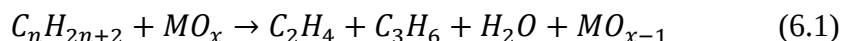
This chapter gives an overview of the kinetics models developed for the oxidative cracking of n-hexane. A reaction mechanism is first proposed based on some assumptions and justifications. Following this, several systems of differential equations were established. The systems of equations were then solved, and various kinetics parameters were determined. The last section discussed the physical significance of these parameters.

6.2 Oxidative Cracking of n-Hexane Reaction Network

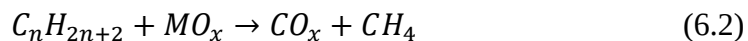
The kinetics studies of n-hexane cracking reaction over $\text{VO}_x/\text{SrO-Al}_2\text{O}_3$ catalysts were conducted at three reaction temperatures between 525 °C to 575 °C and 10s, 15s, the 20s and 25s reaction time. It is observed that light olefins are produced as the desired product and carbon oxides mainly result from unwanted side products. In addition, light paraffin is produced as an intermediate during the oxidative cracking reaction. In this work, a trace amount of methane was also formed as a byproduct due to excessive cracking of the feed. The result obtained suggests a variation of n-hexane conversion, olefin selectivity, and carbon oxides selectivity during the reaction time from 10 s to 25 sec. This variation in feed conversion and product distribution can be attributed to the competing reactions taking place in the oxidative catalysis.

In this light, one can consider the following reaction routes:

Desired reaction:



Undesired reaction:



Keeping the above arguments in focus, one can consider the proposed reaction network for the series-parallel reactions. This reaction network is proposed by our previous research team (el-Badawi et al 2017) since the experiment is performed under the same condition.

Oxidative aided conversion of n-hexane to light olefins involves both competing series and parallel reactions as shown in Figure 27. In such a reaction network, olefins formation and carbon oxides formation mainly depends on the available oxygen participating in the reaction. The type of oxygen released in this reaction scheme has been the subject of intense discussions[142], [169].

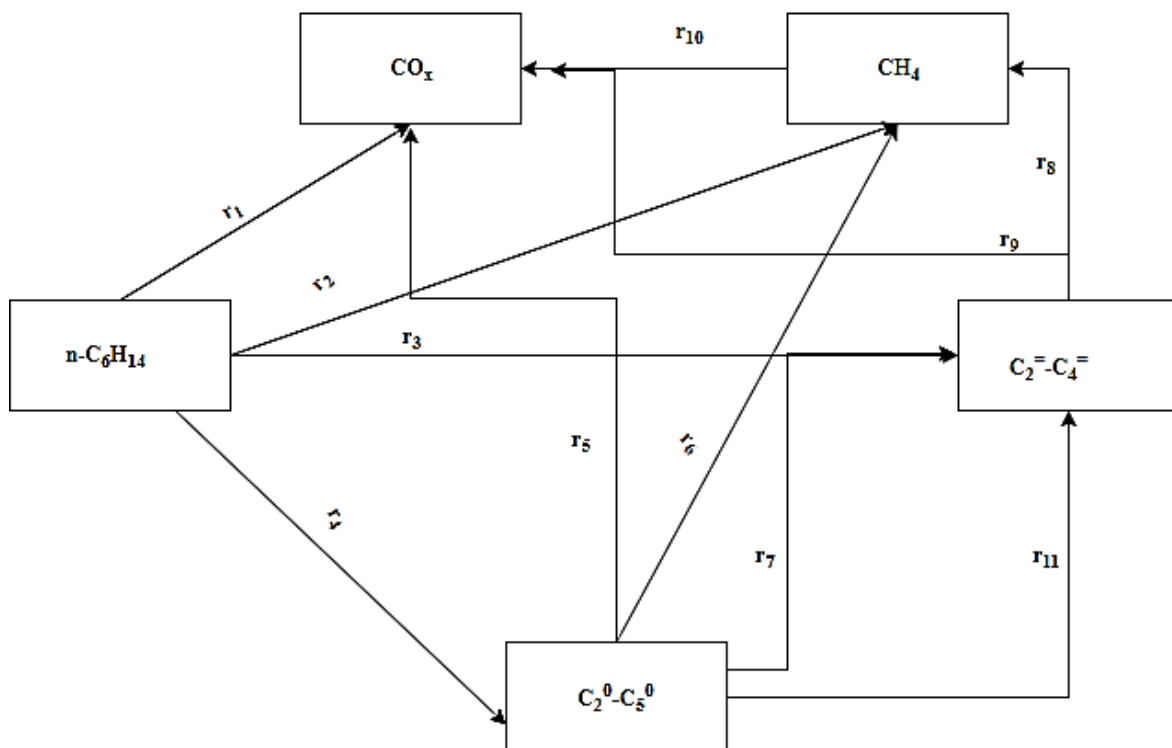


Figure 27: Proposed reaction network for n-hexane oxidative cracking

6.3 Model Development

The kinetic model formulation is an important consideration in the determination of intrinsic parameters. In this study, the kinetic model was formulated based on the reaction network present in Fig 27. Consequently, the reaction mechanisms for this reaction network follows the following steps.

6.3.1 Cracking

In this study, the reaction mechanism follows the carbenium ion mechanism according to the following steps:

Active species V adsorbed on the substrate molecule A



An intermediate substrate formed based on the reaction in Eqn 6.3



Isomerization of the reactive specie AV^*



Cracking reaction from C-C bond fission in an irreversible manner



Cracked molecules desorbed reversibly from the catalyst's active sites



Cracking reaction through chain mechanism reactions



here, A represents the n-hexane feed, V is the site of adsorption, P and R represents the products of the reaction (1) A is reactants hydrocarbon species, (2) V is adsorption site, (3) P, R are reaction products AV*, PV* are the activated adsorbed species.

In this study, the following elementary reactions listed below are used for the formation of rate equations. Accordingly, the following intermediates reaction are enumerated.

$$r_{AV} = k_{ad} C_A C_V - k_{des} C_{AV} = 0 \quad (6.9)$$

$$r_{AV^*} = k_{reac} C_{AV} - k_{iso} C_{AV^*} C_{AV} - k_{fission} C_{AV^*} = 0 \quad (6.10)$$

$$r_{AV^*} = k_{reac} C_{AV} - k_{iso} C_{AV^*} C_{AV} - k_{fission} C_{AV^*} = 0 \quad (6.11)$$

$$r_{PV^*} = k_{fission} C_{AV^*} - k_{des} C_{PV^*} = 0 \quad (6.12)$$

$$r_P = k_{des} C_{PV^*} \quad (6.13)$$

$$C_{AV} = \frac{k_{ad} C_V C_A}{k_{des}} \quad (6.14)$$

$$C_{AV^*} = \frac{k_{reac} C_{AV}}{k_{fission} + C_V k_{iso}} \quad (6.15)$$

$$C_{PV^*} = \frac{k_{fission} k_{reac} k_{fission} C_V C_A}{k_{des}^2 (k_{fission} + C_V k_{iso})} \quad (6.16)$$

Consequently, the rate equation can be expressed as follows:

$$r_A = \frac{k_{fission} k_{reac} k_{fission} C_V C_A}{k_{des} (k_{fission} + C_V k_{iso})} \quad (6.17)$$

Then, the general rate equation is expressed as

$$r_i = \frac{k_{fission} k_{reac} k_{fission} C_V C_A}{k_{des}(k_{fission} + C_V A k_{iso})} \quad (6.18)$$

where, $i = 1, 2, \dots, 10$, the cracking reactions as shown in the reaction network above.

6.3.2 Oxidative Dehydrogenation (ODH)

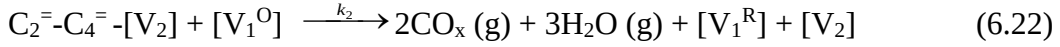
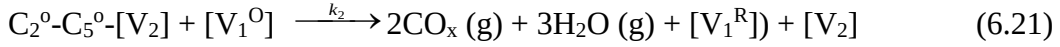
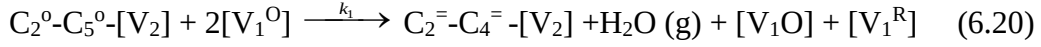
The oxidative conversion of n-hexane in light of olefins formation. It is important to note that the cracking step also forms C₂-C₅ alkanes. Consequently, these C₂-C₅ alkanes produce olefins due to the reaction in the lattice oxygen/molecular oxygen. In these reactions with vanadium oxide catalyst, light olefins are formed due to the subsurface lattice oxygen produced by the catalyst while undesired carbon oxides are also formed because of surface oxygen present on the catalyst. In the open literature, the Mars van Krevelen mechanism and Langmuir–Hinshelwood mechanism have been used to describe the mechanisms of this type of reaction. In principle, the Mars van Krevelen (MVK) mechanisms assume that catalysts' lattice accompanied product desorption while the Langmuir–Hinshelwood mechanism suggests that both the surface lattice oxygen and subsurface lattice oxygen contribute to the oxidation reactions. Nonetheless, this study uses the Langmuir–Hinshelwood mechanism, which occurs according to the following elementary reactions:

Consequently, the mechanisms below are developed:

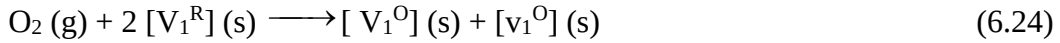
Adsorption of C₂^o-C₅^o alkanes on a site [S₂] on the catalyst surface:



Surface reaction



Desorption of products:



ultimately, the rate expression of the ODH reaction can be expressed as follows:

$$r_{11} = \frac{k_{11}P_{C_2^0-C_5^0}}{1+K_{12}P_{C_2^0-C_5^0}+K_{15}P_{C_2^--C_4^--}+K_{14}PCO_x+K_{14}PCH_4} \quad (6.25)$$

where, $[V_1^O]$ represents lattice oxygen in an oxidized site, $[V_1^R]$ is the surface oxygen vacancy in a reduced size, and $[V_2]$ is the alumina-based sites:

Also in this work, $C_2^0-C_5^0$ are lumped $k_{C_2-C_5}^k$ and $k_{11} = k_{C_2-C_5}^k \times K_{12}$ is the kinetic constant in $\text{mol/g}_{\text{cat}}\cdot\text{s}$.

6.3.3 Catalyst Reduction and Deactivation

catalytic deactivation occur due to coke formation and depletion of the lattice oxygen. Considering these two types of deactivations, the catalyst activity function $\Phi(T, t)$ is defined as :

$$\Phi(T,t)= \alpha (T) \psi(t) \quad (6.26)$$

where

$\psi(t)$: catalyst deactivation term as a result of coke formation.

$\alpha(T)$: catalyst deactivation due to the amount of reduced vanadia

Typically, the equation below is used to define the reaction term as a result of coke formation.

$$\psi(t) = \exp(-\lambda t) \quad (6.27)$$

Here λ is a constant and t means the reaction time

The catalyst deactivation due to catalyst reduction can be neglected due to the small amount of coke formation in this work.

6.4 Rate Equations for the Reacting Species

Herein, we lumped the products into four lumps: (i) short alkanes (C_2 to C_5) is grouped as (C_2^0 - C_5^0), (ii) short olefins ($C_2^=$ to $C_4^=$) are grouped as ($C_2^=-C_4^=$), (iii) methane and (iv) carbon oxides (CO and CO_2) grouped as CO_x . The experimental runs carried out in a CREC Riser Simulator can be described as a well-mixed batch reactor. Accordingly, the following continuity equations can be developed

For a batch reactor

$$\frac{dN_i}{dt} = r_i V \quad (6.28)$$

$$\frac{1}{V} \frac{dN_i}{dt} = r_i \quad (6.29)$$

$$\frac{dC_i}{dt} = r_i \quad (6.30)$$

The weight of catalyst is given by W_c while the volume of the reactor is V_r , putting this in equation implies

$$r_i = \frac{V_r}{W_c} \frac{dC_i}{dt} \quad (6.31)$$

Letting the concentration of a species be expressed in terms of its mass fraction. The following are derived

$$C_i = \frac{y_i W_1}{MW_i V_r} \quad (6.32)$$

$$dC_i = \frac{W_1}{MW_i V_r} dy_i \quad (6.33)$$

$$r_i = \frac{V_r}{W_c} \cdot \frac{W_1}{MW_i V_r} \frac{dy_i}{dt} \quad (6.34)$$

Where W , y_1 , y_2 , y_3 , y_4 , and y_5 are the mass of the n-hexane feed, light olefins, carbon oxides, light paraffin and methane

$$\frac{dPC_{6H_{14}}}{dt} = -\frac{WRT}{V} (r_1 + r_2 + r_3 + r_4) \quad (6.35)$$

$$\frac{dP_{C_2^0-C_5^0}}{dt} = \frac{WRT}{V} (r_4 - r_5 + r_6 + r_7 - r_{11}) \quad (6.36)$$

$$\frac{dP_{C_2^- - C_4^-}}{dt} = \frac{WRT}{V} (r_3 + r_7 + r_{11} - r_8 + r_9) \quad (6.37)$$

$$\frac{dPCO_X}{dt} = \frac{WRT}{V} (r_1 + r_5 + r_9 + r_{10}) \quad (6.38)$$

$$\frac{dPCH_4}{dt} = \frac{WRT}{V} (r_2 + r_8 + r_6 - r_{10}) \quad (6.38)$$

The intrinsic rate constant can be evaluated from the Arrhenius equation

$$k = k_o \cdot e^{-\frac{E}{RT}} \quad (6.40)$$

k_o = Frequency factor or pre-exponential factor

k =reaction rate constant

Considering the centering temperature, an additional equation is obtained as shown below

$$k_c = k_o \cdot e^{-\frac{E}{RT_m}} \quad (6.41)$$

$$\frac{k}{k_c} = e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)} \quad (6.42)$$

$$k = k_c e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)} \quad (6.43)$$

Van Hoff's equations can also be used to determine the adsorption equilibrium constants given below

$$K_i = e^{-\frac{\Delta H_{ads,i}^o}{RT}} \quad (6.44)$$

$$K_i = K_{i_c} e^{-\frac{\Delta H_{ads,i}^o}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)} \quad (6.45)$$

6.5 Kinetics Parameters Estimation

The set of the nonlinear differential equation was solved by fitting the experimental data using the parametric NDSOLVE built-in Mathematica function. A good fit was observed between experimental data and the kinetic model with $R^2 > 0.98$. The MatLab ODE 45 and LSQCURVEFIT built-in function was then employed to estimate the kinetic parameters.

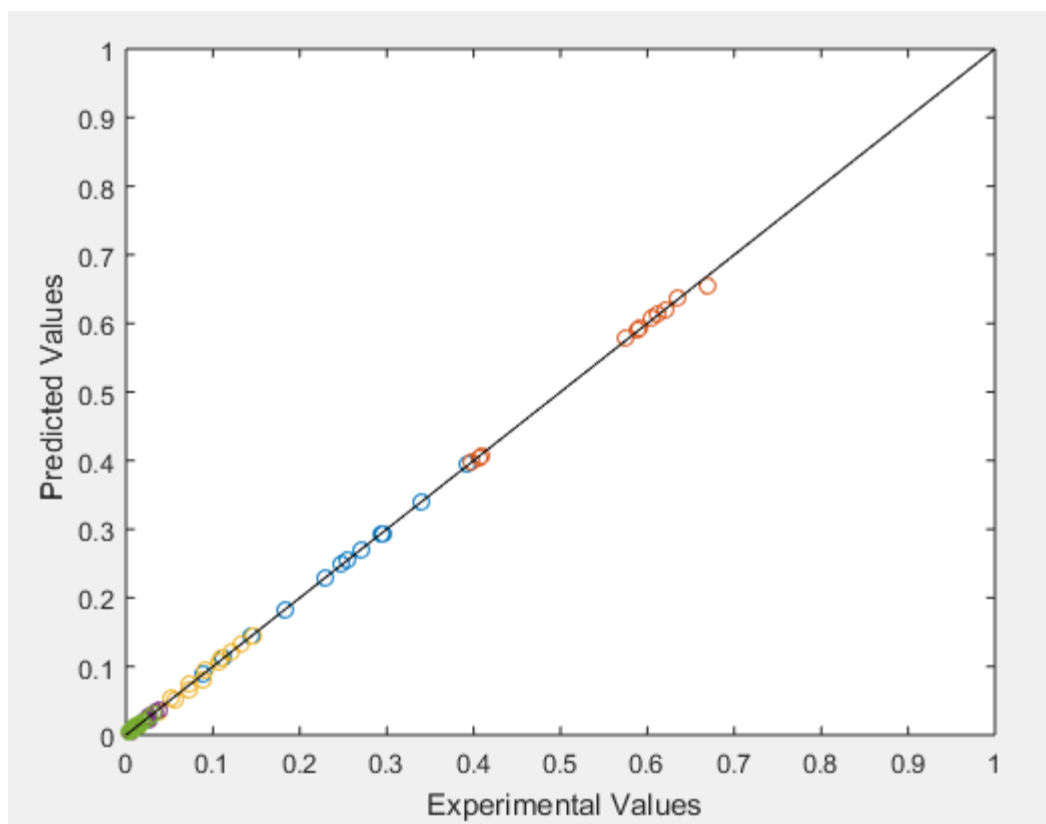


Figure 28: Model predicted values vs experimental value

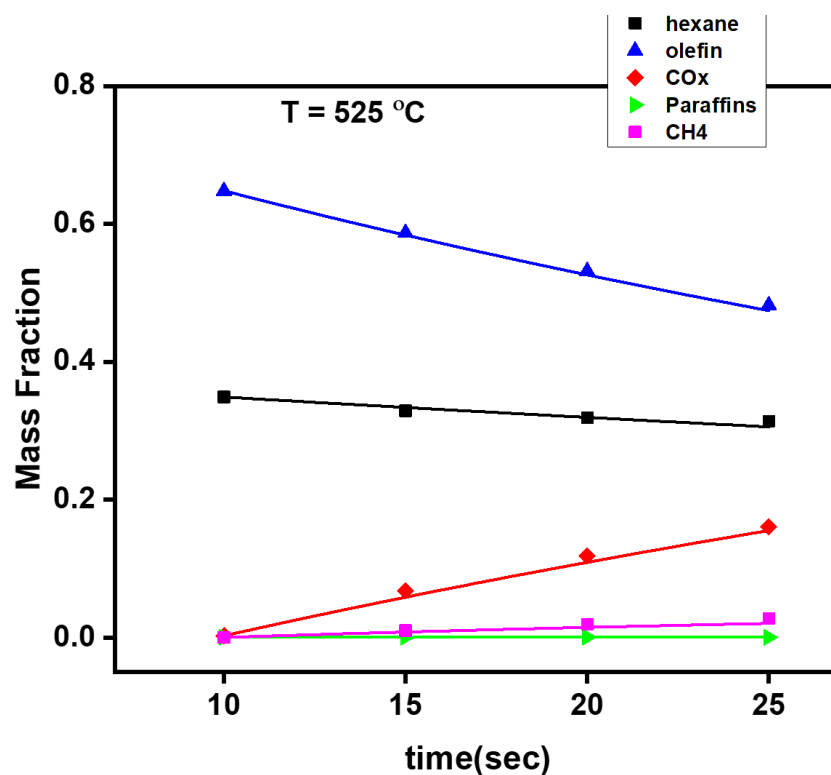
Table 19 (below) presents the kinetic parameters of the present study. The values concur with our prediction of competing reactions during the oxidative cracking reactions. The performance of a catalyst is measured by its ability to lower the barrier of a reaction. The relative higher activation energies in olefin formation compared to the values obtained during its(olefin) disappearance explains why olefin selectivity is difficult to obtain during the oxidative cracking reaction. This is because olefin is highly reactive and can easily undergo cracking and oxidation reactions. The small activation energies values in r1 and r2 suggest that n-hexane is easily combusted to CO_x due to the initial activation by the metal oxides lattice oxygen and also cracked to give CH_4 due to the

acidic support. This observation point to the fact that our catalyst poses two active sites. One can also observe small specific rate constant and activation energy values for reaction route r9. This implies that olefin formation is relatively stable to oxidation compared to other lumps. In addition, methane formation is also easily oxidized to CO_x which affirms our preposition that CO_x is being produced as both primary and secondary reactions.

Table 19: Estimated kinetic parameters

K_i^o (mol/gcat.s)	Value (10⁻³)	E_i (Kj/mol)	Value
K ₁ ^o	0.0001	E ₁	11.9726
K ₂ ^o	0.11	E ₂	43.5127
K ₃ ^o	32.9	E ₃	16.14
K ₄ ^o	5.67	E ₄	26.19
K ₅ ^o	0.74	E ₅	124.63
K ₆ ^o	3.38	E ₆	123.70
K ₇ ^o	25.7	E ₇	133.14
K ₈ ^o	28.9	E ₈	66.19
K ₉ ^o	14.7	E ₉	28.27
K ₁₀ ^o	2.87	E ₁₀	0.0102
K ₁₁ ^o	6.41	E ₁₁	64.91
λ	0.044		
R ²	0.93		

Figure 29 shows the model prediction mole fraction versus experimental data points of the various components at 525, 550, and 575 °C under different reaction times. Higher rates of k_7 and k_{11} indicate that olefins are the primary product and paraffin is produced as intermediate products.



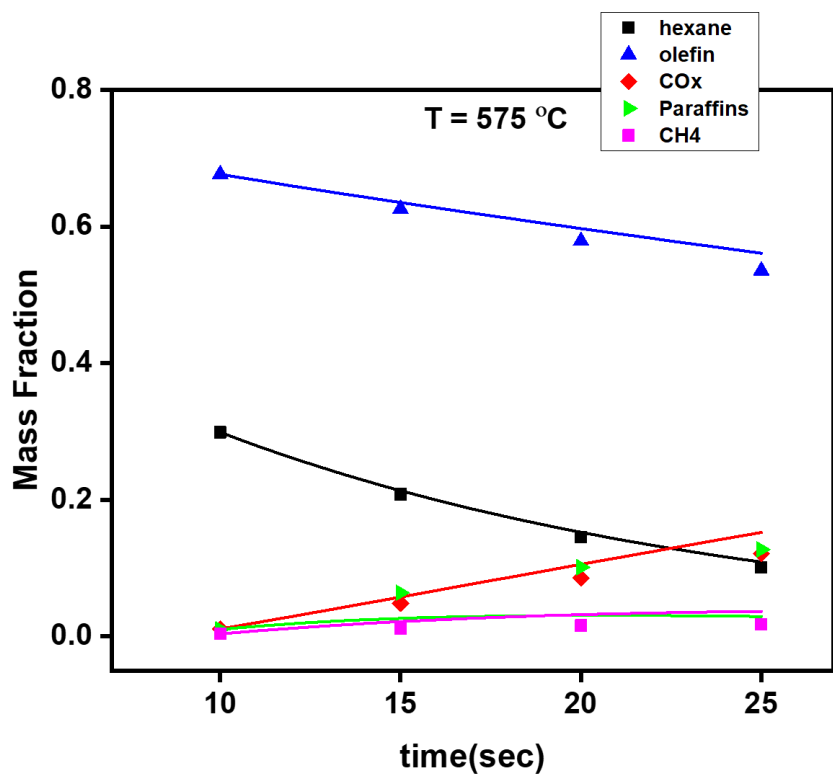
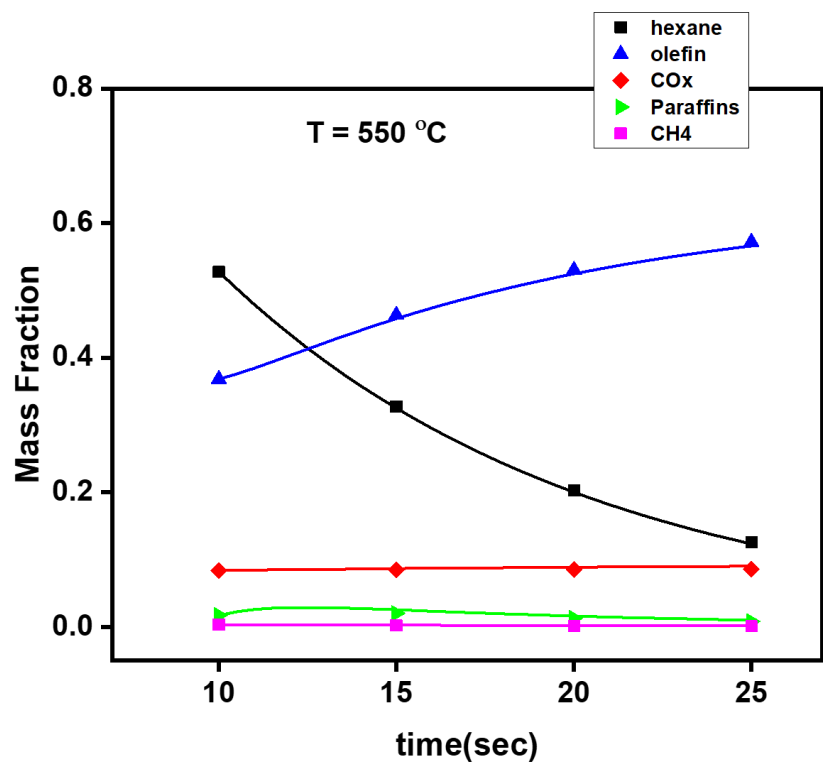


Figure 29: Kinetics data fitting

CHAPTER – 7 CONCLUSIONS AND RECOMMENDATION.

7.1 Conclusions

Different $\text{VO}_x/\text{MO}-\gamma\text{Al}_2\text{O}_3$ ($\text{M} = \text{Mg}$ or Sr) catalysts were synthesized, characterized, and tested in a fluidized bed CREC riser reactor under gas-phase free oxygen conditions. Reaction mechanisms were developed based on cracking, oxidative dehydrogenation, and catalyst deactivation. Based on the developed mechanism, the intrinsic parameters were determined. The conclusions of this research are based on:

7.1.1 Conclusion from the Effect of MgO

A novel fluidizable $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ catalysts were synthesized with varying ratios of $\text{MgO}/\gamma\text{Al}_2\text{O}_3$ for the oxidative cracking of n-hexane. All the catalysts show an increase in n-hexane conversion with temperature. This performance is due to moderate acidities and a controlled amount of lattice oxygen. Among the three samples studied, $\text{VO}_x/\text{MgO}-\gamma\text{Al}_2\text{O}_3$ 1:2 displayed superior performance (i.e. 75.6 - 99.8% n-hexane conversion and 31.35% to 96.17 % light olefin selectivity) due to its moderate acidity which inhibits excessive cracking of hydrocarbons and deep oxidation to CO_x . The selectivity of light olefins reached 96 % at 600 °C and 25s contact time.

7.1.2 Conclusion from the Effect of SrO

Following are the major findings of the present study:

1. The excessive solvent impregnation method is a viable technique to synthesize $\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ catalysts with the desired properties for the oxidative conversion of n-hexane.

2. The newly prepared $\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ catalysts display moderate acidity, good surface area (up to $76 \text{ m}^2/\text{g}$), and moderate metal–support interactions. XRD and FTIR confirmed the presence of SrO and $\gamma\text{Al}_2\text{O}_3$ in the support material, while Raman analysis confirmed the presence of the VO_x active phase.
3. The VO_x species were mainly observed in the amorphous phase with a very small crystalline VO_x phase. NH_3 -TPD showed a reduction in acidity as the amount of strontia is increased in the sample.
4. The new $\text{VO}_x/\text{SrO}-\gamma\text{Al}_2\text{O}_3$ having SrO/ $\gamma\text{Al}_2\text{O}_3$ ratio of 1:1 catalyst performed remarkably in n-hexane conversion (84%) to light olefins (selectivity = 91%) at 25 sec and 550°C .
5. Finally, the presence of SrO controlled the amount of lattice oxygen readily released during the performance evaluation of the catalyst in fluidized bed CREC riser simulator. Above all, the catalyst is active and stable over many repeated redox processes.

7.2 Recommendations

The following recommendations are highlighted for our future research:

- i. Further studies on feed to catalyst ratio should be investigated for the full application of this process for industrial consideration.
- ii. The study of the techno-economic analysis of our novel process should be carried out to determine the viability of our process for commercialization.

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Patents

- **Hussein K. Amusa**, Sagir Adamu, Sameer Al-Ghamdi, Saad Al-Bogami, Mohammad M. Hossain: $\text{VO}_x\text{-SrO}/\gamma\text{Al}_2\text{O}_3$ catalysts for oxidative cracking of n-hexane to olefins under anaerobic environment. ***Applied for UAS Patent***
- **Hussein K. Amusa**, Sagir Adamu, Sameer Al-Ghamdi, Saad Al-Bogami, Mohammad M. Hossain: Novel VO_x Supported on Mixed $\text{MgO-}\gamma\text{-Al}_2\text{O}_3$ for the Selective Oxidative Cracking of n-hexane to Light Olefins. ***Applied for UAS Patent***

Journal Manuscripts

- **Hussein K. Amusa**, Sagir Adamu, Idris A. Bakare, Sameer Al-Ghamdi, Saad Al-Bogami, Shaikh A. Razzak, Mohammad M. Hossain: Novel VO_x Supported on Mixed $\text{MgO-}\gamma\text{-Al}_2\text{O}_3$ for the Selective Oxidative Cracking of n-hexane to Light Olefins. *Manuscript under review by Advisor.*

- **Hussein K. Amusa**, Sagir Adamu, Idris A. Bakare, Abeer S. Arjah³Sameer Al-Ghamdi, Saad Al-Bogami, Shaikh A. Razzak, Mohammad M. Hossain : High performance VO_x on SrO-γAl₂O₃ catalyst for the oxidative cracking of n-hexane to light olefins under anaerobic environment. Prepared for submission. Submitted the Journal of Industrial and engineering chemistry.
- **Hussein K. Amusa**, Sagir Adamu, Idris A. Bakare, Abeer S. Arjah³Sameer Al-Ghamdi, Saad Al-Bogami, Shaikh A. Razzak, Mohammad M. Hossain: Kinetics of oxidative cracking of n-hexane to light olefins over VO_x on SrO-γAl₂O₃ catalyst for the oxidative cracking of n-hexane to light olefins under anaerobic environment. *In progress*

Conference presentations

- **Hussein K. Amusa**, Sagir Adamu, Idris A. Bakare, and Mohammad M. Hossain: Oxidative cracking of n-hexane to olefins Over novel VO_x/MgO-γAl₂O₃. King Fahd University of Petroleum and Minerals, 10th Student Research Forum Final Program. 17th April 2019. Won Second Prize.
- **Hussein K. Amusa**, Afees A. Ayandiran, Sagir Adamu, Sameer Al-Ghamdi, Saad Al-Bogami, Shaikh A. Razzak, Mohammad M. Hossain: Oxidative Dehydrogenation of Propane to Propylene Over VO_x/CaO-Al₂O₃. 29th annual Saudi-Japan Symposium: Nov 3-4, 2019. |