Oxidative dehydrogenation of *n*-octane using morphologically different VMgO catalysts

by

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As the candidate's supervisor I have approved this thesis for submission

Name

Signature

Date

PREFACE

The experimental work described in this thesis was carried out in the School of Chemistry and Physics in the University of KwaZulu-Natal, Westville campus, Durban, from February 2014 to June 2017, under the guidance and supervision of Professor Holger B. Friedrich, Dr Sooboo Singh and Dr Abdul S. Mahomed.

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of work of other it is duly acknowledged in the text.

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- School of Chemistry and Physics, University of KwaZulu-Natal for providing facilities.

DECLARATION-1

I, Ayanda M. Magwenyane, declare that:

- 1 The research reported in this thesis, except where otherwise indicated is my original research.
- 2 This thesis has not been submitted for any degree or examination at any other university.
- 3 This thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
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DECLARATION-2

Part of the work that has been presented at conferences are detailed below:

Poster presentation:

A.M. Magwenyane, M. Fadlalla, H.B. Friedrich, S. Singh, Oxidative dehydrogenation of *n*-octane using morphologically different VMgO, Catalysis Society of South Africa (CATSA), University of the Witwatersrand, Gauteng, RSA, November 2014.

Oral presentation:

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ABSTRACT

Gas phase paraffin oxidative dehydrogenation (ODH) has been explored extensively using medium chain paraffins such as *n*-hexane and *n*-octane as feedstock over various catalytic systems. Among these systems, the activity and stability of magnesium vanadates have been studied during the ODH of these paraffins. In most cases, it was found that 15 wt% vanadium was the optimum loading on the support, i.e. magnesium oxide. In addition, it was found that the morphology of the magnesium oxide influenced the performance of the catalyst. However, this has not been explored in much detail.

In this work, magnesium oxide was synthesized using several methods to produce surfaces that differed morphologically, such as materials with a cubic morphology, denoted MgO-A, spherical morphology (MgO-B) and MgO with a nano-sheet type morphology (MgO-C). These supports were then loaded with 15 wt% vanadium by wet impregnation method using different synthesis methods. They were characterized using X-ray diffraction (XRD), Brunauer-Emmet-Teller technique, inductively-coupled plasma-optical emission spectroscopy, Raman spectroscopy, scanning and transmission electronic microscopy, temperature programed reduction (TPR) and temperature programed desorption (TPD). Electron micrographs generated for all the catalysts confirmed their respective morphologies. The XRD and Raman results showed the formation of magnesium orthovanadate and pyrovanadate phases for the cubic MgO. Only the orthovanadate phase was present for the other VMgO catalysts. This was confirmed by TPR which showed two reduction peaks for VMgO-A and one reduction peak for the other catalysts. The catalysts were tested for the ODH of *n*-octane at 450 °C using air as an oxidant. At an iso-conversion of 14 ± 1 %, VMgO-B (water), whose support had a spherical morphology was more selective towards ODH products, whereas VMgO-A (oxalic acid) where a cubic morphology was observed for the support, carbon oxides (CO_x) were the dominant products and this correlated well with the ammonium-TPD results which showed that catalysts with weak and medium acidic sites promoted the formation of ODH products, whereas catalysts with strong acidic site were more selective towards CO_x , in agreement with published results. Scanning electron microscopy images of the used catalyst showed agglomeration of particles while XRD showed a peak for the reduced phase of magnesium orthovanadate. This study has shown that catalysts with the same formulation but with different morphologies synthesised by methods modified to suit its physical and chemical properties, influenced the variance in the catalysis.

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DEFINITIONS AND CALCULATIONS

Gas hourly space velocity = $\frac{F_T}{V_C}$ where F_T = flowrate in mL h⁻¹ V_C = volume of catalyst bed in mL

1.

2.

Conversion of substrate, $X = \frac{n_a - n_b}{n_a}$ where X = conversion of n-octane $n_a = mols of n-octane in$

 n_b = mols of n-octane in product stream

3. Selectivity of product, $S_P = \frac{n_P}{n_a - n_b}$ where $S_P =$ selectivity of product $n_P =$ mols carbon of product

LIST OF ABBREVIATIONS

BET	:	Brunauer-Emmett-Teller
EDX	:	Energy dispersive X-ray spectroscopy
EM	:	Electron microscopy
FID	:	Flame ionization detector
IR	:	Infrared
GC	:	Gas chromatography
GHSV	:	Gas hourly space velocity
HPLC	:	High performance liquid chromatography
ICP-OES	:	Inductive couple plasma-optical emission spectroscopy
JCPDS	:	Joint Committee on Powder Diffraction Standard
ODH	:	Oxidative dehydrogenation
PXRD	:	Powder X-ray diffraction
SEM	:	Scanning electron microscopy
TCD	:	Thermal conductivity detector
TPD	:	Temperature programmed desorption
TPR	:	Temperature programmed reduction
VMgO	:	Vanadium magnesium oxide

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CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

The increase in price together with the decrease in olefin availability have developed an interest in research to investigate the supply of olefins and to replace them as a feedstock in many chemical processes. Alkanes can be used as an alternate feedstock to produce value added products such as olefins and oxygenates through oxidative dehydrogenation (ODH) due to their abundance [1, 2]. Currently, heterogeneous catalysts appeal to industry as they provide good activity and selectivity towards their desired products and can easily be separated from the reaction mixture, post reaction [3, 4]. Table 1.1 shows a list of some of the heterogeneous oxidation reaction processes in the petrochemical industry.

Reagents	Product	Conversion (%)	Selectivity (%)
methanol	formaldehyde	99	94
<i>n</i> -butane	maleic anhydride	75-80	75
benzene	phthalic anhydride	100	79
naphthalene	phthalic anhydride	100	84
propene (with NH ₃)	acrylonitrile	>99	73-77
propene	acrolein	>90	80-85
acrolein (propenal)	acrylic acid	>95	90-95
isobutene	methacrolein	>97	85-90
methacrolein	methacrylic acid	70-75	80-90
ethene	ethene epoxide	90	80
ethene (with HCl)	1,2-dichloroethane	>95	>95
cyclohexanone	cyclohexanoneoxime	>99	95-98

 Table 1.1 Catalytic oxidation processes in industry [5-7]

In catalytic oxidation reactions, a catalyst activates molecular oxygen forming electrophilic oxygen species and to some extent, nucleophilic oxygen species. Much of the nucleophilic oxygen species reside in the lattice of the catalyst. These oxygen species control the selectivity of the products; electrophilic species activate alkanes to form degraded oxygenated and

completely oxygenated products, while nucleophilic oxygen species typically activate the alkane to form olefinic products [3].

Figure 1.1 shows both electrophilic and nucleophilic catalytic oxidation of *n*-butane [4]. The reaction for electrophilic oxidation proceeds through the activation of molecular oxygen to form O_2^{-} , $O_2^{2^{-}}$ and O^{-} . This process results in the formation of epoxides or saturated ketones. Nucleophilic oxidation, on the other hand results in the formation of olefinic species via the abstraction of hydrogen from the parent alkane. Depending on chain length, poly-unsaturation can take place forming dienes and aromatics. Oxidative dehydrogenation of alkanes to alkenes, dienes and aromatics is thus one of the best examples of nucleophilic oxidation [4].



Figure 1.1 Scheme showing catalytic oxidation via electrophilic and nucleophilic oxygen. [4]

1.1 Oxidative dehydrogenation using vanadium oxides

Gas phase paraffin oxidative dehydrogenation (ODH) has been carried out on lower chain paraffins, as well as hexane and octane feeds employing a wide range of possible catalytic systems [8-13]. Literature has shown that the most used catalytic materials for ODH are vanadium phosphorus oxide (VPO), vanadium oxides, vanadium oxide together with nickel

oxide and molybdates, supported vanadium oxide and other metal oxides, such as mixed systems of Pt, Rh and Pd; Li-MgO; Mo-V-Nb and Cr₂O₃/Al₂O₃ [14-22].

Vanadium oxide has shown good activity in paraffin activation due to its ability to perform hydrogen abstraction at milder reaction conditions than other metal oxides [8]. Vanadium pentoxide, V_2O_5 , exists in a number of forms with varying coordination of vanadium and oxygen atoms since it can exist in many valence states, from +2, to +5. The size of V_2O_5 is controlled by the ionic radius of the vanadium atoms with respect to the oxygen atoms, which are small enough to form four coordinated structures but too small to form a six coordinated structure [4]. The coordination ability of vanadium can be controlled under specific synthesis conditions, e.g. pH and temperature [23].

A major drawback is that unsupported vanadium oxide favours the formation of total oxidation products (CO and CO₂), but delivers high conversion at milder conditions [8]. Vanadium that has been supported on various metal oxides has been shown to reduce the formation of total oxidation products, thereby favouring the formation of dehydrogenated products, usually to the detriment of activity [9-11, 23].

1.2 Unsupported vanadium oxide

Research done on oxidative dehydrogenation using unsupported vanadium oxide catalysts [23] has been reported to show high activity in paraffin activation at low temperatures compared to other metal oxides. The major concern is that unsupported vanadium oxide favours combustion products due to its potential to be reduced when the lattice oxygen in the metal oxide responsible for hydrogen abstraction, is removed [23]. The introduction of external gas phase oxygen replaces the lattice oxygen lost in the catalyst. The reduction-oxidation cycle can be a limiting step since is depends on the redox properties of the material as well as the rate of re-oxidation. Supported vanadia (vanadium oxide) has been prepared and extensively studied in an effort to understand and manipulate the properties of vanadium oxide for ODH reactions.

1.3 Supported vanadium oxide systems

The main use of supports in catalysis is to increase the surface area, reduce sintering of the active material and improve thermal stability of the catalyst. When the active metal oxides are synthesised, the application of relatively high temperatures during calcination results in significant sintering, which lowers the surface area. A few key factors to look for when

choosing a support is that it must act as a heat sink, have good interaction with the active metal as this would aid in minimizing or preventing sintering, and good thermal stability [24]. This is particularly important during exothermic reactions, such as oxidation reactions. The high thermal conductivity helps to remove the heat from the reaction sites and reduce hot spots, which otherwise might activate the desired product to react further and decompose.

Supported vanadium oxide has been tested for short chain alkane feeds in various studies [25-26]. The researchers showed that these catalytic systems can give good activity and selectivity towards oxidative dehydrogenation products and in turn suppress complete oxidation of ODH products. Supports have shown to improve the mechanical strength, increase the thermal stability and the dispersion of vanadium oxide [4, 27]. In some literature, the activity of the supports were not always considered as they were believed to be catalytically inert [28]. However there are reports on the considerable influence of the support on the catalytic activity of such systems [29]. An interaction between vanadium oxide and a support can result in several outcomes which include: [4]

- The crystallite formation of active vanadium oxide
- The monomolecular dispersion of the active component
- The diffusion of the active vanadium oxide into the lattice of the carrier to form a solid solution
- New component formation (various metal vanadates)
- Disruption of the morphology of the support

Supports are usually metal oxides which can be classified into two broad groups, viz. reducible metal oxides (transition metal oxides) and non–reducible metal oxides (alkali and alkaline earth metal oxides). The reducible transition metal oxides are reported to activate paraffin chains at low temperatures than those of alkali and alkaline earth metals [21]. The transition metal oxides have lattice oxygen which are easily removable and create oxygen vacancies. These lattice oxygen species are involved in ODH reactions under oxygen-free conditions. However, lattice oxygen has also controversially been implicated in the formation of carbon oxides [21]. The alkali and alkaline earth metals oxides favour ODH over carbon oxides because of their non-reducible character. The most studied supports, for vanadium oxide, for ODH, are metal oxides such as SiO₂, TiO₂, Al₂O₃, MgO [23, 27], mixed metal oxides incorporating TiO₂/ SiO₂, TiO₂/ Al₂O₃, SiO₂/ Al₂O₃, including calcined hydrotalcites [28-31], molybdates [32] and monolithic ceramic supports and inert ceramic membranes [33].

Magnesium oxide as a support for vanadium oxide has interested researchers due to its nonreducibility, potential to stabilize acid-base properties of V₂O₅, form vanadate phases at different loadings of V₂O₅ and can be synthesized with different morphologies. All these characteristics of MgO make it a suitable support for vanadium oxide, thus providing an efficient ODH catalytic system for various alkanes [12, 13, 23, 27, 30, 33].

Corma et al. [34] studied the effects of various supports with vanadia on propane ODH. They loaded 19 % vanadia on silica, alumina and titania supports and obtained similar activities as those of unsupported V_2O_5 . They also supported vanadia on Sm_2O_3 , MgO and Bi_2O_3 and obtained higher selectivities towards ODH products, 35, 26 and 23 %, respectively, due to the presence of the bulk orthovanadate phase when supported on these basic oxides. This showed that the support had a significant influence on directing the formation of orthovanadate and crystalline vanadium pentoxide phases, which resulted in a change in the catalyst activity and selectivity. The reducible supports behaved like unsupported vanadium pentoxide, while the non-reducible supports tended to favour the desired products.

The effect of the support when vanadium oxide was supported on Al₂O₃, AlNbO₄, AlPO₄ and MgSiO₃ was also compared in the oxidative dehydrogenation of propane by Eon et al. [35]. Only two variables were considered during the evaluation of the catalysts. These were the structure of the surface species and the chemical nature of the support. Isolated and associated vanadate species were both present on the catalysts, the proportion changing with the nature of the support. Isolated vanadate species were dominant on MgSiO₃, while associated vanadate species were abundant on γ -alumina followed by aluminium niobate. A summary of the catalytic results of these catalysts are shown in Table 1.2 [35].

Table 1.2 Catalytic properties in propane oxidative dehydrogenation of dispersed vanadate

 species supported on different oxide materials [35].

Catalyst	θ^a	T (K)	$C_{3}H_{8} / O_{2}$	Conversion		Selectivity	Ref.
			(molar)	(%)	$(\% / g_v)^b$		
VOx / Al ₂ O ₃	0.28	673	2 / 19.6	7.5	2590	58.4	[35]
VO _x / AlNbO ₄	0.23	773	2 / 19.6	9.2	7080	65.0	[35, 38]
VO _x / AlPO ₄	0.23	773	4.2 / 8.4	7.0	700	48.0	[39]
VO _x / MgSiO ₃	0.22	773	4.0 / 8.0	7.5	190	56.7	[34]

^a Extent of vanadia monolayer coverage of the support, ^b Propane conversion per gram of vanadium.

Comparing each catalyst, it is observed that the $VO_x/AINbO_4$ catalyst showed higher activity than VO_x/AI_2O_3 and $VO_x/AIPO_4$ while $VO_x/MgSiO_3$ gave the lowest activity. The overall activities of the catalysts listed in Table 1.2 are more related to the influence of the support than to the structure of the active species. In principle, the bonds formed between the support and vanadate species influence the reactivity of the vanadate species [35].

Some factors which control the catalyst activity are the oxidation state of vanadium, the metalsupport interaction, surface area and acidity [36, 37]. Therefore this causes the interaction of vanadate species and various supports to differ because they become highly dependent on acid– base properties of both the vanadate phase and the support [36].

The preparation method of the support is also an important consideration for improved dispersion of vanadia. The AlNbO₄ support showed that the acidity of hydroxyl groups is a function of the calcination temperature, which was much higher for crystallized oxides than for amorphous solids [38]. Therefore, the amorphous solids were seen to be more active and selective. The γ -alumina adsorbs different vanadate species at different pH, i.e. tetrahedral vanadate species adsorb on γ -alumina at pH 7, while octahedral vanadate species adsorb at pH 2.5-4.5 [35]. Another feature that influences the vanadate phase is temperature of calcination. Vanadium changes to the tetrahedral species during calcination at high temperatures, however depending on the vanadia loading, isolated or associated structures exist [35].

1.4 Properties of magnesium oxide

Apart from advantages mentioned previously, magnesium oxide has been used by researchers in many catalytic reactions as it is a relatively cheap material to purchase or synthesise. The hygroscopic white powder of magnesium oxide (MgO) can occur naturally or obtained by various synthetic methods, including calcination of magnesium hydroxide, magnesium carbonate and magnesium chloride [13]. These different magnesium oxide synthetic processes can result in different morphologies, thus showing varying catalytic activity [13]. Calcining at different temperatures can also have an effect on obtaining different morphologies of MgO. These features have attracted much attention because of their potential application in catalysis, water treatment, sensors and electric power generation [40, 41, 45-51].

The morphology of nano structured material such as MgO is an extremely important feature that has a direct impact on their physical and chemical properties [40-44]. Therefore, researchers have considered the synthesis of MgO with different morphologies, such as nanocrystals, nanoparticles, spheres, nanocubes, nanowires and nano-sheets [52-58]. Various

methods are used to synthesise MgO with different morphologies. MgO characterised as nanoparticles and nanowires are synthesised using the Polyol Mediated Thermolysis (PMT) process, where the concentration of magnesium acetate, polyvinyl pyrrolidone (PVP; capping agent) and ethylene glycol (EG; solvent as well as reducing agent) are monitored to obtain the nanoparticles and nanowires. SEM and TEM images of nanoparticle and nanowire MgO are shown in Fig 1.2 and Fig 1.3 respectively [52, 53].



Figure 1.2 SEM (a) and HRTEM (b) images of MgO nanoparticles [53].



Figure 1.3 SEM image (a), TEM image (b), corresponding selected-area electron diffraction (SAED) pattern (c) and HRTEM image (d) of MgO nanowires obtained from the PMT process [52].



Figure 1.4 TEM image of nanosheet magnesium oxide [57].

Nanosheet MgO can be synthesised by dissolving magnesium ribbons in methanol under a static atmosphere of argon and mixed with 4-methoxybenzyl alcohol (BZ), then dried and calcined (Fig. 1.4) [57].

Nanocubic and spherical MgO are synthesised using a sol-gel method; were magnesium acetatetetrahydrate is treated with oxalic acid (nanocubes) and tartaric acid (spherical) in ethanol to form a gel that is calcined. The SEM images of these materials are shown in Fig. 1.5 while Fig. 1.6 shows the morphology more closely by the use of TEM [58].



Figure 1.5 SEM images of (a) nanocubic MgO and (b) spherical MgO [58].



Figure 1.6 TEM images of (a) nanocubic MgO and (b) spherical MgO [58].

1.5 The effect of vanadia loading on different supports

1.5.1 Vanadium oxide supported on alumina

There have been many studies with alumina supported vanadia catalyst systems due to the thermal stability of alumina. As mentioned previously, there are many possible types of vanadia species. It has been reported that at low loadings of vanadia, amorphous phases of vanadia are observed whose structure form isolated vanadia tetrahedra with high dispersion on the surface [59]. On the other hand, high loadings of vanadia results in the formation of crystalline V_2O_5 with some amorphous vanadia being present [59]. Catalytic activity and selectivity of monolayer vanadia supported on alumina for the oxidative dehydrogenation of lower alkanes [35, 59] are shown in Figure 1.7. The reviewed data was obtained at different temperatures (from 673 to 753 K) with alkane to oxygen ratios ranging from 0.27 to 0.9 in the reaction mixture. The results obtained show the increase in the rate of alkane conversion with the increase in vanadia monolayer coverage, but with a subsequent decrease in the selectivity to butene [59].



Figure 1.7 Catalytic activity and selectivity to lower olefins over the alumina-supported vanadia monolayer in the ODH of lower alkanes. Key: (•) ethane, 753 K, (\Diamond) propane, 673 K, (Δ) butane, 673 K [23].

The uneven distribution of vanadia on alumina also affects the ODH selectivity. The uncovered surface of the alumina support directly influences the ODH selectivity by adsorption of alkenes or other products giving rise to secondary reactions. Using infrared spectroscopy in the DRIFT mode and flushing the alumina–supported vanadia catalysts with ethane/air, adsorbed carbonates on uncovered alumina were observed [59]. The resulting acetate species present were suggested to be formed by uncovered alumina along with Brønsted acid groups of the vanadium oxide layer because they were not detected in bulky vanadium pentoxide. Therefore, it was proposed that uncovered alumina contributes to the formation of total oxidation products [23].

1.5.2 Vanadium oxide supported on silica

Silica is the most commonly used support for catalysts since it enables high dispersion because of its high surface area [23]. The interaction of silica with vanadia was studied using various techniques, such as IR, X–ray absorption, Raman, XPS, UV, oxygen chemisorption and TPR [60-70]. These techniques report that vanadia exists as highly dispersed VO_x monomeric units at low loadings.



Figure 1.8 Catalytic activity and selectivity to alkenes over silica-supported vanadia and bulk V_2O_5 in the ODH of alkanes. Key: (•) ethane, 800 K, (o) ethane, 813 K, (Δ) butane, 793 K [23].

Figure 1.8 shows the catalytic activity and selectivity towards olefins for the oxidative dehydrogenation of ethane and butane over silica-supported vanadia catalysts [23]. The figure shows a decrease in the overall activity when vanadia loadings increase, for the range of data obtained. Le Bars et al. [60] studied the oxidative dehydrogenation of ethane on silicasupported vanadia, while Owens and Kung [11] used butane as a feed. Both reports agreed that lower vanadia loadings showed higher selectivity to alkenes than the higher loadings, while the conversion increased with higher vanadia loading. The decrease in selectivity as the conversion increases occurs much slower over these samples than over higher loaded samples, which indicates that secondary reactions proceed faster on the crystalline V_2O_5 [23]. The data presented in Fig. 1.8 were obtained in a tight temperature range (from 793 to 813 K) but with different reaction mixtures. The graph showed, more importantly, that the varying coverage led to varying vanadate phases which effectively had an impact on the selectivity and activity. Other authors have also shown that the presence of different vanadyl species supported on silica led to a variance in ODH selectivity [11, 71, 72]. The production of carbon dioxide was attributed to the presence of V₂O₅ species, while ODH product selectivity was attributed to the presence of well dispersed isolated vanadia at low loadings. It was proposed that for low loadings, the vanadyl group was bonded to three oxygen ions from the support, as shown in Fig. 1.9.



Figure 1.9 Vanadyl group bonded to three oxygen ions from the silica support

This structure was confirmed by ⁵¹V spin echo and MAS NMR [67], where distorted vanadium tetrahedra were observed. This structure was more selective to ODH products than crystalline V_2O_5 (where the vanadium ion is octahedrally co-ordinated) because it provides reduced availability of electrophilic lattice oxygen. When VO_x species are in contact with air, they react with atmospheric moisture yielding a surface hydrated form and result in acidic hydroxyl groups [60]. The conditions of this surface hydrated form of VO_x closely resemble those observed for bulk crystalline V₂O₅ [38]. These catalysts would then exhibit a more acidic character which enhances the rate of alkane conversion and oxidative dehydrogenation but does not affect the selectivity to the olefin [23].

The silica–supported catalysts with low loading of vanadia were reported [70, 73] to be reduced more easily by hydrogen and ethane more easily than bulk V_2O_5 and crystalline V_2O_5 supported on silica. The mobility of oxygen for the isolated vanadia species can give a higher activity but not higher selectivity to dehydrogenation products [74]. The crystalline V_2O_5 contains V=O bonds, which has been reported to be non-selective towards ODH products and favours complete oxidation [75].

1.5.3 Vanadium oxide supported on titania

It has been reported [34, 76] that V_2O_5 supported on titania was highly active at relatively low temperatures (500 – 600 K) in the oxidative conversion of propane. However, the selectivity obtained was poor, decreasing from 28 % at low loading (5 monolayers) to 12 % for the higher loading (20 monolayers). The V_2O_5 / TiO₂ catalyst promoted with potassium was reported to decrease the overall activity, but increase the ODH selectivity [77]. This was explained by proposing that potassium hinders the formation of the electrophilic O⁻ species that are responsible for total oxidation.

Butane oxidative dehydrogenation yielded only carbon dioxide over both monolayer and multilayer vanadia-titania catalysts with no formation of ODH products being reported [77]. The rate of the reaction at various concentrations of oxygen was found to be proportional to the amount of V=O species in the catalyst [78]. The TiO₂ support was reported to retard the activity, since both anatase and rutile supported catalysts were shown to have lower activity than unsupported V₂O₅ [78, 79].

When TiO_2 supported vanadia was compared with the SiO_2 and Al_2O_3 supported vanadia catalysts, the TiO_2 supported catalyst was less selective to oxidative dehydrogenation products. Haber et al. [78] reported that the nature of a vanadia monolayer on TiO_2 is different from those of silica and alumina. A high concentration of monovandate species form on the titania support which gives a higher overall oxygen capacity to the vanadia monolayer. The oxygen is easily removed from the catalyst and replaced eventually by gas phase oxygen. The removed oxygen from the catalyst were then assumed to be inserted into the reaction molecule, favouring the formation of oxygenated products [23].

1.5.4 Vanadium oxide supported on magnesium oxide

The activity and stability of magnesium vanadates have been investigated in considerable detail for ODH reactions [80]. They are reported as active and stable catalysts and their activity significantly increases from 750 K upwards. The main reactions taking place are oxidative dehydrogenation and combustion. Different researchers have investigated the activity and selectivity of VMgO catalysts in the oxidative dehydrogenation of propane [8, 22, 32, 81] as shown in Figure 1.10. In this figure, the overall activity is expressed by the conversion and reaction rate for different vanadia loadings (0–100 %). The vanadia loading from 15 – 20 % had high reaction rates and conversion (above 65 %). The selectivity to propene was maximum at a vanadia loading of approximately 60 % [22].

The data for butane using the same catalysts is shown in Figure 1.11. Corma et al. [34] found a low selectivity towards butene for butane ODH due to a higher oxygen to butane ratio in the reaction mixture. In another study, Baes and Mesmer [22] obtained a butene selectivity of 60 % with a 30 wt% V_2O_5 loading on the magnesium oxide.



Figure 1.10 Catalytic activity and selectivity over VMgO in the ODH of propane at 813-823 K as a function of the vanadia content in the catalysts. Key: (Δ), VMgO synthesised using wet impregnation by Chaar et al. [9]; ($\mathbf{\nabla}$), VMgO synthesised using citrate method by Gao et al. [80]; (\diamond), VMgO synthesised using wet impregnation by Sam et al. [81]; (*), VMgO synthesised using wet impregnation by Blasco and Lopez Nieto [27].



Figure 1.11 Catalytic activity and selectivity over VMgO in the ODH of butane at 773-823 K as a function of the vanadia content in the catalysts. Key: (*), VMgO synthesised using wet impregnation by Corma et al. [34]; (Δ), VMgO synthesised using wet impregnation by Chaar et al. [9].

Tetrahedral VMgO species are believed to be part of the active centers for ODH reactions, where the reaction mechanism takes place through the reduction–oxidation cycle between V^{5+} and V^{4+} [82]. Three VMgO phases can form using different synthetic methods, viz magnesium orthovnadate (Mg₃V₂O₈), magnesium pyrovanadate (Mg₂V₂O₇) and magnesium metavanadate (MgV₂O₆).

These phases are active centers in VMgO systems for ODH reactions. However, there are contradictory opinions regarding these phases as active centers. Kung and Kung [83] suggested that magnesium orthovanadate (Mg₃V₂O₈) is the active phase, while Sam and co-workers [81] reported magnesium pyrovanadate (α -Mg₂V₂O₇) to be the active phase and the orthovanadate phase to be responsible for total oxidation. The catalytic results for VMgO phases to propene selectivity for ODH of propane at isoconversion reportedly decreased as follows: Mg₂V₂O₇ > MgV₂O₆ > Mg₃V₂O₈. The stability of V⁴⁺ ions associated with oxygen vacancies in magnesium pyrovanadate has been related to the high selectivity obtained for this phase [84].

Table 1.3 show the catalytic properties of the vanadate phases as well as V_2O_5 with respect to H-abstraction selectivity and oxygen insertion ability. The isolated VO₄ units are said to be responsible for the high selectivity associated with the orthovanadate phase. These isolated VO₄ units are separated from each other by MgO₆ units. The V⁵⁺ and Mg²⁺ are bridged by lattice oxygen atoms. The orthvanadate phase does not have V⁵⁺-O- V⁵⁺ groups which are associated with total oxidation and are typically present in the metavanadate and pyrovanadate phases [8].

Phase	Vanadium species	H-abstraction selectivity	Oxygen insertion power
Mg ₃ V ₂ O ₈ (Magnesium orthovanadate)	Isolated VO ₄	†	1
MgV ₂ O ₆ (Magnesium metavanadate)	Isolated VO ₆		
Mg ₂ V ₂ O ₇ (Magnesium pyrovanadate)	VO ₃ -O-VO ₃		
V ₂ O ₅ (Vanadium pentoxide)	VO ₂ -O-VO ₂		Ļ

 Table 1.3 Catalytic properties of vanadium based catalysts [8]

The report on selectivities of pyrovanadate and orthovanadate are at times, contradicting. This controversial subject suggests that one phase alone inadequately explains catalytic performance. The co-existence of orthovanadate phase, either with pyrovanadate phase or with

an excess of the magnesium oxide phase, is considered to give optimum catalytic performance [8].

Typically, physical mixing of V₂O₅ and MgO, followed by calcination is the easiest method to prepare magnesium vanadates [8]. Differential thermal analysis (DTA) studies have confirmed the formation of pure magnesium vanadates using physical mixtures, however, this synthesis results in a low surface area material [85]. To obtain high surface area materials, the preferred technique is impregnation [8]. Different synthetic methods for magnesium vanadates have been reported that influence the formation of different vanadate phases thus affecting the surface areas. To achieve this, magnesium precursors such as ammonium metavanadate, magnesium hydroxide [82], magnesium oxide [85] and magnesium oxalate were studied [86]. Kung and Kung [83] also used a method that included KOH in the synthesis of the magnesium vanadates to try and achieve a high surface area phase. They found that only the orthovanadate phase was formed in samples prepared without KOH, however a large amount of the pyrovanadate phase was observed in samples prepared with KOH, even though the aim was to prepare a pure orthovanadate phase. They found that residual potassium lowered the ODH selectivity, especially for reaction with butane.

VMgO has been analysed by XPS [32, 81] and the results show that magnesium and vanadium are present on the surface mainly as Mg^{2+} and V^{5+} species respectively. In the catalysts prepared by a citrate method, a small amount of reduced vanadium species, probably V^{4+} , was detected [87]. This is because the citrate method has been reported to form the pyrovanadate phase with a vanadia loading of more than 60 wt%, whereas those prepared by wet impregnation [32] contain the orthovanadate phase, however at much lower concentration of vanadia. The V^{5+}/V^{4+} surface atomic ratios were constant for catalysts prepared by both the citrate method and wet impregnation, indicating that the difference between this ratio on the surface and bulk compositions is probably small. A surface enrichment in magnesium was observed for catalysts with a vanadia content greater than 50 wt%. The surface composition and binding energies did not change after catalytic reactions, implying that the catalyst was stable.

Gao et al. [80] reported that the coexistence of magnesium orthovanadate and pyrovanadate phases or excess magnesium oxide during the ODH of propane can improve the selectivity to ODH products. The conversion and selectivity to propene obtained from the coexistence of magnesium pyrovanadate and metavanadate phases were typically from the metavanadate phase. Gao et al. concluded that the phase purity affects the catalytic behaviour of the vanadate

phase and one phase being present in the VMgO system is not enough to improve the catalytic performance.



Figure 1.12. Catalytic activity and selectivity over VMgO in the ODH of propane vs. V/Mg surface ratio. Symbols and reaction conditions as in Figure 1.10 [23].

Corma et al. [34] studied the effect of the V/Mg surface ratio on the catalytic behavior of VMgO catalysts in the oxidative dehydrogenation of propane. Figure 1.12 shows that the surface ratios had no impact on the selectivity to propene at constant conversion. They also reported that there is a relationship between the selectivity and surface oxygen energy; if the binding energy of the 1s orbital improves, the selectivity to propene also improves. Therefore, if the nucloephilicity of lattice oxygen is high, the catalyst will favour the ODH products of propane. The mixing of magnesium oxide and vanadium oxide forms a mixture of magnesium vanadates, viz magnesium orthovanadate (MgV₂O₆), depending on the method used in the preparation.

When ammonium vanadate reacts with magnesium hydroxide below 1173 K, the following phase transitions are possible [81]:

$$2\text{NH}_{4}\text{VO}_{3}(s) \rightarrow \text{V}_{2}\text{O}_{5}(s) + 2\text{NH}_{3}(g) + \text{H}_{2}\text{O}(g)$$

$$Mg(\text{OH})_{2}(s) \rightarrow MgO(s) + \text{H}_{2}\text{O}(g)$$

$$MgO(s) + \text{V}_{2}\text{O}_{5}(s) \rightarrow \alpha - Mg\text{V}_{2}\text{O}_{6}(s)$$

$$2MgO(s) + \text{V}_{2}\text{O}_{5}(s) \rightarrow \alpha - Mg\text{V}_{2}\text{O}_{7}(s)$$

$$3MgO(s) + \text{V}_{2}\text{O}_{5}(s) \rightarrow Mg3\text{V}_{2}\text{O}_{8}(s)$$

$$\alpha - Mg\text{V}_{2}\text{O}_{6}(s) \rightarrow \beta - Mg\text{V}_{2}\text{O}_{6}(s)$$

$$V_{2}\text{O}_{5}(s) \rightarrow \text{V}_{2}\text{O}_{5}(l)$$

$$2\beta - Mg\text{V}_{2}\text{O}_{6}(s) \rightarrow \alpha - Mg_{2}\text{V}_{2}\text{O}_{7}(s) + \text{V}_{2}\text{O}_{5}(l)$$

$$\alpha - Mg\text{V}_{2}\text{O}_{7}(s) \rightarrow \beta - Mg_{2}\text{V}_{2}\text{O}_{7}(s)$$

The oxygen atoms around the vanadium atom arrangement in these vanadate phases are shown in Figure 1.13.



Figure 1.13 The local environment of vanadium in (a) $Mg_3V_2O_8$, (b) α - $Mg_2V_2O_7$, (c) MgV_2O_6 and (d) V_2O_5 (distances are given in nanometres). The black spheres represent vanadium and the brown spheres represent oxygen (Redrawn from [81]).

The structure of α -Mg₂V₂O₇ has V₂O₇ units formed by corner–sharing VO₄ tetrahedra [8]. The V₂O₇ units form rows that have long vanadium–oxygen bridges within them (Figure 1.14) [41].

The V_2O_7 groups have the terminal oxygen atoms that are shared with two magnesium atoms, but the oxygen with the shortest bond (0.163 nm) is shared with one magnesium atom [8]. The pyrovanadate vanadium–oxygen bonds are less covalent than orthovanadate vanadium–oxygen bonds [81].



Figure 1.14 Structure of the magnesium pyrovanadate phase (α -Mg₂V₂O₇) [88].

The structure of MgV_2O_6 has VO_5 octahedra joined by bridges and connected together through MgO_6 octahedra (Figure 1.15) [89]. The bonds of vanadium and oxygen possess ionic character



Figure 1.15 Structure of the magnesium metavanadate phase (MgV₂O₆) [90].

Figure 1.16 shows the structure of $Mg_3V_2O_8$ which is made up of MgO_6 octahedral units sharing corners linked by isolated VO₄ tetrahedra [8]. Vanadium and magnesium atoms are bridged by oxygen atoms and all the oxygen atoms in the structure are involved in this bridging. The packing of oxygen atom layers in this structure is near cubic with the magnesium atoms in octahedral sites and the vanadium atoms in tetrahedral sites [91]. The bonding between vanadium and oxygen atoms are covalent.



Figure 1.16 Structure of the magnesium orthovanadate phase (Mg₃V₂O₈) [89].

Magnesium orthovanadates have shown to be good in converting alkanes to their respective alkenes and other products, but the behaviour of active sites and chemistry that occur on the oxide's surface is not well understood. In catalysis, there are inter-related parameters of composition that influence the reactivity, e.g. the crystal morphology and size. Large single crystals of magnesium orthovanadate are difficult to grow with the flux method because Mg₃ (VO₄)₂ does not melt uniformly [92, 93]. The flux method involve the heating of synthesised Mg₃ (VO₄)₂ at 1220°C and subsequent cooling to 1100 °C at 2°C h⁻¹. The material is further cooled to room temperature at 60°C h⁻¹. However, the crystals obtained with the flux method are too small (< 2 mm) to define it crystallographic orientation [92]. Pless et al. [91] reported the growth of large single crystals of magnesium orthovanadate by the optical floating zone technique. The peak positions of the diffraction patterns matched the calculated pattern taken from Krishnamacheri and Calvo [93]. The growth of single crystals were in the [010] direction and developed facets in the [201] direction during the crystal growth.

The structure of magnesium orthovanadate is similar to its reduced phase, $Mg_3V_2O_6$ [92, 93]. The oxide surface can undergo multiple redox cycles, where the cation deficient spinel, $Mg_3V_2O_6$ can be formed, under reduction conditions with hydrogen [92]. During this reduction, there is a migration of vanadium atoms from tetrahedral sites to octahedral interstices, where the octahedral magnesium atoms rearrange to equally occupy the tetrahedral and octahedral sites [92, 93].



Figure 1.17 Comparison of magnesium orthovanadate and pyrovanadate and other metal oxides for propane conversion [8].

The catalytic performance of the orthovanadate phase and pyrovanadate phase in comparison to other vanadia catalytic systems are shown in Figure 1.17 for the oxidative conversion of propane. Comparing the orthovanadate and pyrovanadate phases from the graph, the pyrovanadate phase shows a higher conversion, but lower selectivity. The orthovanadate phase is already in a partially reduced state, hence its oxygen species would be likely nucleophilic compared to the pyrovanadate oxygen species, therefore it is reported to be more selective towards propene [94].

Some catalytic processes have been known to be structure sensitive, which influences the catalytic activity and selectivity [95]. The change of the structure of the catalyst depends on the method used for the preparation. The structure sensitivity on ethylene to ethylidyne conversion has been studied by comparing the chemical reactivity of single crystal platinum (Pt) exposed surfaces with different orientations [96, 97]. These studies were also extended to catalytic rate measurements using pressure cells [98-100]. The sintering of nanoparticles limited study of the surface of the material in terms of structural shape evaluation, as a result, the idea of metal nanoparticles dispersed on a model oxide surface was implemented [99, 101].


Figure 1.18 Onset temperature for 2-propanol oxidation over Pt nanoparticles (NPs) dispersed on a γ -Al₂O₃ nanocrystalline support versus the average number of missing bonds at the nanoparticle (NP) surface, calculated by using the idealized model shapes shown in the insets [102].

Mostafa et al. [103] worked on platinum with similar size distribution, around 1 nm in diameter, but with different shapes. These prepared nanoparticles were dispersed on a γ -alumina support. The summary of the different shapes is shown in Figure 1.18. The catalytic activity of these nanoparticles was tested for 2-propanol oxidation. The conclusion from the study showed that un-coordinated Pt atoms are the most active sites for 2-propanol oxidation. The effect of surface structure and nanoparticle shape of platinum was also investigated on selectivity associated with the isomerisation of olefins, shown in Figure 1.19 [95]. The TEM images and isomerisation conversion graphs conclude that the tetrahedral platinum particles favour the cisisomer, while more rounded particles display a reverse selectivity towards the trans-isomer [95, 104].



Figure 1.19 Kinetic catalytic data and TEM images showing the correlation that exists between the structure (shape) of platinum nanoparticles and their selectivity in alkene *cis*-trans isomerization conversions [104].

The physical properties of various MgO morphologies have been reported, but for Claison-Schmit reactions, involving benzaldehyde with acetophenone [104]. Table 1.4 summarises how varying the MgO morphologies resulted in catalysts with different surface areas and crystallite sizes, which ultimately impacted on catalytic performance. It is clear from the data that the morphology does impact such characteristics as surface area, but may also influence other characteristics, such as acid-base properties.

Morphology	Surface area (m^2/g)	Crystallite size (nm)	^a Yield (%)
Rod	115	6	99
Big flowers	82	7	99
House of cards	91	6	97
Small flowers	87	6	94
Random flowers	97	6	96
Spheres	62	8	83
Cubes	33	9	57
Plates	75	7	89
Bulk	28	27	23

Table 1.4 Textural and catalytic properties of synthesized MgO with various morphologies

 [104].

^a Yield of 1,3-diphenyl propenone in Claisen-Schmidt condensation.

Li *et al.* [105] studied the oxidation of benzyl alcohol to benzaldehyde using gold (Au) supported on nanoactive MgO and nano-sheet MgO (111) with surface areas of 230 and 146 m^2/g , respectively. When Au was added to the support, the surface areas reduced to 74 and 33 m^2/g for nanoactive Au/MgO and nanosheet Au/MgO (111), respectively. The catalytic results for this study are shown in Table 1.5. Due to similar lattice constants of Au (111) and MgO (111) planes, the interaction of Au with nanosheet MgO influenced the activity and selectivity towards benzaldehyde more significantly compared to nanoactive Au/MgO. The high activity of Au/MgO (111) is due to the partial removal of the hydrogen passivation from the MgO(111) support (which has significant hydroxyl coverage), as well as to the electronic transfer that occurs at the Au–MgO (111) interface. The former showed higher conversion at all temperatures studied, however, selectivity decreased as the conversion increased because of the over oxidation of benzyl alcohol.

Temperature	Catalyst	Conversion (mol%)	Selectivity to
(°C)			benzaldehyde (mol%)
100	MgO (nano-active)	1.03	80.62
	MgO (nano-sheet)	1.21	83.21
	Au/MgO (nano-active)	1.17	70.45
	Au/MgO (nano-sheet)	6.55	92.96
120	MgO (nano-active)	2.89	80.47
	MgO (nano-sheet)	3.12	82.01
	Au/MgO (nano-active)	3.05	78.21
	Au/MgO (nano-sheet)	14.71	82.44
140	MgO (nano-active)	3.71	82.14
	MgO (nano-sheet)	3.62	76.37
	Au/MgO (nano-active)	3.59	76.84
	Au/MgO (nano-sheet)	17.23	56.66

Table 1.5 Comparative data for oxidation of benzyl alcohol over Au supported on different morphologies of MgO [105].

^a MgO materials were subjected to the same procedure as the Au/MgO catalysts, but without gold

1.6 *n*-Octane oxidative dehydrogenation over vanadium supported catalysts

The challenge with the long chain paraffins is to obtain a high selectivity to value added products at high conversions. Therefore there is the tendency to use temperatures in the range 450-500°C to achieve low conversions, thus maintaining high selectivity towards value added products [3].

Many studies have been carried out on *n*-octane oxidative dehydrogenation over vanadium supported catalysts. Mahomed and Friedrich [106] have studied the oxidative dehydrogenation of *n*-octane to styrene using catalysts derived from hydrotalcite-like precursors. The Mg and V hydrotalcite-like compounds were prepared with different Mg/V ratios, ranging from 1:1 to 4:1. Various synthetic procedures were used to investigate the effect of precipitating agents and temperatures. Styrene was the dominant product and the best results were obtained with a Mg/V ratio of 2:3 giving a 19 % selectivity, corresponding to 14 % yield. The catalyst synthesized from sodium salts performed better, compared to those synthesised from potassium salts.

Dasireddy et al [12] studied the activation of *n*-octane over supported vanadium alkaline earth hydroxyapatites. The wet impregnation method was used to support vanadium pentoxide on calcium, strontium, magnesium and barium hydroxyapatite with 2.5 and 10 wt% loadings. The XRD and IR analyses showed the vanadium pentoxide phase for both loadings but the 10 wt% loading had an additional pyrovanadate phase present. The catalysts were tested for the oxidative dehydrogenation of *n*-octane. The phase composition of the catalyst as well as the optimum *n*-octane to oxygen molar ratio were reported to be responsible for the selectivity towards the desired products. The selectivity towards aromatics and octenes were obtained for a *n*-octane to oxygen molar ratio of 1:0.5, whereas for aromatics and oxygenates it was obtained at 1:2 [11]. The 2.5 wt% V₂O₅ loaded hydroxyapatite catalyst gave a high selectivity towards octenes, whereas the 10 wt% loaded catalyst showed a decrease in octenes selectivity and a significant increase towards aromatics.

Elkalifa and Friedrich [82] studied the oxidative dehydrogenation of *n*-octane using vanadiummagnesium oxide catalysts with different vanadium loadings, prepared by the wet impregnation method. The loadings of vanadia were: 5, 15, 25 and 50 wt%. Both textural and chemical properties of the catalysts were reported to be affected by the vanadia concentration. The vanadia concentration also affected the catalytic activity and selectivity towards the desired products (octenes and aromatics). The crystalline $Mg_3V_2O_8$ phase was observed with all vanadia loadings, while crystalline $Mg_2V_2O_7$ was only observed with 50 wt% vanadia loading. A 15 % vanadia loading was found to have the best catalytic activity and selectivity towards the desired products, especially towards 1-octene and styrene. This confirmed that the orthovanadate phase was selective towards the desired products in coexistence with magnesium oxide. The vanadia loadings with more than 15 wt% resulted in a catalyst with V₂O₅, orthovanadate and pyrovanadate phases. The used catalyst did not show any phase changes.

In another study, the oxidative dehydrogenation of *n*-octane was carried out using 15 % vanadia supported on magnesium oxides obtained from different precursors (MgC₂O₄ and Mg(OH)₂) and different precursor treatments (under vacuum and under static air) [107]. Different MgO precursors and precursor treatment led to changes in morphology, crystallite size, vanadium dispersion, reducibility and surface acidity of the resultant VMgO catalysts. The performances of the catalysts were also different [107]. The catalysts were reported to consist of magnesium oxide and magnesium orthovanadate phases only. Different MgO precursors led to the manifestation of a different orthovanadate phase. The orthovanadate phase with rough surfaces was reported to favour ODH products [107].



Figure 1.20 Scheme showing the pathway for various products formed from the nucleophilic and electrophilic oxidation of octane.

1.7 Aim of the study

The aim of this study was to synthesise 15 wt% vanadium loaded catalysts with different morphologies of the support (MgO). These catalysts were then used to obtain the corresponding octenes and aromatics from *n*-octane via ODH. It is believed that a variation in the morphology of MgO by using different synthetic methods can influence the surface properties and thus improve catalytic activity and selectivity of the corresponding VMgO catalysts.

References

- G. Centi, F. Cavani, and F. Trifiro, Selective Oxidation by Heterogeneous Catalysis, Kluwer Academic / Plenum Publishers, New York, (2001) 1-4.
- 2. M. Baerns and O. Buyevskaya, Catal. Today. 45 (1998) 13-22.
- 3. J. Haber and W. Turek J. Catal. 190 (2000) 320–326.
- 4. V.D.B.C. Dasireddy, Ph.D Thesis, University of KwaZulu-Natal, South Africa, 2012.

- D. Olaf, H. Knözinger, K. Kochlefl and T. Turek, *Heterogeneous and solid catalysis*, Ullmann's Encyclopedia of Industrial Chemistry (2009).
- 6. F. Cavani and F. Trifiró, Catal. Today, 34 (1997) 269-279.
- 7. F. Cavani and F. Trifirò, Appl. Catal. 88 (1992) 115-135.
- 8. J. Chetty, Ph.D Thesis, University of KwaZulu-Natal, South Africa, 2006.
- 9. M.D. Chaar, D. Patel and H. Kung, J. Catal. 109 (1988) 463-467.
- 10. R. Valenzuel, E. Mamodov and V.C. Corberan, Catal. Lett. 55 (1995) 213-220.
- 11. L. Owens and H. Kung, J. Catal. 162 (1996) 250-259.
- 12. V.D.B.C. Dasireddy, S. Singh and H.B. Friedrich, Appl. Catal. 456 (2013) 105-117.
- 13. E.A. Elkhalifa and H.B. Friedrich. J. Mol. Catal. A: Chem., 392 (2014) 22-30.
- 14. S.J. Conway and J.H. Lunsford, J. Catal. 131 (1991) 513-522.
- 15. M. Huff and L.D. Schmidt, J. Phys. Chem. 97 (1993) 11815-11822.
- E.M. Thorsteinson, T.P. Wilson, F.G Young and P.H. Kasai, J. Catal. 52 (1978) 116-132.
- 17. R. Burch and R. Swarnakar, Appl. Catal. 70 (1991) 129-148.
- 18. O. Desponds, R.L. Keiski and G.A. Somorjai, Catal. Lett. 19 (1993) 17-32.
- 19. M. Ilhan and T. Dogu, Chem. Eng. Com. 93 (1995 1-12.
- 20. S. Onen, PhD Thesis, Middle East Technical University, Turkey, 1997.
- 21. S.A Al-Ghamdi, PhD thesis, The University of Western Ontario, London, 2013.
- 22. C.F. Baes and R.E. Mesmer, The hydrolysis of cations, Wiley, 1976.
- 23. E. Mamedov and V.C. Corberan, Appl. Catal. A, 127 (1995)1-40.
- M.S. Wilsona, F.H. Garzona, K.E. Sickafusb and S. Gottesfelda, J. Electrochem. Soc. 140 (1993) 2872.
- B. Solsona, A. Dejoz, M.I. Vazquez, F Marquez and M.J. Lopez Nieto, Appl. Catal. 208 (2001) 99-110.
- J.J.H.B. Sattler, J. Ruiz-Martinez, E. Santillan-Jimenez, and B.M. Weckhuysen, Chem. Rev. 114 (2014) 10613-10653.
- 27. T. Blasco and J.M. Lopez Nieto, Appl. Catal. A, 157 (1997) 117.
- 28. C.H. Bamford and C.F.H. Tipper, Complex Catalytic Processes, 20 (1978) 114-121.
- 29. G.C. Bond, Platinum Metals Rev. 27 (1983) 16.
- 30. S. Albonetti, F. Cavani and F. Trifiro, Catal. Rev. Sci. Eng. 38 (1996) 413.
- 31. M.S. Wainright and N.F. Foster, Catal. Rev. Sci. Eng. 19 (1979) 211.
- 32. D.B. Dadyburjor, S.S. Jewur and E. Ruckenstein, Catal. Rev. Sci. Eng. 19 (1979) 293.

- 33. L.M. Madeira and M.F. Portela, Catal. Rev. Sci. Eng. 44 (2002) 247.
- A. Corma, J.M. Lopez Nieto, N. Paredes, M. Perez, Y. Shen, H. Cao and S.L. Suib, Stud. Surf. Sci. Catal. 72 (1992) 213.
- 35. J. Eon, R. Olier and J. Volta, J. Catal. 145 (1994) 318-326.
- 36. P.P. De Oliveira, J Eon and J. Volta, J. Catal. 137 (1992) 257-266.
- K. Tanabe, Solid Acids and Bases: Their Catalytic Properties, Kodansha, Tokyo, Academic press, New York and London, Elsevier, 2012.
- T. Lindblad, B Rebenstorf, Z. Yan and S.L.T. Andersson, Appl. Catal. A: 112 (1994) 187-208.
- 39. C.L. Yan, D. Xue, L Zou, X Yan and W. Wang, J. Cryst. Growth. 282 (2005) 448.
- Y.S. Ding, X.F. Shen, S. Gomez, H. Luo, M. Aindow and S. L. Suib, Adv. Funct. Mater. 16 (2006) 549.
- 41. F. Zhou, X. Zhao, H. Xu and C. Yuan, J. Phys. Chem. C 111 (2007) 1651.
- 42. T. He, D.R. Chen, X.L. Jiao and Y.L. Wang, Adv. Mater. (2006), 1078.
- 43. G. Zhang, X. Lu, W. Wang and X. Li, Chem. Mater. 19 (2007) 5207.
- L.S. Zhong, J.S. Hu, A. Cao, Q. Liu, W. Song and L. Wan, J. Chem. Mater. 19 (2007) 1648.
- 45. L.S. Zhong, J.S. Hu, A. Cao, Q. Liu, W. Song and L. Wan, J. Adv. Mater. 18 (2006), 2426.
- 46. J.B. Fei, Y. Cui, X.H. Yan, W. Qi, Y. Yang, K.W. Wang, Q. He and J.B. Li, Adv. Mater. 20 (2008) 452.
- 47. M. Cao, X. He, J. Chen and C. Hu, Cryst. Growth Des.7 (2007) 170.
- 48. B. Liu and H.C. Zeng, J. Am. Chem. Soc. 126 (2004) 8124.
- 49. V. Subramanian, H. Zhu, R. Vajtai, P. M. Ajayan, and B. Wei, J. Phys. Chem. B 109 (2005) 20207.
- 50. W.N. Li, J. Yuan, X.F. Shen, S. Gomez-Mower, L.P. Xu, S. Sithambaram, M. Aindow and S. L. Suib, Adv. Funct. Mater. 16 (2006) 1247.
- 51. W.C. Li, A.H. Lu, C. Weidenthaler and F. Schuth, Chem. Mater. 16 (2004) 5676.
- 52. A. Subramania, G.V. Kumar, A.R.S. Priya and T. Vasudevan, Nanotechnology, 18 (2007) 225601.
- 53. S. Makhluf, R. Dror, Y. Nitzan, Y. Abramovich, R. Jelinek and A. Gedanken, Adv. Funct. Mater. 18 (2005) 1708.
- X.S. Fang, C.H. Ye, L.D. Zhang, J.X. Zhang, J.W. Zhao and P. Yan, P. Small 1 (2005) 422.

- 55. S. Stankic, M. Muller, O. Diwlad, M Sterrer, E Knözinger and J. Barnardi, J. Angew. Chem., Int. Ed. 44 (2005) 4917.
- M. Zhao, X.L. Chen, W.J. Wang, Y.J. Ma, X.P. Xu and H.Z. Zhao, Mater. Lett. 60 (2006) 2017.
- 57. K.K. Zhu, D. Wang and J. Liu, Angew. Chem., Int. Ed. 45 (2006) 7277.
- 58. M.S. Mastuli, N. Kamarulzaman, M.A. Nawavi, A.M. Mahat, R. Rusdi and N. Kamarudin, Nanoscale Res. Lett. 9 (2014) 134.
- 59. B. Jonson, B. Rebenstorf, R. Larsson and S.T. Andersson, J. Chem. Soc., Farad. Trans.1: Phys. Chem. Cond. 84 (1988) 1897-1910.
- 60. J. Le Bars, J.C. V6dilne, A. Auroux, S. Trautmann and M. Baerns, Appl. Catal. A, 88 (1992) 179.
- 61. M. Nabavi, F. Taulelle, C. Sanchezand M. Vergagver, J. Phys. Chem. Sol. 51 (1990) 1375-1382.
- 62. B.M. Weckhuysen and D.E. Keller, Catal. Today, 78 (2003) 25-46.
- 63. S.T. Oyama, J. Catal. 128 (1991) 210-217.
- B. Taouk, M. Guelton, J. Grimblot and J. P. Bonnelle, J. Phys. Chem. 92 (1998) 6700-6705.
- 65. I.E. Wachs, Catal. Today, 27 (1996) 437-455.
- N. Das, H. Eckert, H. Hu, I. E. Wachs, J. F. Walzer and F. J. Feher, J. Phys. Chem. 97 (1993) 8240-8243.
- 67. M. Schraml-Marth, A. Wokaun, M. Pohl and H.L. Krauss, J. Chem. Soc., Faraday Trans. 87 (1991) 2635-2646.
- N.K. Nag, K.V.R. Chary, B.R. Rao and V.S. Subrahmanyam, Appl. Catal. 31 (1987) 73-85.
- F. Roozeboom, M. C. Mittelmeijer-Hazeleger, J. A. Moulijn, J. Medema, V. H. J. De Beer and P. J. Gellings, J. Phys. Chem. 84 (1980) 2783-2791.
- 70. S.T. Oyama and G.A. Somorjai, J. Phys. Chem. 94 (1990) 5022-5028.
- A. Dinse, B. Frank, C. Hess, D. Habel and R. Schomacker, J. Mol. Catal. A: Chem. 289 (2008) 28-37.
- J. Kijenski, A. Baiker, M. Glinski, P. Dollenmeier and A. Wokaun, J. Catal. 101 (1986)1-11.
- 73. X. Rozanska, R Fortrie and J. Sauer, J. Phys. Chem.C, 111 (2007).

- L. Balders-Tapia, I. Hernandez-Perez, P. Schacht, I.R. Cordova and G.G. Aguilar-Rios, Catal. Today, 107 (2005) 371-376.
- R. Grabowski, B. Grzybowska, K. Samson, J. Sloczynski, J. Stoch and K. Wcislo, Appl. Catal. 125 (1995) 129-144.
- 76. A. Satsuma, A. Hattori, K. Mizutani, A. Furuta, A. Miyamoto, T. Hattori, Y. Murakami,J. Phys. Chem. 92 (1988) 6052-6058.
- 77. G.C. Bond and S.F. Tahr, Appl. Catal. 71 (1991) 1-31.
- 78. G. Bond, Appl. Catal. 157 (1997) 91-103.
- 79. J. Haber, A. Kozlowska and R. Kozlowski, J. Catal. 102 (1986) 52-63.
- 80. X. Gao, P. Ruiz, Q. Xin, X.X. Guo, B. Delmon, J. Catal. 148 (1994) 56-67.
- 81. D.S.H. Sam, V. Soenen and J. Volta, J. Catal. 123 (1990) 417-435.
- 82. E.A. Elkalifa and H.B Friedrich, Appl. Catal. 373 (2010) 122-131.
- 83. H.H. Kung and M. Kung, Appl. Catal. A, 157 (1997) 105.
- 84. S. Sugiyama, T. Hashimoto, N. Shigemoto, H. Hayashi, Catal. Lett. 89 (2003) 3-4.
- 85. A. Corma, J.M. Lopez Nieto N.J. and Paredes, J. Catal. 144 (1993) 425.
- 86. M.D. Chaar, D. Patel, M.C. Kung and H.H. Kung, J. Catal. 105 (1987) 483.
- 87. C.T. Au, W.D. Zhang and H.L. Wan, Catal. Lett. 37 (1996) 241-246.
- R. Gopal and C. Calvo. Acta Crystal. Section B: Structural Cryst. Cryst. Chem. 30 (1974) 2491-2493.
- 89. W. Oganowski, J. Hanuza and L. Kepiński, Appl. Catal. 171 (1998), 145-154.
- 90. H.N. Ng and C. Calvo, Canadian J. Chem. 50 (1972) 3619-3624.
- 91. J.D. Pless, N. Erdman, D. Ko, L. D. Marks, P. C. Stair, and K. R. Poeppelmeier, Cryst. Growth and Design, 3 (2003) 615-619.
- 92. P.R. Shah, J.M. Vohs, and R.J. Gorte, J. Phys. Chem. 111 (2007) 5680-5683.
- 93. N.T. Krishnamachari and C. Calvo, Canadian J. Chem. 49 (1971) 1629-1637.
- 94. W.S. Chang, Y.Z. Chen and B.L. Yang, Appl. Catal. A: Gen. 124 (1995) 221-243.
- 95. F. Zaera, Catal. Lett. 142 (2012) 501-516.
- 96. F. Zaera, Prog. Surf. Sci. 69 (2001) 1-98.
- 97. G.A. Somorjai, Introduction to Surface Chemistry and Catalysis 2nd Ed. Wiley, New York (2010) 5-27.
- F. Zaera and G.A. Somorjai, Surface Science Series Vol. 23, M.J. Schick, Ed., Marcel Dekker, Inc., New York, 425 (1988) 425-441.
- 99. C.T. Campbell, Adv. Catal. 36 (1989) 1-54.

- 100. J.A. Rodriguez and D.W. Goodman, Surf. Sci. Rep. 14 (1991) 1.
- 101. H.J. Freund, Chem. Eur. J. 16 (2010) 9384–9397.
- 102. J. Croy, S. Mostafa, J. Liu, Y. Sohn, B. R. Cuenya, Em. Catal. Lett. 118 (2007) 1-7.
- S. Mostafa, F. Behafarid, J. R. Croy, L. K. Ono, L. Li, J. C. Yang, A. I. Frenkel, and B. R. Cuenya, J. Am. Soc. 132 (2010) 15714-15719.
- 104. F. Zaera, Acc. Chem. 42 (2009) 1152-1160.
- Z. Li, C. V. Ciobanu, J. Hu, J.P. Palomares-Báez, J.L. Rodríguez-López and R. Richards, Phys. Chem. Chem. Phys. 13 (2011) 2582-2589.
- 106. H.B. Friedrich and A.S. Mahomed, Appl. Catal. 347 (2008) 11-22.
- 107. E.A. Elkalifa and H.B Friedrich, Appl. Catal. 392 (2014) 22-30.

CHAPTER TWO EXPERIMENTAL

2.1 Preparation of catalyst supports

2.1.1 Cubic magnesium oxide

The procedure used is similar to that previously reported by Elkhalifa and Friedrich [1]. A brief description of the preparation of the material involves heating a magnesium acetate solution (53.3 g in one litre of distilled water) in a 2000 mL beaker to 50°C using a hot plate. Thereafter, a stoichiometric amount of hot aqueous solution of oxalic acid (31.52 g in 800 ml) was added slowly, with stirring for 30 minutes, to obtain a precipitate of MgC₂O₄. The magnesium oxalate precipitate was filtered off and washed thoroughly with 20 mL of cold followed by 20 mL of hot water, placed in an oven set at 110°C and left to dry for 12 hours. The dry magnesium oxalate was calcined at 550°C for 6 h and the resulting material was labelled MgO-A.

2.1.2 Spherical magnesium oxide

The procedure used is a treatment of commercial MgO with citric acid according to a method reported previously [2]. Citric acid (13.2 g) was added to 500 mL of distilled water and stirred until the citric acid was completely dissolved. The MgO (12.7 g), purchased from Hopkin and Williams Ltd. England, was added to the citric acid solution slowly while stirring and left to stir continuously for an hour at 70°C to reduce the amount of water. The mixture was filtered and washed with 20 mL of cold water followed by 20 mL of hot water. The mixture was then placed in the oven set at 110°C for 24 h and thereafter, calcined at 550°C for 6 h. The white powder was labelled MgO-B.

2.1.3 Nano-sheet magnesium oxide

The MgO (111) nanosheets were prepared by a modified sol–gel method [3] using 4-methoxyl- α -methyl-benzyl alcohol to direct the formation of the (111) facet. In a typical synthesis, 1.0 g of thoroughly cleaned (using sand paper) Mg ribbon was suspended in absolute methanol overnight under the protection of an argon atmosphere to form magnesium methoxide. Then,

2.32 g of 4-methoxyl- α -methyl-benzyl alcohol was slowly added to the methoxide solution with continuous stirring for 5 hours, before the addition of a mixture of 1.48 mL H₂O and 30 mL methanol. After a further 7 hours of stirring, the solution was transferred to a closed Teflon container and dried by heating to 110°C for 3 days. The obtained aerogel was calcined for 6 hours at 550°C to remove the OH groups. This support material was labelled MgO-C.

2.2 Preparation of vanadium magnesium oxide

The magnesium oxide supports, viz. MgO-A, MgO-B and MgO-C were loaded with 15 wt% vanadium by wet impregnation. A solution of ammonium metavanadate (0.799 g) dissolved in an aqueous solution of oxalic acid (5.5 g in 200 mL distilled water) was added to the respective magnesium oxide support (5.296 g), while stirring. The mixture was continuously stirred and heated at 100°C to evaporate water until a paste formed. The paste was dried in an oven set at 110°C overnight and calcined for 6 h at 550°C obtaining VMgO-A, VMgO-B and VMgO-C. An additional catalyst was prepared using water instead of oxalic acid. Here, ammonium metavanadate (0.799 g) was placed in double distilled water (1000 mL) and heated up to 70°C with stirring, until all the ammonium metavanadate dissolved. This solution was added to a prepared paste of the spherical magnesium oxide, i.e. MgO-B. The mixture was stirred and heated to 100°C to evaporate excess water until a paste formed. The paste was dried in an oven at 110°C overnight and calcined for 6 h at 550°C. The resulting material was labelled VMgO-B-water.

2.3 Catalyst characterization

2.3.1 Infrared spectroscopy

Infrared spectra were obtained using a PerkinElmer Spectrum 100 FT-IR Spectrometer fitted with a Universal ATR Sampling Accessory. A small amount of the powdered catalyst was placed on top of the ATR crystal (composite of zinc selenide and diamond) and a pressure of about 120 Gauge was applied to allow for better contact between the sample and crystal.

2.3.2 Powder X-ray diffraction

X-ray diffractograms were obtained using a Philips 1370/1 instrument operating at 40 kV and 25 mA Co K α radiation on a long line focus (no filter). All data were captured by a Sietronics 122D automated microprocessor. The generator tension and current were 40 kW and 30 mA, respectively and the irradiated length was 12 mm. Samples were scanned in the 5 to 70° 2 θ range at room temperature for 80 min.

2.3.3 Raman spectroscopy

The computer-controlled laser Raman equipped with a monochromator and a back thinned mutli pinned mode (MPP) type charged couple device (CCD) was used. The laser was set to a wavelength of 480 nm and an output level of 75 mW was used as an excitation source. The focus of the laser beam in conjunction with the CCD (70 % quantum yield) provided a spatial resolution of 0.6–0.8 μ m [4]. The sample was placed on a precision X–Y stage and clamped to stay stable during the analysis. An optical microscope allowed for visual identification of the position from which the signal was obtained. The laser beam was focused on the sample surface with a 100X microscope objective taking care to avoid resin tags, which would disturb the measurement. The sample was moved perpendicular to the resin–bonding agent interface in steps of 0.2 μ m, and the spectra were obtained at each position across the dentin–adhesive interface with an integration time of 45 seconds for each measurement. The measurements were done three times per sample [4].

2.3.4 Scanning electron microscopy

A small portion of the sample was mounted directly onto an aluminium stub that was covered with double-sided carbon tape. The sample was then coated with gold and transferred directly into the microscope for analysis. A Zeiss ULTRA 55 instrument was used for analysis and imaging was performed at 3 kV. The working distance was set at approximately 5 mm and a 30 μ m aperture was used for the analysis. Images were obtained at different regions and at various magnifications.

2.3.5 Inductively coupled plasma-optical emission spectroscopy

The elemental composition of the catalysts was determined by inductively coupled plasmaoptical emission spectroscopy (ICP-OES) using an Optima 5300 DV PerkinElmer Optical Emission Spectrometer. Standards (1000 ppm Mg and V), purchased from Fluka were used to prepare (by dilution) the standards ranging from 0.5 to 100 ppm. These standards were used to obtain the calibration graphs from ICP-OES analysis, which was done in triplicate. The VMgO samples for ICP-OES analysis were prepared by digesting the powder (0.02146 -0.02574 g) using 15 mL of concentrated sulfuric acid in a 50 mL beaker. A watch glass was placed over the beaker which was heated on a hot plate to approximately 350°C.

2.3.6 BET surface studies

Nitrogen physisorption analyses were performed on a Micromeritics ASAP 2420 instrument. The samples were accurately weighed (250 - 300 mg), loaded in the glass tube and degassed under nitrogen at 90°C for a minimum of 1 hour, thereafter at 150 °C for an hour. The samples were then heated under nitrogen at 200 °C overnight. After degassing, the samples were weighed to correct for the change in mass. Measurements were carried out with nitrogen adsorbate at -195°C and nitrogen adsorption and desorption isotherms were recorded over a nitrogen pressure range using a preset range of relative pressures, p/po, ranging from 0.02 to 0.98. The surface area was calculated by applying the linearized Brunauer-Emmet-Teller (BET) equation to the data between $0.05 < p/p_o < 0.30$. Total pore volume, average pore diameter and pore size distribution (PSD) of the materials were determined using the Barrett-Joyner-Halenda (BJH) theory on the desorption branch of the nitrogen sorption isotherm. This theory assumes that all pores are shaped as round cylinders.

2.3.7 Temperature programmed analyses

A Micromeritics 2900 AutoChem II Chemisorption Analyzer was used for temperatureprogrammed reduction (TPR) and NH₃-temperature-programmed desorption (TPD) experiments. Before reduction, the catalyst was pretreated at 400°C under a stream of Ar (30 mL/min) for 30 min and then cooled to 80°C still under Ar. For the TPR experiment, 5% H₂ in Ar was used as the reducing agent at a flow rate of 50 mL/min. To account for the difference in vanadium concentrations across the catalysts, different weights were used in the analysis (18–94 mg). The temperature was ramped to 950°C at a rate of 10°C/min. In the TPD experiments, the catalyst was pretreated under a stream of He at 350°C for 60 min. The temperature was then decreased to 80°C and a mixture of 4.1 % ammonia in He at a flow rate of 30mL/min was passed over the catalyst for 60 min. The excess ammonia was removed by purging with He for 30 min. The temperature then was raised to 950°C by ramping at 10°C/min under the flow of He and desorption data was recorded.

2.4 Catalytic testing

Oxidative dehydrogenation reactions of *n*-octane over various catalysts were carried out in a continuous flow fixed bed reactor (down flow mode). The catalysts were placed in a stainless steel reactor tube with an internal diameter of 10 mm and a length of 220 mm. The catalyst with a volume of 1 mL was sandwiched between layers of glass wool and the void spaces in the tube were filled with carborundum. The pellet size of the catalyst ranged between 300 µm and 600 µm. The reactor tube was heated with an electrically heated block, equipped with a temperature controller and a thermocouple. The catalyst bed temperature was controlled with a centred thermocouple which was placed in the middle of the catalyst bed. The *n*-octane concentration in the gaseous mixture was 7% (v/v) and the molar ratio of carbon to oxygen was 8: 2. Air was used as the oxidant and nitrogen as the make-up gas to give a total flow of 100 mL/min. The *n*-octane was delivered to the system by an HPLC pump. The unreacted octane and liquid products were collected in a catchpot which was cooled to ca 2.5°C. The volume of the gaseous effluent was measured by a Ritter drum-type gas meter. All products were analyzed, off line, using a gas chromatograph (PerkinElmer Clarus500) equipped with both FID and TCD. The TCD was used for carbon oxides, hydrogen and oxygen analyses and the FID for all the other products in both the gaseous and liquid phase.

References

- 1. E.A. Elkhalifa and H.B. Friedrich, Appl. Catal. A, 373 (2010) 122-131.
- 2. X. Gao, P. Ruiz, Q. Xin, X. Guo and B. Delmon, Catal. Lett. 23 (1994) 321-337.
- Z. Li, C. V. Ciobanu, J. Hu, J. Palomares-Báez, J. Rodríguez-López and R. Richards, Phys. Chem. Chem. Phys. 13 (2011) 2582-2589.
- 4. M.H. Miyazaki, Dent. Mater. 18 (2002) 576-580.

CHAPTER THREE CATALYST CHARACTERIZATION

In this chapter, the characterisation of the various forms of magnesium oxides that were synthesised and the subsequent vanadium magnesium oxides prepared from them is discussed using various physico-chemical techniques. This was done in an effort to establish the success of the synthesis methods used and to determine the microstructure of the materials synthesised. Ultimately, the characterisation techniques that were carried out were necessary to help us understand how the catalytic behaviour could be correlated to the physical structure and chemical composition of the catalysts prepared. The techniques included XRD, IR, Raman, SEM, TEM, physisorption studies and temperature programmed methods, as well as ICP-OES.

3.1 Powder X-ray diffraction

Figure 3.1 shows the XRD pattern of magnesium oxide obtained from the calcination of the three different magnesium precursors. MgO–A (cubic) was obtained from the magnesium oxalate precursor, MgO–B (spherical) from magnesium citrate and MgO–C (nano-sheets) from the magnesium 4–methoxy– α –methylbenzyl alcohol method of preparation.



Figure 3.1 XRD diffractograms of (a) MgO-A, (b) MgO-B, and (c) MgO-C supports.

The diffractograms of all three support materials show three dominant peaks attributed to pure magnesium oxide, found at 36.5°, 44.2° and 62.5°, corresponding to the crystal planes (111, 200 and 220) respectively [1]. In addition, Figure 3.1 suggests that essentially pure magnesium oxides were synthesised since there were no additional peaks and phases belonging to magnesium precursors that were observed. MgO–B gave shaper peaks than the other systems, followed by MgO–C and then MgO-A. It can also be characteristic of materials with different lattice strain, which could be caused by the lattice dislocation due to the finite growth of the crystal [2].



Figure 3.2 XRD diffractogram of vanadium magnesium oxide catalysts.

The XRD diffractograms of 15 wt% loading of vanadium on the magnesium oxide supports are shown in Figure 3.2. The major peak for the magnesium orthvanadate phase was observed for VMgO-A and VMgO-C at 20 equal to 35° and minor peak for magnesium orthovanadate phase was observed at 20 equal to 37.5° [3, 4]. On the other hand the major peak for the magnesium orthovanadate phase was observed for VMgO-B-water at 20 equal to 37.5°. This suggest that VMgO-B-water is dominated with the magnesium orthovanadate that has a different orientation compared to VMgO-A and VMgO-C. Therefore, catalytic results for VMgO-B-water are expected to be comparable to those of VMgO-A and VMgO-C. For VMgO-C, the vanadate peaks were of low intensity suggesting very small particles of this phase. On the other hand, the vanadate peaks for VMgO-B-oxalic were not observed suggesting that the vanadate phases formed, could be amorphous. The peaks characteristic of

magnesium oxide were also observed for all the supports, at 2θ angles of 44.2° and 62.5° [3, 4].

3.2 Infrared spectroscopy

Figure 3.3 presents the FT–IR spectra for MgO–A, MgO-B and MgO-C. Each has a barely visible peak from 3332 - 3701 cm⁻¹ range, showing O-H stretching for physisorbed water on the surface of the material [5]. The peaks for hydroxyl bending, bonded on the surface of the material were observed at 1426 cm⁻¹, 1440 cm⁻¹, and 1409 cm⁻¹ for MgO–A, MgO-B and MgO-C respectively [5]. The magnesium oxygen vibration band appeared between 865-650 cm⁻¹ in all the synthesised materials [5].



Figure 3.3 IR spectra for magnesium oxide supports, (a) MgO-A, (b) MgO-B and (c) MgO-C.

Figure 3.4 shows the infrared spectra of the VMgO catalysts. VMgO-A shows a weak band at 809 cm⁻¹, which is attributed to the magnesium orthovanadate phase [3, 6]. VMgO-A also shows a peak at 997 cm⁻¹ which is attributed to VO₆ asymmetric stretching indicative of the pyrovanadate phase [7]. Examination of the spectra for VMgO-B-oxalic, VMgO-B-water and VMgO-C, suggests the presence of only the orthovanadate phase. These peaks were observed at 861, 838 and 832 cm⁻¹ respectively, confirming the observations made in the X-Ray

diffractograms. The weak bands observed at 675 and 667 cm⁻¹ for VMgO-A and VMgO-C are attributed to MgO.



Figure 3.4 IR spectra of vanadium magnesium oxide catalysts, (a) VMgO-A, (b) VMgO-B-oxalic, (c) VMgO-B-water and (d) VMgO-C.

3.3 Raman spectroscopy

Raman spectroscopy was carried out to confirm the phases formed in the catalysts. Amongst all laser line frequencies selected, a wavelength of 480 nm showed to give best results, which was used to obtain the spectra presented in Figure 3.5. The Raman spectrum of VMgO-A shows many sharp peaks compared to the other catalysts. This indicates that more than one vanadate phase was formed, confirming the XRD data that complements this catalyst.





Figure 3.5 Raman spectra of vanadium magnesium oxide catalysts, (a) VMgO-A, (b) VMgO-B-oxalic, (c) VMgO-B-water and (d) VMgO-C

The cubic morphology of magnesium oxide lends itself to form crystalline vanadium orthovanadate and pyrovandate phases [3]. VMgO-A shows strong peaks at 883 cm⁻¹ and 863 cm⁻¹ which were assigned to VO₄ stretching attributed to the crystalline orthovanadate phase [7-10]. The peaks at 440, 244, 205 and 121 cm⁻¹ are attributed to isolated species of VO₄ dispersed on the magnesium oxide surface. The peak at 845 cm⁻¹ was assigned to VO₃ isolated species and peaks at 440, 403, 375, 281 and 244 cm⁻¹ were assigned to lattice VO₃, attributed to the pyrovanadate phase [7]. The additional bands at 1090, 1014, 992 and 525 cm⁻¹ indicates the coexistence of isolated VO₄ species ascribed to both orthovanadate and pyrovanadate [7]. VMgO-B-oxalic show a major peak at 829 cm⁻¹ and a hump at 1090 cm⁻¹ which were attributed to stretching in VO₄ tetrahedra and the coexistence of VO₄ isolated species [7]. VMgO-B-water and 809, 865 and 892 cm⁻¹ for VMgO-C, indicated the formation of VO₄ isolated species ascribed to the orthovanadate phase [7].

3.4 Scanning electron microscopy

Scanning electron microscopy was used to ascertain the morphology of the supports resulting from the applied synthetic techniques. Figures 3.6 (a-c) shows the SEM images of the various supports describing their morphology. The method that used magnesium oxalate as a precursor, is observed to have formed cubic magnesium oxide (MgO-A) [11] as shown in Figure 3.6 (a), magnesium citrate formed spherical magnesium oxide particles (MgO-B) [8] and the use of magnesium-4-methoxyl- α -methyl-benzyl alcohol formed nano-sheet magnesium oxide (MgO-C) [12], when calcined at 550°C.



Figure 3.6 SEM micrographs of different magnesium oxide supports, (a) MgO-A, (b) MgO-B and (c) MgO-C.

Oxalic acid, citric acid and 4-methyl-methoxyl- α -methyl-benzyl alcohol complexing agents play an important role in size and shape formation by fixing the metal ions prior to the

formation of the MgO [13]. Figure 3.7 shows the complexation sites for all three complexing agents used.



Figure 3.7 The complexation sites available in the complexing agents, (a) oxalate, (b) citrate and (c) 4-methyl-methoxyl- α -methyl-benzyl alcohol.



Figure 3.8 Growth mechanism of MgO using oxalic acid complexing agent



Figure 3.9 Growth mechanism of MgO using citric acid complexing agent

Citric acid shows the most number of sites compared to oxalic acid and 4-methyl-methoxyl- α -methyl-benzyl alcohol. The oxalic acid, due to its two complexation sites, can fix less Mg²⁺ ions (Figure 3.8) compared to the larger citrate molecule, resulting in stacked polymerised MgO, forming cubes. The citric acid molecule has more complexation sites and will be able to fix a larger number of Mg²⁺ ions (Figure 3.9), thus producing branched polymerized MgO. The complex branching that subsequently arises from this arrangement results in the formation of spherical particles. 4-methyl-methoxyl- α -methyl-benzyl alcohol has only one complexation site, and coupled with the presence of the aromatic ring, this allows for the fixing of one Mg²⁺ ion (Figure 3.10) resulting in a layer of polymerized MgO, thus forming a sheet.



Figure 3.10 Growth mechanism of MgO using the complexing agent, 4-methyl-methoxyl-αmethyl-benzyl alcohol

The proposed mechanisms were further discussed by Mastuli et al. [13] as shown in Fig. 3.11, who studied the effect of oxalate and tartrate as complexing agents. When oxalate complexes

with magnesium, it forms a linear polymer network, while tartrate complexes to form a branched polymer network at temperatures less than 450°C. At 450°C the oxalate complex remain linear while the tartrate complex starts to decompose forming small crystals. Raising the temperature to 500°C breaks the linear chain of the oxalate complex forming small seed crystals, stacked to form the cubic MgO, and while spherical shaped MgO crystals grow after the decomposition of the tartrate complex. The annealing at 950°C for 36 h results in small cubic MgO crystals obtained from the oxalate complex and larger MgO crystals obtained from the titrate complex.

<450°C

450°C

500°C

950°C



Linear polymer network

At this temperature the

polymer complex is still in

linear structure and not yet

decomposed

Bond breaking of linear

chain at 500 °C forming small seed crystals



Branched polymer network



The polymer complex starts to decomposed at 450 °C forming small seeds crystals



Crystal still growing



Larger MgO crystals formed after annealing at this temperature for 36 h

Figure 3.11 A schematic diagram for crystal growth of the MgO samples [13].

Small MgO crystals formed

after annealing at this

temperature for 36 h

Figure 3.12 shows the SEM images after impregnation of the respective MgO supports with vanadium using ammonium metavanadate in oxalic acid. The morphology of the catalysts after vanadium loading was changed somewhat when compared to the morphology of the respective support. VMgO-A appears to have maintained a cubic morphology although the cubes do not appear as sharp as the support (Fig. 3.6 (a)). VMg-B-oxalic is showing a prismatic morphology which is far removed from the spherical morphology of the precursor support (Fig. 3.6 (b)).



Figure 3.12 SEM images of vanadium magnesium oxide catalysts, (a) VMgO-A, (b) VMgO-B-oxalic, (c) VMgO-C and (d) VMgO-B-water.

Similarly, VMgO-C (Fig. 3.12 (c)) shows a transformation in its morphology after impregnation with vanadium when compared to the morphology of the support (c.f. Fig. 3.6 C) from which it was prepared. In this case, a cubic morphology was observed not too dissimilar from VMgO-A, however, with nano sheets visible on some of the cubes. VMgO-B was then prepared using water only as the solvent as described in the experimental section 2.1.5, instead of the water-oxalic acid solvent mixture used to prepare VMgO-B-oxalic. After this treatment, the morphology of the support appeared to be retained as shown in Fig 3.12 (d).

However, the spheres appeared much larger when compared to the support, suggesting agglomeration during the impregnation step.

3.5 Elemental analysis and surface studies

ICP-OES was used to confirm the weight loadings of vanadium on the MgO support as shown in Table 3.1.

Catalyst	Surface area	Pore volume	Pore diameter	Crystallite	Wt% of
	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	(Å)	size (nm) ^a	V_2O_5
MgO-A	20	0.07	23.0	-	-
MgO-B	22	0.1	38.7	-	-
MgO-C	100	0.3	8.91	-	-
VMgO-A	170	0.60	14.4	2.31	15.5
VMgO-B-oxalic	162	0.23	38.7	2.29	14.9
VMgO-B-water	78	0.45	19.2	10.82	15.6
VMgO-C	202	0.67	57.5	2.71	15.7

Table 3.1 Nitrogen physisorption, ICP and crystallite size analysis.

^a obtained from XRD

All the VMgO catalysts synthesised have a vanadium weight loading of approximately 15 wt% \pm 1%. Nitrogen physisorption was used to obtain information about the surface area and porosity of the materials prepared. MgO-A and MgO-B had a similar surface area of approximately 20 m²/g, while MgO-C, which are nano-sheets, gave the highest surface area of 100 m²/g. MgO-C also showed a larger pore volume of 0.3 cm³/g compared to the cubic MgO-A and the spherical MgO-B which were 0.071 cm³/g and 0.11 cm³/g respectively The loading of vanadium on the magnesium oxide supports resulted in catalysts with a higher surface area. The obtained surface areas were 170, 162, 78 and 201 m²/g for VMgO-A, VMgO-B water and VMgO-C, respectively. VMgO-A, VMgO-B oxalic, VMgO-B water and VMgO-C also have large pore volumes compared to their corresponding supports. During loading of vanadium oxide, vanadium interacts with the support resulting in the formation of magnesium vanadate phases, thus disturbing the morphology to some extent as discussed previously, resulting in a change in the observed surface area [3]. The vigorous

evaporation of the solvent during calcination may have created larger pores in the catalysts [3]. Closer inspection of the SEM images of the various catalysts also show that the particles appeared to have a more rough outer texture when compared to the support. The surface area increased with the pore volume for all the catalysts except for VMgO-B water, where the pore volume was high, but the surface area is lower than other catalysts. We thus suspect that the lower surface area of VMgO-B, despite having a high pore volume, was affected more by its particle size growth, as shown by the SEM images.



Figure 3.13 N₂ adsorption/desorption isotherms of VMgO catalysts

The N₂ adsorption/desorption isotherms of the VMgO catalysts are shown in Figure 3.13. VMgO-A and VMgO-C show type IV isotherms, while VMgO-B-oxalic shows a type IV type isotherm but whose hysteresis closure point is at a much lower pressure than the saturation pressure of the material. VMgO-B-water shows behaviour similar to materials with type II isotherms which is indicative of lower surface area material and unrestrictive coverage of the adsorbent [15, 16]. Apart from VMgO-A, which shows typical behaviour of microporous materials, all the other catalysts are indicating macroporous character [15, 16].

3.6 Temperature programmed reduction

In Figure 3.14 (a), the broad peak for VMgO-A most probably indicates that vanadium exists in two phases, viz. the orthovanadate and pyrovanadate phases. According to Elkhalifa and Friedrich [3], the pyrovanadate phase was observed at higher loadings of vanadium pentoxide and the reduction temperature increased as the loading increased. Therefore, orthovanadate is reduced at a lower temperature compared to pyrovanadate.



Figure 3.14 TPR profile of (a) VMgO-A and (b) VMgO-B-water, VMgO-B-oxalic, VMgO-C

The reduction peak at 584°C and broad peak at 733-773°C for VMgO-A confirms the formation of octahedrally coordinated species, in addition to the tetrahedrally coordinated ones

[19]. In contrast to VMgO-A, VMgO-B-water and VMgO-B-oxalic (Fig. 3.14b) show one dominant peak indicating a monophasic material. VMgO-C also shows a dominant peak and a broad hump. This may suggest a dominant phase with the possibility of minor amounts of a second vanadate phase present. However, based on observations made from the previous analyses, it is more likely to be composed of a single vanadate phase [20, 21]. The average oxidation state of vanadium, as shown in Table 3.1, reflects the extent of reduction for each of the catalysts. VMgO-A has the lowest average oxidation state of all the catalysts prepared showing that the vanadium appears in a form that is more reducible, or perhaps a mixture as has been already suggested from the host of previous analytical discussions [4]. The average oxidation state of V for the other catalysts give a value closer to 4 or just above 4, showing again the presence of a common vanadate phase which is difficult to reduce.

The reducibility of the vanadates is an important characteristic that affect the selectivity to ODH products, i.e. the more reducible the catalyst, the less selective it is to ODH products [20, 21]. From this argument, it would appear that VMgO-A should show the lowest selectivity to ODH products.

Catalyst	Temp. (°C)		Total moles of	Average	
	Peak 1	Peak 2	Peak 3	$(cm^3/g STP)$	vanadium
VMgO-A	584	733	773	25.98	3.4
VMgO-B-water	641	-	-	15.73	3.7
VMgO-B-oxalic	589	-	-	13.95	4.2
VMgO-C	635	-	-	23.45	3.9

Table 3.2 Temperature programmed reduction and average oxidation state.

3.7 Ammonia-temperature programmed desorption

The NH₃-TPD profile and acidic sites distribution presented in Figure 3.15 and Table 3.3 show that there are two types of acidic sites observed for VMgO-A, strong (790-806°C), and medium acid sites (449-549°C) [4, 22] which is reported to be due to the presence of the pyrovanadate phase [18]. VMgO-B-oxalic, VMgO-B-water and VMgO-C exhibit both weak and medium

acidic character [3, 23]. VMgO-B-water has high total acidity, which is due to a high amount of medium acidic sites being present, therefore the catalytic products favoured by medium acidic sites are expected to dominate on this catalyst.



Figure 3.15 Ammonia TPD profile of (a) VMgO-A, VMgO-B-oxalic and VMgO-B-water and (b) VMgO-C

A high medium acid site content is beneficial from an ODH selectivity perspective, since it allows for increased interaction with the parent alkane, while at the same time, it is not so strong as to over oxidise the olefins that will form. VMgO-B-oxalic and VMgO-C have almost

the same number of acidic sites and same total acidity. As the density of weak acidic sites increases, the medium acidic sites also show an increase.

Catalysts	Weak acidic sites (mmol NH ₃ /g) (111-122°C)	Medium acidic sites (mmol NH ₃ /g) (445-549°C)	Strong acidic sites (mmol NH ₃ /g) (790-806°C)	Total acidity (mmol NH ₃ /g)
VMgO-A		0.21	0.22	0.43
VMgO-B-oxalic	0.37	0.42	-	0.80
VMgO-B-water	0.64	1.24	-	1.87
VMgO-C	0.40	0.40	-	0.80

Table 3.3 Ammonia TPD acidic sites distribution of catalysts

References

- 1 L.Z. Pei, W.Y. Yin, J.F. Wang, J. Chen, C.G. Fan, Q.F. Zhang, Mat. Research, 13 (2010) 339-343.
- 2. V. Mote, Y. Purushotham and B. Dole, J. Theo. Appl. Phys. 6 (2012) 1-8.
- 3. E.A. Elkhalifa and H.B. Friedrich, Appl. Catal. A, 373 (2010) 122-131.
- 4. E.A. Elkhalifa and H.B. Friedrich, J. Molecular Catal. A, 392 (2014) 22-30.
- 5. M. Sharma and P. Jeevanandam, J. Alloy Comp. 509 (2011) 7881-7885.
- L. Balders-Tapia, I. Hernandez-Perez, P. Schacht, I.R. Cordova and G.G. Aguilar-Rios, Catal. Today, 107 (2005) 371-376.
- G. Ricchiardi, D.S.H. Sam, and J.C. Volta, J. Chem. Soc. Faraday Trans. 90 (1994) 1161-1170.
- A.P.S. Dias, L.D. Dimitrov, M.C.R. Oliveria, R. Zavoianu, A. Fernades and M.F. Portela, J. Non-Cryst. Solids, 356 (2010) 1488-1497.
- A. Dejoz, J. M. López Nieto, F. Melo, and I. Vázquez, Ind. Eng. Chem. Res. 36 (1997) 2588-2596.
- 10. J. Chetty, Ph.D Thesis, University of KwaZulu-Natal, South Africa, 2006.

- 11. E.A. Elkhalifa and H.B. Friedrich, Arab. J. Chem. (2014).
- Z. Li, C. V. Ciobanu, J. Hu, J. Palomares-Báez, J. Rodríguez-López and R. Richards, Phys. Chem. Chem. Phys. 13 (2011) 2582-2589.
- M.S. Mastuli, N. Kamarulzaman, M.A. Nawavi, A.M. Mahat, R. Rusdi and N. Kamarudin, Nanoscale Res. Lett. 9 (2014) 134.
- 14. J. Jia, P. Zhang and L. Chen, Catal. Science Techn. (2016).
- R. Haul, Berichte der Bunsengesellschaft für physikalische Chemie, 86 (1982) 957-957.
- Y. Kamiya, E. Nishikawa, A. Satsuma, M. Yoshimune and T. Okuhara, Microporous Mesoporous Mater. 54 (2002) 277-283.
- R.J. White, V. Budarin, R. Luque, J. H. Clark and D.J. Macquarrie, Chem. Soc. Rev. 38 (2009) 3401-3418.
- T. Yamada, K.I. Johkan and T. Okuhara, Microporous Mesoporous Mater. 26 (1998) 109-115.
- 19. O.R. Evans, A.T. Bell and T.D. Tilley, J. Catal. 226 (2004) 292-300.
- 20. H.H. Kung and M.C. Kung, Appl. Catal. A 157 (1997) 105–116.
- 21. T. Blasco and J.M. Lopez Nieto, Appl. Catal. A 157 (1997) 117–142.
- S.R. Ginjupalli, S. Mugawar, P. Rajan, P.K. Balla and V.R.C. Komandur. Appl. Surf. Sci. 309 (2014) 153-159.
- 23. V.D.S. Dasireddy, S. Singh and H.B. Friedrich, Appl. Catal. A, 421 (2012) 58-69.

CHAPTER FOUR

RESULTS AND DISCUSSION: CATALYTIC TESTING

The synthesised catalysts were tested in a fixed bed reactor as described in Chapter 2, to determine their effectiveness towards *n*-octane oxidative dehydrogenation. VMgO-A was first tested, over the temperature range of 350 °C-550°C with a temperature increment of 50°C at a GHSV of 4000 h⁻¹ and C:O ratio of 8:2. The activity of all the catalysts were compared at *iso*-conversion of 14 ± 1 mol C % under the same reaction conditions. The results shown in this chapter are based on the steady state conversions, from time on stream experiments performed, usually achieved after a few hours of start-up. Multiple samples were taken to monitor the reaction to ensure steady state was reached before actual testing could begin. The carbon balances were in the range of 98 %-101 %. The main products obtained by the catalysts were octenes, C8 aromatics and carbon oxides. Cracked products and octadienes were also obtained, but in lower amounts.

4.1 Activity and product evaluation of VMgO-A

Figure 4.1 shows the activation of *n*-octane over VMgO-A in the temperature range of 350°C to 550°C. The data shows that the conversion of *n*-octane increased from 350°C up to 450°C (8 % to 14 %), thereafter remained constant from 450 °C to 550 °C. The constant conversion at the higher temperatures is likely due to insufficient oxygen being present, as deduced from the almost complete conversion of O2 at these temperatures. The octene selectivity increased steadily from a value of 30 % at 350°C to 39 % at 500°C and then decreased slightly to 36% at 550°C. ODH reactions can proceed via nucleophilic attack or electrophilic attack of the paraffin [1]. This is dependent however, on the oxidation state of the cation and its environment, which influences the polarization strength of the M=O bond. Nucleophilic oxygen species favour deprotonation of the paraffin, which then leads to ODH product formation, while weakly polarized M=O bonds will favour homolytic reactions as in allylic olefin dehydrogenation [1]. In the case of electrophilic activation, electrophilic attack occurs on conjugated bonds, i.e. double bonds or aromatic rings, by the M=O bond, forming oxygenates and CO_x [1]. Therefore in VMgO-A, we postulate that there were more nucleophilic adsorbed oxygen species at the lower temperatures, up to about 400°C, which controlled both the conversion and selectivity.


Figure 4.1 Conversion and selectivity of ODH of *n*-octane over VMgO-A with GHSV fixed at 4000 h^{-1} and C:O ratio fixed at 8:2.

As the temperature increased beyond 400 °C, the selectivity towards ODH products increased steadily with a concomitant decrease in CO_x selectivity. Since the characterisation of VMgO-A showed that it possessed both orthovanadate and pyrovanadate phases, we surmise that the orthovanadate phase is more active toward ODH activity at the higher temperatures, since it has been reported to have more nucleophilic oxygen species associated with it compared to the pyrovanadate phase [1].

The selectivity towards CO_x decreased from 59 % to 32 % as the temperature was increased from 350 °C to 550 °C due to the arguments presented. The stable aromatic nucleus in styrene, ethylbenzene and xylene represents the driving force for their formation and thereby reduces the production of carbon oxides, especially the contribution from secondary combustion [2]. Pradham et al. reported that at lower temperatures, the non-selective oxygen species are more active than selective oxygen species [3]. As the temperature rises, the selective oxygen species are activated, which leads to a competitive relationship of selective and non-selective oxygen species during ODH processes. Hence, an increase in temperature leads to an increase in octene selectivity and a decrease in CO_x selectivity. The cracked products (C1 to C7 alkanes and alkenes) exhibit low selectivity (around 4%) at temperatures below 450°C, however, the selectivity increases significantly between 500-550°C (7-16%). Thus, at the high temperatures (500-550°C) octene is less stable and more susceptible to cracking over the VMgO-A.

4.2 Comparison of catalyst selectivity at *iso*-conversion

All the catalysts were tested at *iso*-conversion at 450°C, since the lower temperature showed to give the best selectivity to octenes and aromatics. Figure 4.2 shows the selectivity obtained over the various catalysts at *iso*-conversion.



Figure 4.2 Selectivity at *iso*-conversion of *n*-octane over VMgO catalysts at 450°C with C:O ratio fixed at 8:2.

The rate of the reaction is determined by the ease of C-H bond breaking in alkane activation, while the selectivity is determined by the reducibility of the catalyst, i.e. the more reducible, the less selective the catalyst is towards ODH products [4, 5, 6]. However, this was further found to be unlikely, rather the acid-base properties of the catalyst was thought to have more influence. VMgO-B-water and VMgO-C show higher selectivity towards octene isomers (\approx 45 %) implying that the orthovanadate phase and magnesium interaction led to a change in the acid-base characteristics of these systems compared to VMgO-A. This is indicated in the acidity measurements as shown in Table 3.3. The data suggests that the higher density of weak

to medium sites favour higher olefin selectivity, while the strong acid sites in VMgO-A, favours CO_x formation, even though its total acidity is low. This may imply a highly active site associated with the strong acid sites. VMgO-B-oxalic, however, appears to go against this trend. Further analysis of this material shows that the argument of reducibility may play a role in describing this system. TPR data (Table 3.2) shows this catalyst to be least reducible with the highest average V oxidation state, suggesting that nucleophilic species proliferate on the surface leading to the higher CO_x selectivity. Thus, the comparative difference in selectivity for VMgO-B-water, VMgO-C and VMgO-A can be explained by the variance in acidity whilst activity of VMgO-B-oxalic is controlled by the reducibility.

Figure 4.3 shows the Mars and van Krevelen (MvK) mechanism for the oxidative dehydrogenation of paraffins.



Figure 4.3 Systematic description of the MvK mechanism where oxygen is used as the oxidant in the reaction [10]

The metal oxide catalysts lose oxygen from the lattice, which leaves a vacancy on the catalyst. The vacancy is replenished by atmospheric oxygen [7, 8]. For a catalyst to be more selective towards ODH products, a substrate must react with lattice nucleophilic oxygen from the surface of the catalyst, while CO_x production is favoured by electrophilic oxygen on the surface of the catalyst. Unfortunately, it is difficult to evaluate the contribution of the different pathways, since there are equations describing only the overall reaction rate are known [9].

The rate of oxygen incorporation from gas phase to metal oxide and evolution of O_2 gas is in dynamic equilibrium. In this process, oxygen gas dissociates to both electrophilic and

nucleophilic oxygen ions on the surface of the catalyst and recombine to form molecules that desorb as dioxygen. Therefore, the catalyst with highest rate of dynamic equilibrium of oxygen between catalyst and gas are highly covered with electrophilic oxygen species on the surface, while the catalysts with no dynamic equilibrium are covered by nucleophilic oxygen species on the surface [9].

All VMgO catalysts showed to have a dynamic equilibrium of O_2 and dissociated oxygen species but with different rates, therefore there is a competition between electrophilic and nucleophilic oxygen species on the surface of the catalysts. VMgO-A had the highest rate of dynamic equilibrium as it produced more CO_x , followed by VMgO-B-oxalic and then VMgO-C. VMgO-B-water showed to have the lowest rate of dynamic equilibrium as it was more selective towards ODH products.

Figures 4.4 and 4.5 show the distribution of octene isomers and C8-aromatic compounds, respectively. The octene isomers observed were 1-octene, cis-2-octene, trans-2-octene, trans-3-octene and trans-4-octene.



Figure 4.4 Octenes selectivity over VMgO catalysts at iso-conversion



Figure 4.5 Aromatic selectivity over VMgO catalysts at iso-conversion

The aromatics were ethylbenzene, styrene and *o*-xylene. 1-octene and styrene were given special attention as they are used as starting materials in the polymer industry [11, 12]. An alternative arrangement of oxygen and magnesium species for nano-sheet MgO results in the formation of polar monolayers of oxygen anions and magnesium cations, which makes the surface of MgO to have a strong electrostatic field [13, 14]. Therefore, the MgO-orthovanadate interaction resulted in VMgO-C having a high density of weak acidic sites, favouring octenes selectivity. The proposed mechanism for alkane activation suggests that the transformation of *n*-octane can be initiated by hydrogen abstraction, which is a slow step to form an octyl species [7, 8, 15]. The second hydrogen is eliminated from the hydrocarbon from an adjacent carbon atom (fast step), which leads to the formed alkyl species reacts [8, 16]. The VMgO catalyst has been reported to favour a dehydrogenation route, rather than routes which favour cracking and oxygenates formation [8, 17]. Therefore, the formed octenes may either desorb from the less acidic catalyst's surface or go through more dehydrogenation steps that eventually lead to cyclization and aromatics formation [11].

The formation of aromatics results from cyclization of octenes and octadienes via C1 to C6 (path I and II in Figure 4.6) or C2 to C7 (path III in Figure 4.6) to form a six membered carbon ring [18-20]. It is reported that in this process, the C1 to C6 cyclisation might lead to the

formation of ethylbenzene or styrene, while path III will form *o*-xylene [21]. The acidic sites play an important role in this case because VMgO-B-water showed a selectivity shift from 1-octene to ethylbenzene and styrene because of the high number of medium acidic sites present. The other catalysts in Figure 4.5 showed a lower selectivity to aromatics than VMgO-B-water. In comparison to the other catalysts, VMgO-B-water had the highest density of medium acidic sites, which emphasizes the role these sites possibly play in allowing octenes to readsorb and be further dehydrogenated, and then cyclising to form styrene.



Figure 4.6 The formation of aromatics via cyclization of octene



Figure 4.7 ODH selectivity versus CO_x selectivity over the various catalysts at *iso*-conversion

Figure 4.7 shows a comparison of CO_x selectivity to ODH selectivity for the various catalysts. In the figure, it can be deduced that VMgO-B-water, which has spherical morphology was more selective towards ODH products compared to the catalysts having cubic morphology (VMgO-A, VMgO-B-oxalic and VMgO-C). Thus, the morphology of the supports is shown to have an influence on the selectivity of the products formed and is linked possibly to the formation and distribution of the vanadate phases on these catalysts. VMgO-A was shown to have both orthovanadate and pyrovanadate phases, which were heterogeneously distributed. The distribution of these phases on VMgO-A led to it being more selective towards CO_x . The data in Figure 4.8 compares the rate of depletion of *n*-octane, normalised against the surface area of the various catalysts. The graph shows that VMgO-B-water is most active, followed by VMgO-B-oxalic, VMgO-A and VMgO-C. This suggests that the arrangements of the vanadate phases obtained from spherical MgO improves not just the selectivity, but also the activity of this phase, thus providing a better yield. When looking at the SEM images in Figures 3.3 and 3.7, the cubic morphology has a more organised and ordered shape, while the catalyst having a spherical morphology shows to have a rough texture and is slightly more disordered. The combination of these physical properties has shown a positive influence on the selectivity of the desired reactions.



Figure 4.8 Normalisation of activity with surface area

4.3 Selectivity vs acidity of the catalysts

The acid-base character of vanadia-based catalysts is reported to have an influence on the selectivity of the final products [7, 23, 24]. Referring to Table 3.2 in Chapter 3, NH₃-TPD results shows that VMgO-A has strong acidic sites.



Figure 4.9 Comparison of selectivity of products vs weak acidic sites.



Figure 4.10 Comparison of selectivity of products vs. medium acidic sites

This resulted in VMgO-A being more selective towards CO_x compared to other catalysts. This is probably because the strong acidic sites have high probability to adsorb olefins and therefore enhance the formation of aromatics, or to further react and form CO_x [11, 25]. VMgO-B-water, VMgO-B-oxalic and VMgO-C selectivities show a trend toward having more weak and medium acidic sites. The graphs in Figures 4.9 and 4.10 show that the catalysts with more weak and medium acidic sites are more selective towards ODH products. VMgO-C has a similar distribution of medium acid sites as VMgO-B-oxalic, and also a similar morphology, hence it shows a similar product selectivity profile when compared to VMgO-B-oxalic.

References

- [1] G.E. Vrieland and C.B. Murchison, Appl. Catal. A, 134 (1996) 101-121.
- [2] E.A. Elkhalifa and H.B. Friedrich, Appl. Catal. A, 373 (2010) 122-131.
- S. Pradhan, J.K. Bartley, D. Bethell, A.F. Carley, M. Conte, S. Golunskli, M.P. House,
 R.L. Jenkins, R. Lloydand G.J. Hutchings, Nature Chem. 4 (2012) 134-139.
- [4] T. Blasco and J.M. Lopez Nieto, Appl. Catal. A, 157 (1997) 117–142.
- [5] B.K. Hodnett, Wiley, New York, USA, (2000) 65–101.
- [6] H.H. Kung and M.C. Kung, Appl. Catal. A 157 (1997) 105–116.
- [7] C. Doornkamp and V. Ponec, J. Mol Catal. A, 162 (2000) 19-32.
- [8] M. Pepera, J.L. Callahan, M.J. Desmond, E.C. Milberger, P.R. Blum and N.J. Bremer, J. Amer. Chem. Soc. 107 (1985) 4883.
- [9] J. Haber and W. Turek, J. Catal. 190 (2000) 320-326.
- [10] P. Mars and D.W. van Krevelen, Chem. Eng. Sci. 3, Supplement 1 (1954) 41-59.
- [11] E.A. Elkhalifa and H.B. Friedrich, J. Molec. Catal. A, 392 (2014) 22-30.
- [12] T. Pintauer and K. Matyjaszewski, Chem. Soc. Rev. 37 (2008) 1087-97.
- [13] P.W. Tasker, J. Phys. C: Solid State Phys. 12 (1979) 4977.
- [14] Z. Li, C. V. Ciobanu, J. Hu, J. Palomares-Báez, J. Rodríguez-López and R. Richards, Phys. Chem. Chem. Phys. 13 (2011) 2582-2589.
- [15] E.A. Mamedov and V. Cortes Corberan, Appl. Catal. A 127 (1995) 1–40.
- [16] H.H. Kung and P.M. Michalakos, ACS Symposium Series, Washington DC, (1993) 389–408.
- [17] J.P. Lange R.J. Schoonebeek, P.D.L. Mercera and F.W. Van Breukelen. Appl. Catal. A, 283 (2005) 243–253.

- [18] J. Fung and I. Wang, J. Catal. 130 (1991) 577–587.
- [19] P. Meriaudeau, A. thangaraj, C. Naccache and S. Narayanan, J. Catal. 146 (1994) 579– 582.
- [20] B. Shi, B.H. Davis, J. Catal. 157 (1995) 626–630.
- [21] V.D.B.C. Dasireddy H.B. Friedrich and S. Singh, Appl. Catal. A, 467 (2013) 142-53.
- [22] E.A. Mamedov and V. Cortés Corberán, Appl. Catal. A, 127 (1995) 1-40.
- [23] T. Blasco, J.M. Lopez Nieto, A. Dejoz and M.I. Vazquez, J. Catal. 157 (1995) 271-82.
- [24] M.A. Chaar, D. Petl, M.C. Kung and H.H. Kung, J. Catal. 105 (1987) 483-98.
- [25] A. Coelho, G. Caeiro, M.A.N.D.A. Lemos, F. Lemos and F. Ramoa Ribeiro, Fuel, 111 (2013) 449-60.

CHAPTER FIVE CHARACTERIZATION OF USED CATALYSTS

The used catalysts were analysed to establish the stability of the catalysts with respect to the morphology of the supports and the corresponding VMgO phases that formed. In most cases, when the MvK mechanism takes place during ODH, the catalysts are stable. However, there is a possibility of restructuring of the catalysts since the rate of removal of oxygen may exceed the rate of its replacement in the catalyst. In some cases, the catalyst may re-structure itself in a different way before the replacement of the lattice oxygen, leading to the formation of new reduced phases and the disruption of the morphology. Various characterisation techniques such as XRD, IR and SEM were used to provide this type of information about the catalysts.

5.1 Powder X-ray diffraction

Figures 5.1 and 5.2 compares the X-ray diffractograms of the fresh and used catalysts. The fresh catalysts (Figure 5.1) show the common magnesium oxide peaks at 44.2° and 62.5° and the major peak for the magnesium orthvanadate phase was observed for VMgO-A and VMgO-C at 2 θ equal to approximately 35°. The used catalysts in Figure 5.2 show the absence or lower intensity (as in the case of VMgO-A) peak at 35° and the appearance of a peak representing a new reduced form of magnesium orthovanadate at 37.2° [1]. A reduced form of magnesium orthovanadate (Mg₃V₂O₆) has a spinel structure that can re-oxidise to Mg₃V₂O₈ when the oxygen gas is introduced. We surmise that during the reaction the cations migrate from VO₄ to VO₆ sites in the cell transforming Mg₃V₂O₈ to Mg₃V₂O₆ (reduced orthovanadate) [1]. The catalysts that were more easily reduced (cf. Table 3.2), showed a peak for Mg₃V₂O₆ with higher intensity. VMgO-A shows sharper peaks of the reduced orthovanadate phase compared to the other catalysts. The used VMgO-B-oxalic also shows a peak for the reduced magnesium orthovanadate phase, even though there were no vanadate peaks visible before the reaction. This suggests that for this catalyst, the vanadate particles or phases present on the surface of MgO were highly dispersed.



Figure 5.1 XRD diffractograms of fresh VMgO catalysts



Figure 5.2 XRD diffractograms of used VMgO catalysts

5.2 Infrared spectroscopy

Figures 5.3 and 5.4 compares the spectra of the fresh and used VMgO catalysts, respectively. Figure 5.4 shows that peaks for the magnesium orthovanadate phase for VMgO-A, VMgO-Boxalic, VMgO-B-water and VMgO-C at 854 cm⁻¹, 850 cm⁻¹, 863 cm⁻¹ and 856 cm⁻¹, respectively, are more prominent than the fresh catalysts. The peak for the pyrovanadate phase for VMgO-A was not observed at 997 cm⁻¹, suggesting that during the reaction the pyrovanadate phase restructures itself to form the orthovanadate phase. The reduced orthovanadate phase was not observed, which is known to appear around 619 cm⁻¹, although it was observed in XRD. The bands in the region of 920-950 cm⁻¹ indicating V=O stretching were not observed [2]. The characteristic peaks of V₂O₅ in the region of 1020-1060 cm⁻¹ were also not observed [3].



Figure 5.3 IR spectra of fresh vanadium magnesium oxide catalysts, (A) VMgO-A, (B) VMgO-B-oxalic, (C) VMgO-B-water and (D) VMgO-C.



Figure 5.4 IR spectra of used vanadium magnesium oxide catalysts, (A) VMgO-A, (B) VMgO-B-oxalic, (C) VMgO-B-water and (D) VMgO-C.

5.3 Scanning electron microscopy

The SEM images in Figure 5.5 compares the morphology of the catalysts after undergoing a reaction cycle. The images show that the morphology of the used catalysts have changed significantly and bear no similarity to that of the fresh catalysts. This shows that during the reaction, the abstraction of lattice oxygen deforms the structure of VMgO, which leads to a new morphology that presents itself as amorphous clumps. The SEM images show that the particles agglomerated together during the reaction to form larger particles.



Figure 5.5 SEM images of fresh and used vanadium magnesium oxide catalysts

References

- X. Wang, H. Zhang, W. Sinkler, K.R. Poeppelmeier and L.D. Marks, J. All. Comp. 270 (1998) 88–94.
- Y.M. Liu, Y. Cao, N. Yi, W.L. Feng, W.L. Dai, S.R.Yan, H.Y. He and K.N. Fan, J. Catal.224 (2004) 417-428.
- 3. B.K. Hodnett, Wiley, (2000) 65-101.

CHAPTER SIX CONCLUSIONS

Varying the synthetic methods resulted in different magnesium precursors which were calcined to obtain morphologically different magnesium oxides as follows; cubic (MgO-A) was obtained from magnesium oxalate, spherical (MgO-B) was obtained from magnesium citrate and nano-sheet (MgO-C) was obtained from magnesium 4-methoxyl- α -methyl-benzyl alcohol. Varying the morphologies led to different physico-chemical properties for the various magnesium oxides prepared. The number of complexation sites in the complexing agents used, appear to direct the morphology of the prepared supports. All the MgO supports showed to be pure after calcination, and after being analysed using XRD and IR. MgO-C had the highest surface area (100 m²/g) because of its high pore volume (0.3 cm³/g). There was a significant difference between surface areas and pore volumes of MgO-A (20 m²/g; 0.07 cm³/g) and MgO-B (22 m²/g; 0.1 cm³/g) when compared to MgO-C.

The loading of vanadium using oxalic acid as a solvent changed the MgO-B morphology, therefore, water was used as a solvent for vanadium loading on MgO-B. Oxalic acid as complexing agent directed cubic morphology, while water as complexing agent directed the formation of spherical and sheet-like morphology. As a result, three types of morphologies were obtained for the catalysts, viz. cubic (VMgO-A, VMgO-B-oxalic), spherical (VMgO-Bwater) and a mixture of cubic and sheets (VMgO-C). IR and Raman showed that VMgO-A contained magnesium oxide, magnesium orthovanadate and magnesium pyrovanadate phases, heterogeneously distributed, while the other catalysts contained magnesium oxide and magnesium orthovanadate phases which were more homogeneously distributed. The catalysts showed different physisorption properties and crystallite sizes. The vanadium loaded reacted with the MgO to form vanadia phases, which increased the pore volumes resulting in VMgO phases having higher surface areas compared to their respective MgO supports. VMgO-C having the highest surface area (200 m^2/g), influenced by the high pore volume and small crystallite size (2.71 nm) while VMgO-B-water had lower surface area (78 m^2/g) which is a result of the larger crystallite size (10.82 nm). The pyrovanadate phase in VMgO-A resulted in the catalysts having strong acidic sites and being more easily reduced, while catalysts with only the orthovanadate phase had weak and medium acidic sites only. ICP-OES confirmed that all the VMgO catalysts synthesised had a vanadium weight loading of approximately 15 wt% $\pm 1\%$.

The chemical and physical properties of the catalysts influenced the catalytic performance of each catalyst. The temperature influenced the oxygen species in VMgO-A. The selectivity toward ODH products increased while COx production decreased as the selective oxygen species were activated by an increase in temperature. There was no increase in conversion of octane from 450 °C to 550 °C which was limited by a depletion in oxygen.

At iso-conversion, VMgO-B-water, which has spherical morphology was shown to be more selective towards ODH products compared to the catalysts having cubic morphology (VMgO-A, VMgO-B-oxalic and VMgO-C). VMgO-A was shown to have both orthovanadate and pyrovanadate phases, which were heterogeneously distributed which led to it being more selective towards COx. The strong electrostatic field perpendicular to the surface of VMgO-C resulted in it having more weak acidic sites and was observed to be more selective towards 1octene compared to other catalysts. The spherical morphology of the support resulted in VMgO-B-oxalic and VMgO-B-water having more medium acidic sites and thus being more selective towards aromatics, and which also contributed to VMgO-B-water being more selective towards ODH products. The reduction and acidity studies clearly showed that VMgO-A consumed more hydrogen amongst all the catalysts, but because of its strong acidity, it took longer for a substrate to desorb from the surface of the catalyst, hence causing electrophilic oxygen species to form during the catalyst's re-oxidation. Thus, these electrophilic oxygen species further oxidised the substrate to favour CO_x production. There was a high consumption of hydrogen by VMgO-C, while having a weak acidic surface, therefore favouring octenes. VMgO-B-oxalic and VMgO-B-water consumed less hydrogen but in combination with their medium acidic surface, favoured the aromatics. Therefore, the catalytic activity and selectivity was influenced not just by the phases formed and the distribution of these phases, but also strongly influenced by the redox properties and acid-base characteristics of the catalysts. These properties of the catalysts were controlled, to some extent, by the morphology of the supports and synthetic conditions.

The XRD and IR shows that the pyrovanadate phase observed in a fresh VMgO-A catalyst restructured to the orthovanadate phase during the ODH reaction. The orthovanadate phase in all catalysts was partially reduced from $Mg_3V_2O_8$ to $Mg_3V_2O_6$. The TPR and XRD of the used catalysts agreed to the assertion that the more reduced the catalyst was the higher the propensity to form the $Mg_3V_2O_6$ phase. It also suggests that the catalysts with resistance to re-oxidise to $Mg_3V_2O_8$ were less selective towards ODH products.

SEM images showed that after reaction, the morphologies were changed and did not bare any resemblance to the starting material. They all showed a powdery appearance suggesting that ultimately the micro surface structure were very similar after a certain period of being exposed to the oxidative/reductive atmosphere that is paraffin oxidative dehydrogenation.

APPENDIX

A1. GC-Method used for analyzing organic (gaseous and liquid) samples

Channel Parameters:

Run Time: 30.00 min

Sampling Rate: 3.1250 pts/s

Carrier Parameters:

Carrier A Control: He (300 Kpa)

Column A length: 50.00 m

Vacuum Compensation: Off

Diameter: 530 µm

Split Ratio: 150:1

Initial Set point: 2.0 mL/min

Valve Configuration and Setting:

Valve 1: SPLIT On

Valve 2: NONE

Valve 3: NONE

Detector Parameters:

	Detector A
Detector	FID
Range	1
Time Constant	200
Autozero	ON
Polarity	-
Detector A Gas Flows	

Air: 450.0 mL/min

Hydrogen: 45.0 mL/min

Heated Zones:

Injector A: CAP

Setpoint: 220°C

Detector A: 250°C

Oven Program:

Cryogenics: Off

Initial Temp: 40°C

Initial Hold: 15.0 min

Ramp 1: 20.0°C/min to 100°C, hold for 5.0 min

Ramp 2: 20.0°C/min to 200°C, hold for 2.0 min

Processing Parameters:

Bunch Factor: 2 points

Noise threshold: $50 \mu V$

Area Threshold: 100.0 μV

Peak Separation Criteria:

Width Ratio: 0.2

Total Run Time: 30.0 min Max. Temp: 300°C Equilibration Time: 0.2 min

A2. GC-Method used for analysing carbon oxides

Channel Parameters:

Run Time: 7.0 min

Sampling Rate: 6.25 pts/s

Carrier Parameters:

Carrier B Control: He (300 KPa)

Column B length: 30.00 m

Vacuum Compensation: Off

Diameter: 530 µm

Split Flow: 500.0 mL/min

Initial Set point: 6.0 mL/min

Valve Configuration and Setting:

Valve 1: SPLIT On

Valve 2: NONE

Valve 3: NONE

Detector Parameters:

	Detector B
Detector	TCD
Range	3
Time Constant	200
Autozero	ON
Polarity	-
Detector B Gas Flows Helium:	30.0 mL/min
Heated Zones:	

Injector B: CAP

Set point: 220°C

Detector B: 250°C

Oven Program:

Cryogenics: Off

Initial temp: 40°C

Initial Hold: 2.50 min

1: 20.0°C/min to 80°C, hold for 2.5 min

Processing Parameters:

Bunch Factor: 2 points

Noise threshold: $1 \ \mu V$

Area Threshold: 100.0 μV

Peak Separation Criteria:

Width Ratio: 0.2

Valley-to-peak Ratio: 0.01

Total Run Time: 7.0 min Max. Temp: 250°C Equilibration Temp: 0.5 min

Table A1	Standards	used for	calibration
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Chemical	Supplier	Purity (%)
<i>n</i> -octane	Merck	98
1-octene	Aldrich	98
trans-2-octene	Fluka	98
cis-2-octene	AlfaAesar	98
trans-3-octene	Aldrich	98
trans-4-octene	Fluka	98
cis-4-octene	AlfaAesar	97
1,7-octadiene	Fluka	97
ethylbenzene	AlfaAesar	99
<i>o-x</i> ylene	AlfaAesar	99
styrene	Aldrich	99
ethylcyclohexane	Fluka	99
<i>n</i> -heptane	Fluka	99.8
1-heptene	Aldrich	97
<i>n</i> -hexane	ACROS	99.5
1-hexene	ACROS	97
<i>n-n</i> onane	Fluka	99
cyclooctane	Fluka	99
cis-cyclooctene	Aldrich	95
1,5-cyclooctadiene	Fluka	98
propylcyclopentane	Fluka	98
2,4-dimethylhexane	Fluka	99
2-ethyl-1-hexanol	Fluka	98
1-octanol	AlfaAesar	99
octanal	Aldrich	99
2-octanone	Fluka	97
3-octanone	Fluka	97

Mixture	Component	Percentage (%)
Mixture 1	ethane	3.0
	ethene	6.0
	<i>n</i> -butane	9.2
	nitrogen	81.8
Mixture 2	methane	2.0
	propane	4.0
	propene	6.0
	nitrogen	88.0
Mixture 3	carbon monoxide	5.0
	carbon dioxide	15.0
	nitrogen	80.0

Table A2Gaseous standards used for calibration

A3. FID Sampling



<Sample Information>

: Maild August 2015 Final Octane.gcm					
rator					
rator					

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	2.704	2806	3008	0.000	ppm	V	Methane
2	2.731	38768	22704	0.000	ppm	V	Ehene
3	2.843	53659	35528	0.000	ppm		Propene
4	3.124	39053	23242	0.000	ppm		Butene
5	3.219	2392	1512	0.000		V	
6	3.302	2969	1940	0.000			
7	3.853	30687	17177	0.000		V	
8	4.086	2396	1262	0.000			
9	4.198	2287	1213	0.000			
10	5.786	14846	6482	0.000		V	
11	8.234	4696	1391	0.000		V	
12	18.929	7688	2068	0.000			
13	20.123	3862	1071	0.000	ppm		1-Octene
14	20.797	4851	1244	0.000	ppm		Tr-3-Octene
15	20.947	291263	90438	0.000	ppm	V	Octane
16	21.242	3422	1046	0.000	ppm		Tr-2-Octene
Total		505645	211325				

Figure A1 GC-FID chromatogram for a gaseous sample



<Peak Table>

FID1							
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.282	2332	1007	0.000	ppm	V	Hexene
2	7.299	13624	4372	0.000	ppm	V	Benzene
3	14.564	8177	1658	0.000			
4	17.066	7782	1330	0.000		V	
5	19.169	113023	16286	0.000	ppm		1-Octene
6	20.169	69079	9296	0.000	ppm		Tr-4-Octene
7	20.611	182384	20432	0.000	ppm	V	Tr-3-Octene
8	21.133	12073618	1149514	0.000	ppm	V	Octane
9	21.477	193571	37662	0.000	ppm	V	Tr-2-Octene
10	22.059	5614	1269	0.000			
11	22.385	152344	30886	0.000	ppm		Cis-2-Octene
12	22.882	11780	1902	0.000		V	
13	23.157	6554	1361	0.000		V	
14	23.983	10220	2103	0.000		V	
15	25.502	10504	2904	0.000	ppm		Octadienes 01
16	25.636	110515	27284	0.000	ppm	V	Ethyle beneze
17	25.733	24603	6302	0.000	ppm	V	Octadienes 02
18	26.331	15320	4070	0.000	ppm		Octadienes 03
19	26.622	6396	1786	0.000			
20	27.643	99325	27770	0.000	ppm		Styrene
21	27.963	37792	10412	0.000	ppm	V	O-xylene
Total		13154559	1359607				

Figure A2 GC-FID chromatogram for an organic sample

A4. TCD sampling



Figure A3 TCD chromatogram for a gaseous hydrogen and CO_x analysis



Figure A4 TCD chromatogram for a gaseous oxygen analysis before catalytic reaction





A5. Analysis of temperature programmed reduction, oxidation and desorption

Calculation of average oxidation state of vanadium in TPR

Degree of reducibility (%) = $\frac{\text{moles of hydrogen consumed}}{\text{moles of vanadium in the sample}} \times 100$

Average oxidation state of vanadium = 5- $\frac{(moles of hydrogen consumed \times 2)}{moles of vanadium in the sample}$

Calculation of number of acidic sites from TPD

No. of acidic sites (acidity) = $\frac{\text{moles of ammonia consumed}}{\text{mass of the catalyst}}$

A6. SEM Mapping









<u>5μm</u>

<u>5μm</u>



Figure A6 SEM images and mapping of VMgO-A





<u>5μm</u>



Figure A7 SEM images and mapping of VMgO-B





V Kα1



5µm

Figure A8 SEM images and mapping of VMgO-C

A7. TEM images





Figure A10 TEM images of (a) MgO-A, (b) MgO-B and (c) MgO-C



Figure A11 TEM images of (a) VMgO-A, (b) VMgO-B-oxalic,(c) VMgO-B-water and VMgO-C