

## Heterogeneous vanadium Schiff base complexes in catalytic oxidation reactions

Christiana Abimbola Salubi<sup>a\*</sup>

<sup>a</sup>Department of Chemistry, Faculty of Natural Science, University of the Western Cape, Western Cape, South Africa

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### ABSTRACT

The chemistry of Schiff base has received remarkable attention in different applications, both organic synthesis and industries. Over the past few years many reports have been on the synthesis, characterization and application of vanadium Schiff base complexes. However, heterogeneous vanadium Schiff base catalysts are active for various oxidation reactions, making catalytic oxidation of hydrocarbons a great interest. This review summarizes the recent development of organic substrate oxidation with heterogeneous vanadium Schiff base catalysts.

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## 1. Introduction

Vanadium has the symbol “V” in group 5, and it is the lightest among the elements in the group. In 1801 a Spanish mineralogist named Andre Manuel Del Rio discovered vanadium by isolating it from brown lead ore ( $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ , also known as vanadinite. At high temperatures, vanadium reacts readily with carbon, nitrogen and oxygen. In the past 50 years, the chemistry of vanadium has received notable activity. Many reviews have been on the catalysis of vanadium compounds because of their wide application.<sup>1</sup> Recently, research was done on the coordination chemistry of vanadium complexes because of their interesting structural features,<sup>2,3</sup> catalytic applications<sup>4</sup> and biological functions.<sup>5</sup> Vanadium exhibits different oxidation states from +2 to +5, -1 to +5 and the rare oxidation state of -3 exists in  $\text{V}(\text{CO})_5^{3-}$ . There is a charge-transfer transition from the ligand to the metal ion or vice versa in a coordination complex. A change in the oxidation state of the metal, either by swapping or adding ligands, affects its coordination environment by changing the energetics of the charge transfer transition, leading to a change in the colour of the complex<sup>6</sup>.

Vanadium is the seawater’s second most abundant transition element after Zn (zinc). In the 20<sup>th</sup> century, vanadium was recognized as a biological relevant element till 1980. The relevance of vanadium started receiving much interest in the early 70s. A group of Chasteen developed a study of vanadium binding to protein using EPR and  $\text{V}(\text{IV})\text{O}^{2+}$  as a spin probe, giving more information on metal sites, its functional roles in proteins and characterizing the binding of  $\text{V}(\text{IV})\text{O}^{2+}$  to proteins. In the last 30 years, the study of vanadium chemistry has been broad, and the achievement has been enormous<sup>7</sup>.

Schiff bases, also known as “Azomethine or Imine” are formed from the condensation reaction of primary amines with an aldehyde or ketones. The Schiff base ligand binds with a metal ion via nitrogen lone pair electron.<sup>8,9</sup> Schiff base plays a significant role as a chelating ligand in transition metal coordination chemistry because they bind with non-transition, transition actinide and lanthanide metal ions to form complexes with excellent properties for practical applications and

\* Corresponding author.

E-mail address [3878010@myuwc.ac.za](mailto:3878010@myuwc.ac.za) (C. A. Salubi)

theoretical studies.<sup>10</sup> Vanadium metal has been known since 1831, but its importance in enzymatic medicinal chemistry came to the limelight in the 1980s.<sup>11</sup>

Furthermore, Schiff base complexes show excellent catalytic reactivity at high temperatures and are easily synthesized forming complexes with virtually all metal ions. However, reports show that the application of vanadium Schiff base as a homogeneous or heterogeneous catalyst in various reactions increases the performance of the reactions which are polymerization,<sup>12, 13</sup> bromination,<sup>14-17</sup> coupling,<sup>18-20</sup> degradation,<sup>21</sup> epoxidation,<sup>22, 23</sup> hydroxylation,<sup>24, 25</sup> oxidation,<sup>26-28</sup> sulphoxidation,<sup>29-31</sup> dehydrogenation,<sup>1</sup> dehydroperoxidation reactions and synthesis of some compounds.<sup>8, 32</sup>

## 2. Vanadium Schiff base-catalyzed reaction

Vanadium Schiff base complexes are efficient catalysts both in heterogeneous and homogeneous reactions; also, the metal ions, coordination sites and the type of ligand affect the activity of the Vanadium Schiff complexes. The catalytic activity of Vanadium Schiff base complexes has been analyzed in different reactions as given below. Due to the catalytic and biological importance of vanadium, there has been an increased interest in vanadium coordination chemistry in past decades. Schiff base ligands can be modified using an appropriate ring substituent containing oxygen and nitrogen atoms, their steric and electronic properties and versatility makes them essential and an area of interest today.<sup>33</sup> Vanadium complexes are well recognized because they are abundant in nature, eco-friendly, low toxic and less sensitive to moisture.<sup>34</sup> More importantly, vanadium complexes coordination chemistry has been explored due to the structural features in polynuclear and mononuclear complexes and their catalytic use for epoxidation of olefins and oxidation of alcohol and sulfide.<sup>35</sup>

Vanadium is an essential component of a catalyst that participates in different chemical processes such as olefin epoxidation, toluene to benzonitrile, oxidation of propylene and propane to oxidation of propane. Also, they are applied in the field of catalysis with many reviews and research paper reports.<sup>36</sup> This review aims to provide readers with an outline of oxidation reactions catalyzed by Vanadium Schiff base complexes published in the last decade.

Schiff base complexes show excellent catalytic reactivity and are easily synthesized, forming complexes with virtually all metal ions. Over the past few years many reports have been made on the application of vanadium Schiff base as a homogeneous or heterogeneous catalyst in catalyzing various reactions.<sup>8</sup>

## 3. Catalyst supports

A heterogeneous catalyst is prepared by immobilizing the homogeneous catalyst onto the surface of the solid supports to modify its stability and recyclability. There are different types of solid supports for heterogeneous catalysts, namely, zeolite, graphene oxide,<sup>37</sup> carbon, magnetic nanoparticles (MNPs) SBA-15,<sup>38</sup> MCM-41 (silica materials), multiwalled carbon nanotubes (MWCNTs),<sup>39</sup> clay, and polymer.<sup>40</sup> Also, the advantage of this heterogeneous catalyst in the field of catalysis is its easy separation, recyclable, thermally stable, highly selective and long catalytic lifetime.<sup>41</sup> Magnetic nanoparticle (MNPs) is also another type of solid support that is gaining more attention in the synthesis of heterogeneous catalyst because of their availability, low cost, easy functionalization, diversity, and a high surface area. More so, the nanocatalyst is active, reusable (easy separation magnetically), environmentally friendly and stable.<sup>42, 43</sup>

The disadvantages and drawbacks of using a homogeneous catalysts are instability, deactivation, controlled desired product, expensive catalyst recycling, difficulty in recovery of the final product, and only use in the solution phase<sup>40, 44</sup>. However, homogeneous complex is bound to a solid support to overcome these challenges.

## 4. Oxidation reactions

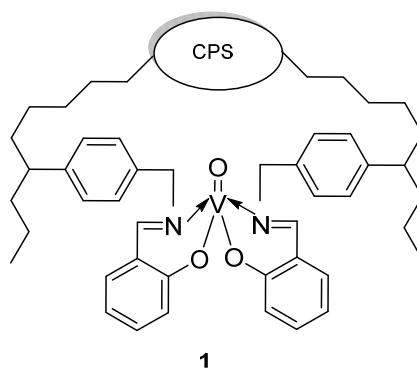
The oxidation reaction is one of the significant reactions in organic synthesis, catalysis and industries. From a scientific point of view, the oxidation reaction is very important in organic chemistry; without it, life would not exist.<sup>45</sup> However, the study of vanadium complexes with Schiff base is very important because of their ability to insert oxygen into the organic substrate from Schiff base precursor.<sup>33</sup> Furthermore, epoxides with an electron-withdrawing group undergo further oxidation; the heterogeneous catalyst synthesized by Hosseini and co-workers possesses excellent selectivity and conversion for oxidation of alkenes and alkanes; also there is less loss of activity when reused several times. The heterogeneous catalyst was used for selective oxidation of alkyl aromatic, benzene, alkenes and alkanes in the presence of hydrogen peroxide as oxidants. The catalyst was derived from the condensation reaction of salicylaldehyde and benzhydrazide to form hydrazine Schiff base, which reacts with vanadium(IV), the complexes are immobilized onto the surface of functionalized silica gel. However, oxidation of allylbenzene, norbornene, and 1-decene gave a low yield, probably because of the low solubility of acetonitrile.<sup>26</sup>

A heterogeneous catalyst  $[V^{VO_2}(\text{pydx-dmen})]-Y$ , reported by Maurya *et al.*<sup>46</sup> was synthesized systematically by condensation of N,N-dimethylethylenediamine and pyridoxal then reacted with  $[V^{IVO}(\text{acac})_2]$ , to form complexes  $[V^{IVO}(\text{acac})(\text{pydx-dmen})]$  then converted to oxidoperoxidovanadium(V) complex  $[V^{VO}(\text{O}_2)(\text{pydx-dmen})]$  in the presence of 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).  $[V^{VO}(\text{O}_2)(\text{pydx-dmen})]$  is encapsulated on nano-cavity of zeolite-Y to form the heterogeneous catalyst  $([V^{VO_2}(\text{pydx-dmen})]-Y)$ . The catalytic activity of the complexes was determined in the oxidation

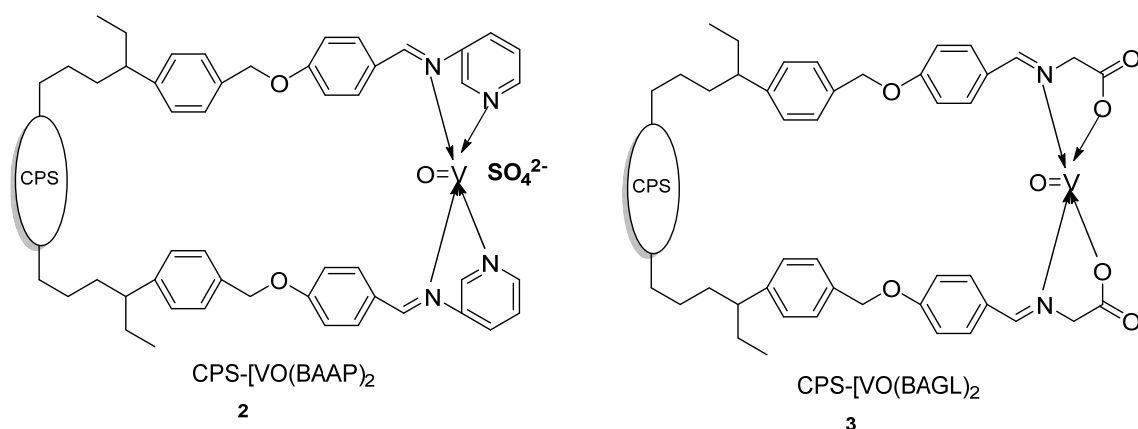
of cyclohexene, methyl phenyl sulfide, styrene and diphenyl sulfide in the presence of  $\text{H}_2\text{O}_2$  as oxidant. The heterogeneous catalyst shows to have excellent recyclability. In addition, the catalyst  $[\text{V}^{\text{V}}\text{O}_2(\text{pydx-dmen})]\text{-Y}$  shows different catalytic actions for oxidation of methyl phenyl sulfide and diphenyl sulfide while oxidation of styrene gave four different products which are phenylacetaldehyde styrene oxide, benzoic acid, benzaldehyde and 1-phenylethane-1,2-diol. High selectivity was obtained for benzaldehyde, which may be due to the attack between styrene oxide and hydrogen peroxide (nucleophilic). Secondly, the formation of benzaldehyde is favoured by oxidative cleavage of the double bond on styrene through a radical mechanism.

Graphene oxide is efficient and convenient as support for grafting; it has good surface chemistry and low dimensionality. A heterogeneous catalyst synthesized by immobilizing oxo-vanadium Schiff base on 3-aminopropyltrimethoxysilane (APTMS) grafted graphene nanosheets exhibit high efficiency and reactivity for oxidation of alcohols compared to the homogenous complexes. The synthesized graphene-based heterogeneous catalyst is convenient, inexpensive, and stable at room temperature. The complexes were recycled and recovered with minimal loss in their catalytic activity. Although, the homogeneous analogue has equal efficiency as the graphene-bound oxo-vanadium Schiff base. Substituted aromatic alcohol was reported to be more reactive compared to aliphatic and alicyclic secondary alcohols.<sup>47</sup>

A heterogeneous catalyst (CPS-[VO(SAAM)<sub>2</sub>] microspheres **1**) developed by Gao *et al.*<sup>48</sup> as shown in **Fig. 1**, effectively catalyze the oxidation reaction of ethylbenzene by molecular oxygen because of vanadium atom character; it has two high valence oxidation states. The complexes provide an excellent condition giving high catalyst selectivity and activity for oxidation of ethylbenzene and can also be recycled and reused. The oxidation of ethylbenzene is strongly influenced by temperature and the quantity of the catalyst used.<sup>49</sup> In addition, two different heterogeneous catalysts, CPS-[VO(BAAP)<sub>2</sub>] **2** and CPS-[VO(BAGL)<sub>2</sub>] **3** (**Fig. 2**) synthesized, exhibit different activity because of the stability VO(BAAP)<sub>2</sub> than VO(BAGL)<sub>2</sub>. The two complexes catalyze the oxidation of benzyl alcohol and cyclohexanol using molecular oxygen as the oxidant. However, CPS-[VO(BAAP)<sub>2</sub>] **2** has higher catalytic activity, recyclability and stability than microspheres. The immobilized VO(BAAP)<sub>2</sub> is more stable than VO(BAGL)<sub>2</sub>; this makes CPS-[VO(BAAP)<sub>2</sub>] have excellent catalytic properties than CPS-[VO(BAAP)<sub>2</sub>], VO(BAGL)<sub>2</sub> gave 58% yield for benzaldehyde.



**Fig. 1.** Heterogeneous catalyst CPS-[VO(SAAM)<sub>2</sub>] microspheres.



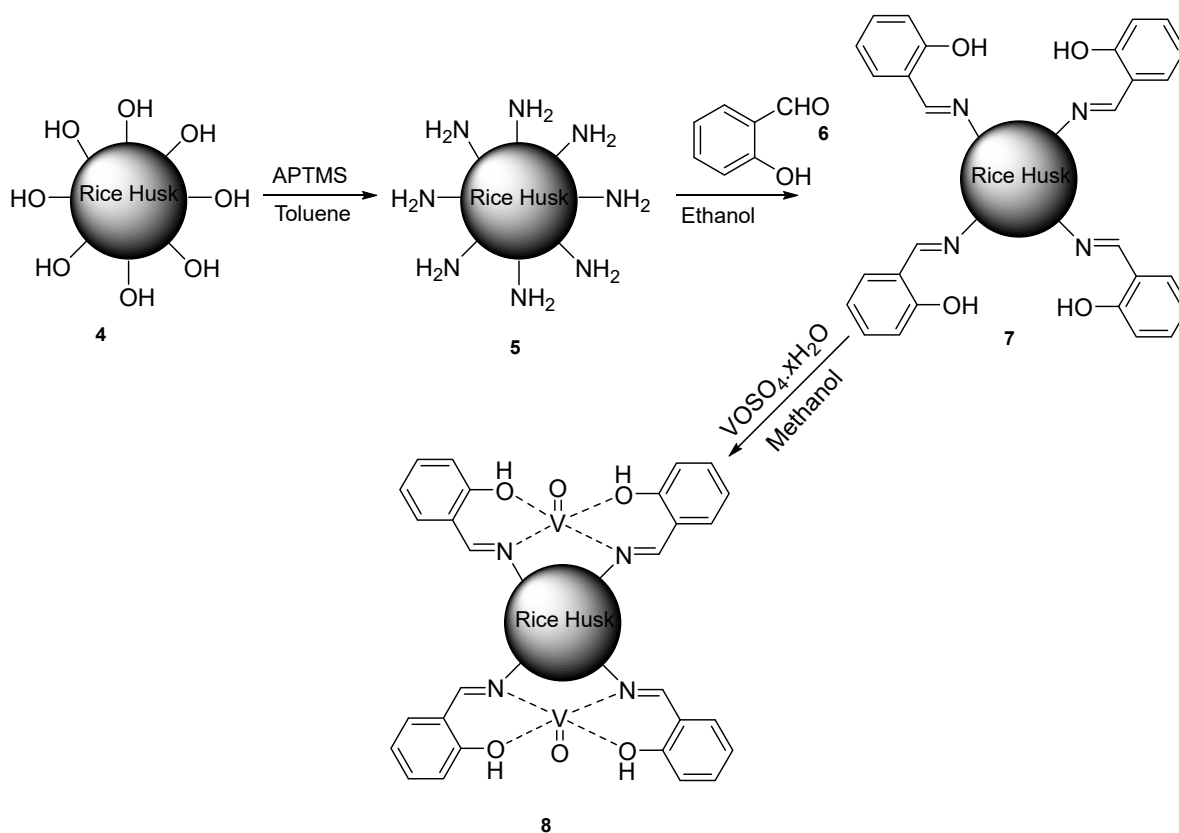
**Fig. 2.** Structural formula of CPS-[VO(BAAP)<sub>2</sub>] and CPS[VO(BAGL)<sub>2</sub>] microspheres.

The mechanism of styrene oxidation follows the proper arrangement of atoms on vanadium by nucleophilic attack of coordinated electron-deficient styrene and peroxy oxygen, then the formation of pseudocyclic dioxametallocyclopentane by rearranging of styrene between vanadium–oxygen bond ( $\sigma$ - $\pi$  rearrangement). A new  $\mu$ -oxido divanadium compound  $[(\text{VOL})_2(\mu\text{-O})]$  synthesized by reacting vanadium compound with aliphatic hydrazone ligand ( $\text{LH}_2 = (\text{E})\text{-N}^1\text{-(1-(2-hydroxyphenyl)ethylidene)acetohydrazide}$ ), the complexes was further infused on alumina ( $\text{Al}_2\text{O}_3$ ) to give a heterogeneous

catalyst. The catalytic activity of the heterogeneous catalyst tested on oxidation of styrene were reported to be recycled when supported over alumina. Therefore, 99.7% conversion yield and 88.1% selectivity for benzaldehyde formation were obtained because styrene oxide can be easily converted to benzaldehyde by nucleophilic attack of  $\text{H}_2\text{O}_2$  with styrene oxide.<sup>50</sup> A new heterogeneous catalyst oxo-vanadium(IV) supported on a polymer for oxidation toluene gives an oxygenated product. The heterogeneous catalyst was synthesized by reacting 2,4-dihydroxy benzaldehyde,  $\text{VO}(\text{acac})_2$  and nano-silica  $\text{NH}_2$ -functionalized. The catalyst was reported to be recycled several times without significant loss in its catalytic activity, chemically stable and efficient for the oxidation reaction. However, the catalyst gave a high selectivity and excellent yield. In addition, the catalyst retains its catalytic activity when reused at least eight times, has easy recovery from the product and is chemically stable. Although, an increase in catalyst concentration decreases selectivity for benzaldehyde, increases the conversion of toluene and decreases turnover number. Toluene with electron-donating substituent gives excellent conversion and selectivity for the formation of aldehydes.<sup>51</sup>

The heterogeneous catalyst is prepared by immobilizing vanadium oxo Schiff base on graphene oxide as the support using a covalent bonding to catalyze the oxidation of furfural and 5-hydroxymethylfurfural to maleic anhydride. Hydroxyl functional groups makes both sides of the graphene oxide sheet an anchor by using them as scaffolds connecting the oxovanadium Schiff base and organometallic nodes. Oxovanadium Schiff base has an active site, and the residual oxygen group adsorb 5-hydroxymethylfurfural (HMF) to regulate the concentration of the reactants surrounding the catalyst. Hence, the catalyst ( $\text{VO-NH}_2\text{-GO}$ ) gave high selectivity towards maleic anhydride and efficiency. The catalyst was reported to give 95.3% and 62.4% yields for the conversion of 5-hydroxymethylfurfural (HMF) and furfural to maleic anhydride.<sup>52</sup>

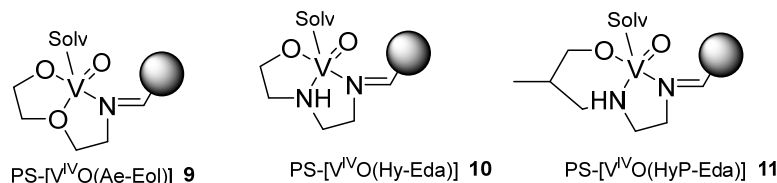
Also, a heterogeneous catalyst was synthesized using rice husk (low cost/renewable) as support to catalyze the oxidation reaction of tertiary amines. However, substituted pyridines are less reactive compared to substituted aliphatic amines. Although the complexes were efficient and gave a good yield in the oxidation of tertiary amine, it is chemically stable and can be recycled five times without losing their activity. In addition, pyridine with an electron-donating group is very reactive, while amine with steric hindrance gives a good conversion yield. This heterogeneous catalyst was synthesized as shown in **Scheme 1** by functionalizing rice husk (RH) **4** with amino-propyltrimethoxysilane (APTMS), reacting it with salicylaldehyde **6** to give rice husk- functionalized Schiff base, which is further reacted with vanadyl sulphate.<sup>53</sup>



**Scheme 1.** Schematic representation of the synthesis of RH-grafted oxo-vanadium Schiff base<sup>53</sup>.

A heterogeneous catalyst derived from chloromethylated polystyrene as solid support is cost-effective, readily available, functionalized and possesses high thermal stability. However, three heterogeneous catalysts (**Fig. 3**) were synthesized from chloromethylated polystyrene (solid support) for the oxidation of alkenes (styrene, cyclohexene, allylbenzene, and *cis*-

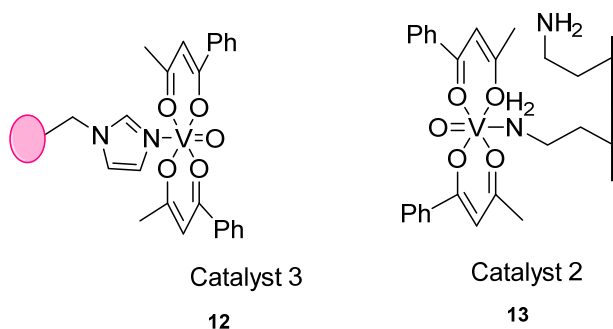
cyclooctene). Therefore, an excellent catalytic activity toward oxidation of styrene and cyclohexane with complexes **9** and **11** shows 99.86% and 95.12% conversion with complex **9**, while complexes **11** gave 95.42 and 92.84% conversion. Also, catalyst **2** gave the least catalytic activity of 79.1% conversion for cyclohexene compared to catalysts **1** and **3** with 95.1 and 92.8% conversion. The complexes are eco-friendly and cost-effective for the oxidation of alkenes. The catalyst was synthesized by reacting polymer anchored Schiff base ligand with  $[\text{VO}(\text{acac})_2]$  to give Polymer anchored vanadium complexes  $\text{PS}-[\text{V}^{\text{IV}}\text{O}(\text{Ae-Eol})]$  **9**,  $\text{PS}-[\text{V}^{\text{IV}}\text{O}(\text{Hy-Eda})]$  **10**, and  $\text{PS}-[\text{V}^{\text{IV}}\text{O}(\text{HyP-Eda})]$  **11**. The complexes are thermally stable and recycled several times without loss in their catalytic activity.<sup>54</sup>



**Fig. 3.** Polymer-anchored metal complexes.

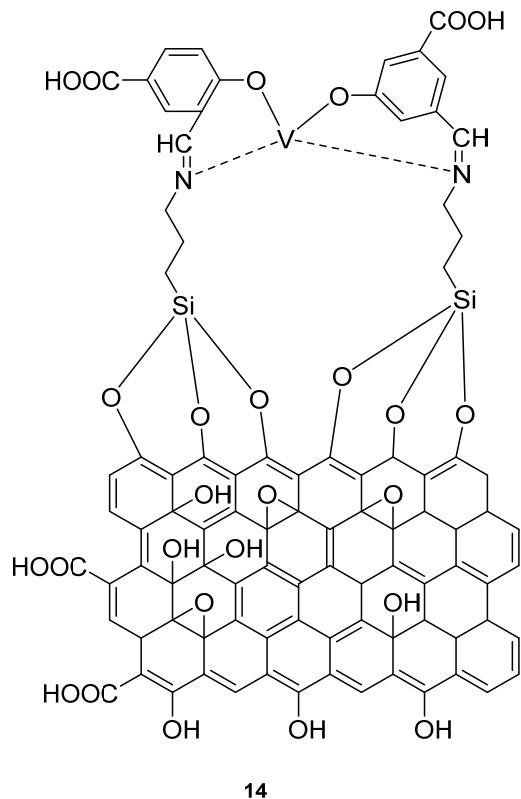
The central metal ion in complexes is depends on catalyst's effectiveness for the oxidation reaction.<sup>55</sup> A neat vanadium complex as a homogeneous catalyst and encapsulating zeolite -Y complexes (Heterogeneous catalyst) were synthesized and compared toward cyclohexene, benzene, phenol and styrene oxidation. Therefore, this oxidation reaction involves the transfer of oxygen atoms from peroxovanadium(V) intermediate species to the substrate, which occurs from the interaction between hydrogen peroxide and the catalyst. Encapsulated zeolite-Y complexes showed weak activity in the oxidation of styrene compared to benzene and phenol, this is associated with zeolite pores selective effects not letting large substrates enter the catalytic centres and products exiting freely from the channels. The heterogeneous catalyst was synthesized by encapsulating zeolite -Y with the complexes 7-amino-5-aza-4-methyl-hept-3-en-2-one and 4,4'-(ethane-1,2-diyl dinitrilo)dipentan-2-one). The heterogeneous catalyst was reported to possess high turnover frequency, good selectivity, efficiency and environmentally friendly. Oxidation of phenol gave catechol and hydroquinone; without catalyst the reaction gave 1% conversion, with H-Y zeolite as catalyst 3.5% phenol conversion was obtained whereas, V-exchanged zeolite gave a higher phenol conversion; this indicates that the presence of a ligand in the catalyst increases the catalytic activity of the catalyst. However homogenous complexes are reported to be more active for oxidation reaction than the encapsulated VO(IV) complexes.<sup>56</sup>

Based on Kesharwani *et al.*<sup>57</sup> findings, product selectivity and substrate conversion depend on the nature of solid support in a heterogeneous catalyst. Therefore, two heterogeneous catalysts from the vanadium(IV) oxido complex of 1-Phenyl-1,3-butanedione  $[\text{V}^{\text{IV}}\text{O}(\text{bzac})_2]$  were supported on imidazole-modified polystyrene beads and APTMS modified graphene oxide while studying the effect (solid support) on oxidation of thioethers (catalyst 2: graphene oxide supported GO-APTMS- $[\text{V}^{\text{IV}}\text{O}(\text{bzac})_2]$  complex **12**, catalyst 3: polymer anchored PS-im- $[\text{V}^{\text{IV}}\text{O}(\text{bzac})_2]$  complex **13** (**Fig. 4**). Hence, good substrate conversion was exhibited for both catalysts **2** and **3**, but catalyst **3** gave better performance for oxidation of thioether than catalyst **2**.



**Fig. 4.** Graphene oxide and PS-anchored  $[\text{V}^{\text{IV}}\text{O}(\text{bzac})_2]$  complexes.

Tautomerization effect, low basicity of  $\pi$ -electron group or steric hindrance is reported to affect the conversion rate in epoxidation reaction. However, in the epoxidation reaction of cyclooctene and cyclohexene with V(IV) Schiff-base/GO catalyst **14**, the aromatic/allyl group had the highest conversion rate. Hence, the reaction gave the following conversion rate; 54 % (allyl alcohol), 77 % (allyl bromide), 91 % (styrene), 96 % (1-octene), and 98 % (cyclooctene). The catalyst shows an exceptional efficiency for epoxidation reaction with excellent effectiveness and durability after six subsequent cycles because graphene oxide is structurally robust and has a strong interaction between chelating moieties and Vanadium (IV). The reaction gave 99% selectivity and approximately ~93% yield with 50mg catalyst. The heterogeneous catalyst (**Fig. 5**) was synthesized from the immobilization of vanadium (IV) Schiff base-amine on graphene oxide.<sup>58</sup>



**Fig. 5.** V(IV) Schiff-base GO catalyst

Polymer particles with a small diameter favour catalysis, but a decrease in the size of the beads makes the separation more difficult. Vanadium complexes immobilized on polymerized as the support. Catalyst immobilisation on polymerize supports gives a high turnover number and is also highly effective and recyclable compared to a homogenous catalyst. Heterogeneous catalysts are prepared by binding the ligand and polymer, then further binds to the vanadium complex.<sup>59</sup> Also, oxovanadium complexes can effectively promote and catalyze alkane functionalization under moderate and mild conditions.<sup>60</sup>

The comparison between the homogenous catalyst and solid supported vanadium catalyst, shows that immobilization of support such as carbon materials or zeolites on oxidovanadium complexes facilitates recyclability and easy separation, although, oxidovanadium complexes exhibit efficient activity toward epoxidation of allylic alcohol and alkenes. Also, the presence of azine fragments ligands (C=N-N=C) in complexes is responsible for its catalyst selectivity and efficiency towards alkanes oxidation, but the use of 2-pyrazinecarboxylic acid (PCA) as a promoter increases the catalyst efficiency.<sup>61, 62</sup>

The stability of oxido, non-oxido and dioxidovanadium centre is depends on either the ligand or reaction conditions.<sup>63</sup> However, Salen complexes with metals are applied as a catalyst for asymmetric synthesis, also Salen vanadium complexes immobilized on a support such as zeolites, polystyrene and silica have been extensively exploited for therapeutic use. Vanadium-salen complexes produce a stable product by releasing a labile ligand.<sup>64</sup>

A CeO<sub>2</sub> supported vanadium catalyst was synthesized with different vanadium loading for oxidation of H<sub>2</sub>S to sulfur and water (either selective or partial oxidation reaction). However, high catalytic activity was observed with 92% H<sub>2</sub>S conversion and approximately 4% selectivity toward SO<sub>2</sub>. Between 300-370 °C temperature range, the catalyst was reported to effectively inhibit the formation of SO<sub>2</sub>, because the conversion of H<sub>2</sub>S is close to equilibrium value while the selectivity of SO<sub>2</sub> is below equilibrium calculation. Although, catalyst deactivation was observed due to the deposition of sulfur and there was no formation of SO<sub>3</sub>.<sup>65</sup>

Several studies have proven that a heterogeneous catalyst has a high catalytic performance than a homogeneous catalyst, Similarly, oxidovanadium(V) **15** and dioxidovanadium(V) **16** functionalized with carbon materials show efficient catalytic oxidation and activity with good recyclability for four cycles compared to its homogeneous environment with no recyclability. There was a decrease in the vanadium content due to the catalyst recycle and some loss of catalyst activity which was more evident in complex **15** than **16**. The two oxidovanadium catalysts (oxidovanadium(V) **15** and dioxidovanadium(V) **16**) shown in **Fig. 6** below were synthesized and immobilized on functionalized activated carbon and

carbon nanotubes. Both homogeneous and heterogeneous catalyst was evaluated for oxidation of cyclohexane, and the effect of microwave irradiation time was studied on the catalytic activity.<sup>66</sup>

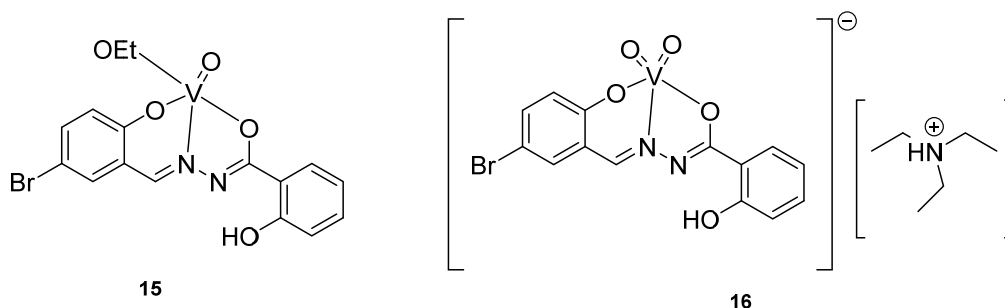


Fig. 6. Oxidovanadium catalysts

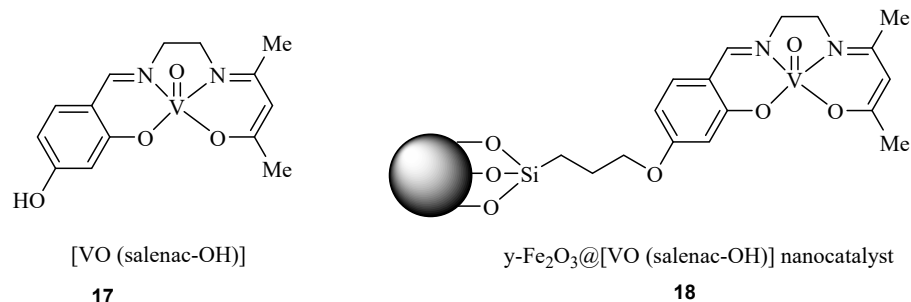
Furthermore, to explore the importance of vanadium, doped Co and V were designed by an energy-efficient method as an electrocatalyst for oxidation of water in energy conversion. DFT calculation and systematic experiment show that the doped catalyst can optimize free energy for adsorbed intermediates and electronic structure. The novel doped catalyst (Co, V)-FeOOH is rich in Fe, which exhibits excellent electrocatalytic performance with a low over potential of 230 and 322 mV. Also, the surface area is electrochemically active and V and Co have a concerted effect which is responsible for the superior performance of the nanoribbon catalyst (Co, V)-FeOOH.<sup>67</sup>

Vanadium oxide supported on two different mesoporous silica (SBA-15 and MCF-17) was synthesized either by wet or dry impregnation. The catalyst (VOx /m-SiO<sub>2</sub>) was investigated in the oxidation of methane to formaldehyde. The dry impregnation method VOx/m-SiO<sub>2</sub> catalyst supported on MCF-17 was proven as the best in the direct conversion of methane oxidation to formaldehyde, 1% of VOx/MCF-17(DI) catalyst gave 20.2% conversion at 600 °C, this is because of the large pore size and surface area, high dispersion of vanadium loading. The characterization techniques also indicated that VOx/m-SiO<sub>2</sub> catalysts produce tetrahedral monovanadate in the dry impregnation method than in the wet impregnation (WI).<sup>68</sup>

The catalytic study of Heterobimetallic vanadium complexes reported by Kumar *et al.*<sup>69</sup> has shown to be very effective for the oxidation of alcohols. However, complexes 1 and 4 show more effectiveness in the oxidation of alcohol to aldehyde and ketones. Vanadium in all the complexes has an oxidation state of +5 and d<sup>0</sup> electronic configuration. Primary Benzylic alcohol with an electron-donating group gave a higher yield and conversion to aldehydes than primary benzylic alcohol with an electron-withdrawing group. In addition, Primary benzylic alcohols with meta and ortho electron-donating or electron-withdrawing substituents oxidized to a lower yield than substituents at the para position on primary benzylic alcohols. Six heterobimetallic catalysts were synthesized from two dihydrazones as ligands (bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H4nph) and disalicylaldehydeoxaloyldihydrazone (H4slox)) and vanadium pentoxide [M<sub>6</sub>[VO(μ-O)]<sub>2</sub>(μ-OH)<sub>4</sub>(μ<sub>4</sub>-slox/nph)].n DMF]<sub>∞</sub> where M = Na, K, and Cs; n = 1 complex (1), 0 for complexes (2)-(6).

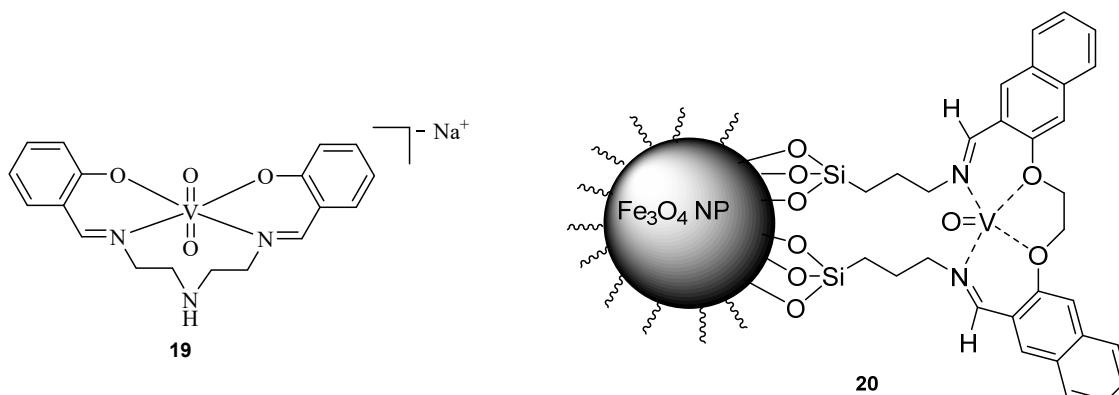
Polymer catalysts have high reactivity and activity, after several recyclables, they still retain their catalytic activity. The polymer-bound metal complexes synthesized as a catalyst for oxidation of alkene exhibit excellent recyclability (up to 3 cycles) after checking the IR, electronic and EPR spectral patterns with the original spectra before use, also this polymer does not leach which attests to the heterogeneous nature. The polymer catalyst was synthesized from functionalized ligands and ligand precursors to give a polymer-bound ligand (through covalent bonds), and further reaction of polymer-bound ligands with the metals (V<sub>2</sub>O<sub>5</sub>) gave polymer-anchored complexes.<sup>70</sup> In comparison, cyclopentane oxidation to cyclopentanol and cyclopentanone with V-scorpionate complex catalyst exhibits a lower catalytic activity and turnover number than cyclohexane. However, the dioxovanadium complex [VO<sub>2</sub>(SO<sub>3</sub>C(pz)<sub>3</sub>)] gave the highest activity towards cyclohexane oxidation and a maximum turnover number (TON) of 117 which is higher than the turnover number of Vanadium oxides (47) that is commercially available. Silva *et al.*<sup>71</sup> reported the first V-scorpionate complex catalyst used for carboxylation of alkanes. It was synthesized by reacting [VO(OEt)<sub>3</sub>] with the scorpionate ligands (HC(pz)<sub>3</sub> and SO<sub>3</sub>C(pz)<sub>3</sub>). The oxidation reaction of cyclohexane with dioxygen (green oxidants) was studied using a V-scorpionate complex [VCl<sub>3</sub>(HC(pyrazolyl)<sub>3</sub>)] and [VCl<sub>3</sub>(SO<sub>3</sub>C(pz)<sub>3</sub>)] as a catalyst. The catalyst [VCl<sub>3</sub>(HC(pyrazolyl)<sub>3</sub>)] gave 13% conversion of cyclohexane into ketone and alcohol and high activity, the conversion rate was increased to 15% by adding pyrazinecarboxylic acid (PCA).<sup>72</sup>

At room temperature, a nanocatalyst  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] **18** (Fig. 7) selectively oxidizes sulfide into sulfoxide with no unwanted by-products with excellent yield, whereas in the absence of a catalyst, no complete oxidation reaction occurs after for 24 hours. Hence, oxidation of diethyl sulphide gave a good yield compared to diphenyl sulphide because it is sterically hindered. The catalyst was recycled five times with no loss in the catalytic activity and recovered magnetically using an external magnet. Also, the catalyst was synthesized by immobilizing oxo-vanadium(IV) complex [VO(salenac-OH)] **17** on the surface of magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles **18**.<sup>73</sup>



**Fig. 7.** Structural formula of the oxo-vanadium(IV) Schiff base complex and nanocatalyst

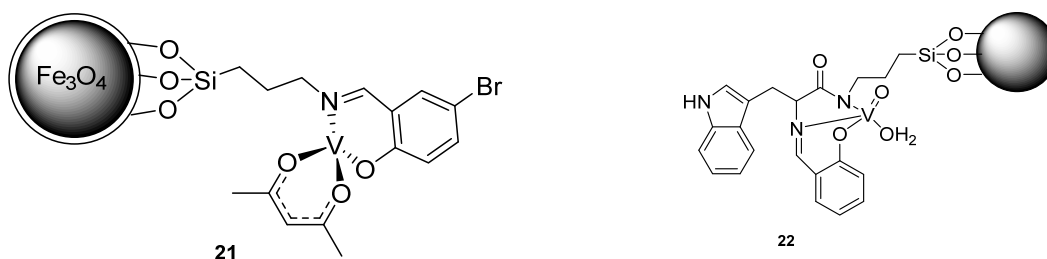
Moreover, with the environmental issue associated with the use of solvent for synthesis, a green synthesis approach was used in synthesizing Vanadium (V) complex  $\text{Na}[\text{VO}_2\text{L}]$  **19** (Fig. 8), by grinding vanadyl sulfate, salicylaldehyde and diethylenetriamine. The complex was utilized as a catalyst for the oxidation of alcohol and organic sulphides with conventional heating and microwave irradiation. Based on the result obtained the complex has shown to be efficient and selective in oxidizing benzyl alcohol and methyl phenyl sulfide. Hence the oxidation reaction under the microwave occurs faster than the conventional heating<sup>74</sup>. Similarly, microwave heating proves to be the best method for vanadium(V)-catalyzed oxidation of methyl p-tolyl sulfide and cyclooctene because it gave a high sulfide conversion within a short time (20–100 s), temperature range of 32– 50 °C and high product selectivity with no formation of sulfone.<sup>75</sup>



**Fig. 8.** Structure of  $\text{Na}[\text{VO}_2\text{L}]$  complexes

**Fig. 9.** Structure of  $\text{VO}(\text{BINE})@\text{Fe}_3\text{O}_4$  nanocatalyst

More importantly, vanadium complexes have more attention because of their widespread use as heterogeneous, homogeneous and industrial oxidation processes. Numerous heterogeneous vanadium nanocatalysts have been employed for the oxidation reaction. The nanocatalyst  $\text{VO}(\text{BINE})@\text{Fe}_3\text{O}_4$  **20** (Fig. 9) has also proved to be efficient, reusable and employed as a green catalyst for oxidation of sulfides to sulfoxides, thereby making the nanocatalyst a proper catalyst to selectively oxidize sulfides. The reaction occurs at room temperature within a short time to obtain sulfoxides in high yield; the catalyst was recycled eight times (8) and recovered magnetically with no loss in activity or leaching. Similarly, the method has several advantages: short reaction times, catalyst recyclability, excellent chemoselectivity, mild reaction conditions, high yield, practicability, chemically stable and cheap oxidant. Hence, the oxo-vanadium/Schiff-base complex synthesized was immobilized on the surface of the magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles.<sup>76</sup> Additionally, magnetic nanoparticle  $\text{VO}(\text{acac})@\text{Sb}@\text{SMNPs}$ , **21** (Fig. 10) synthesized by immobilizing vanadyl acetylacetonate complex,  $[\text{VO}(\text{acac})_2]$  onto the surface of a silica magnetite nanoparticles were utilized for oxidation of sulfides and epoxidation of alkenes.<sup>77, 78</sup>



**Fig. 10.** Structural of the magnetic nanoparticle  $\text{VO}(\text{acac})@\text{Sb}@\text{SMNPs}$

**Fig. 11.** Structural representation of the nanoparticle catalyst



Furthermore, protein–vanadium complex hybrid was utilized to catalyse the oxidation of methyl phenyl sulfide, the vanadium complexes crystal structure was analysed with a single crystal X-ray diffraction, and hybridized proteins serve as an enzyme. In addition, the disadvantage of the enzyme catalysts is that it is sensitive to changes in temperature. At a high-temperature rate of reaction, conversion and yield improve but further increase deactivates the artificial enzyme, while at a lower temperature, the rate of reaction decrease, thereby improving enantioselectivity.<sup>79</sup>

Also, amino acids play an important role in homogeneous and heterogeneous vanadium complexes. However, an amino acid Schiff base (N-salicylidene-L-tryptophan and N-salicylidene-L-histidine) ligand was utilized to synthesize a heterogeneous catalyst VO(Sal-His)/AmpSCMNP and VO(Sal-Tryp)/AmpSCMNPs **22** (Fig. 11) for epoxidation of olefins and allyl alcohols. It was confirmed that the reaction gave excellent selectivity, conversion, and high yield, while the catalyst is easy to separate, chemically stable and recyclable with no desorption during epoxidation reaction.<sup>80</sup>

As proven by Dabiri *et al.*<sup>81</sup> the use of catalyst is essential and plays a vital role in the selectivity and yield obtained in the oxidation of sulfides to the sulfoxide; little sulfoxide was formed in the absence of catalyst while the addition of only vanadium catalyst (in the absence of SiO<sub>2</sub>) or only SiO<sub>2</sub> do not bring a significant yield unless the in situ catalyst is prepared and used, which gave an excellent and improved yield. The catalyst VSBC@NS **23**, as shown in Fig. 12, gave a good yield towards alcohol oxidation with excellent selectivity to give carbonyl compounds. Also, the VSBC@NS **23** is reusable and recyclable. As shown below in Table 1, the oxidation reaction of different substrates catalysed by several heterogeneous vanadium Schiff base complexes was compared.

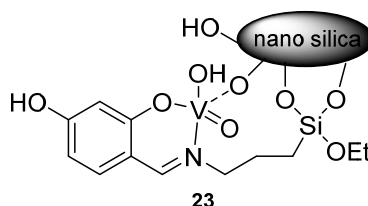


Fig. 12. Vanadium nanocatalyst VSBC@NS

Table 1. Comparison of the efficiency of several heterogeneous vanadium Schiff base catalysts in the oxidation of reaction

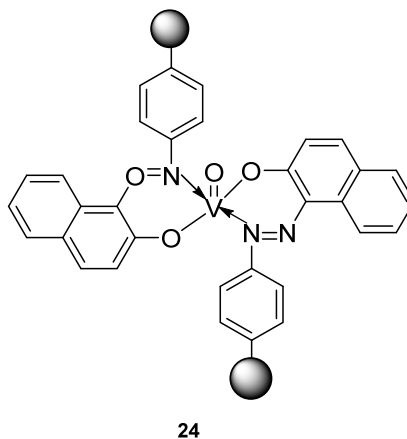
Entry	Catalyst	Substrate	Condition	Yield/Selectivity(%)	References
1	VO(Schiff) complex grafted on MCM-41	methyl phenyl sulfide	CH <sub>2</sub> Cl <sub>2</sub> , 298 K, 6 hours	70-96	82
2	VO(IV)-MCM-41.	methyl phenyl sulfide	Urea Hydrogen Peroxide (oxidant), r.t.	95	83
3	V-IFBNPs	cyclooctene	CCl <sub>4</sub> , TBHP	80-92	84
4	PSim[VVO <sub>2</sub> (bzpy-fah)] <sup>+</sup> polymer-supported dioxovanadium(V) complex	isoeugenol	80°C, acetonitrile, H <sub>2</sub> O <sub>2</sub> , 2 hours		85
5	Vanadium complex grafted on starch nanoparticle	benzhydrol	<i>t</i> -BuOOH, 65 °C, 1 hour	94	86
6	[VOL(OMe)]/ MNPs	methylphenylsulfide	H <sub>2</sub> O <sub>2</sub> , EtOH, reflux, 15mins	92	42
7	[VOL]Cl <sub>2</sub> @mont	cyclohexene	TBHP, 8 hours, ACN	100	41
8	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PTMS@Mel-NaphVOcomplex	cyclooctene	TBHP, CH <sub>3</sub> CN, reflux.	100	43
9	Fe <sub>3</sub> O <sub>4</sub> @VO (salen)	Methyl phenyl sulfide	H <sub>2</sub> O <sub>2</sub> , r.t, solvent-free	96	87
10	VO-salen-MCM-41	Benzyl methyl sulfide	H <sub>2</sub> O <sub>2</sub> , 45 min	98	88
11	SBA-NH <sub>2</sub> -VO <sup>2+</sup>	5-hydroxymethylfurfural	Toluene, 110 °C	26.1	38
12	VO-GO	styrene	8 hours, CH <sub>3</sub> CN, air	55.3	89
13	V/SBA-15	Methyl phenyl sulphide/sulfides	DCM (dichloroethane), r.t, H <sub>2</sub> O <sub>2</sub>	85/ 93	90
14	VO-Sal-CMK-3	Styrene	CH <sub>3</sub> CN, TBHP	73.9	91
16	Cu <sub>3</sub> (BTC) <sub>2</sub> -AMP-PA-V	cyclooctene	TBHP, 3 hours, 90 °C	-	92

Also, a heterogeneous catalyst [VO(VTCH<sub>2</sub>)<sub>2</sub>]-Y synthesized by entrapping VO(IV) complexes into the zeolite-Y nanopores catalyses the oxidation of limonene, thereby exhibiting a high catalytic activity compared to the VO(IV) complexes. Although the catalytic activity of the heterogeneous catalyst decrease when reused due to a reduction in the vanadium content.<sup>93</sup> In addition, Saeed *et al.*<sup>94</sup> synthesized a similar heterogeneous catalyst (VOL-Y) for the oxidation of alkenes and aldehyde reduction oxovanadium(IV) was encapsulated into the nanocavities of zeolite-Y. However, oxidation

of alkenes gave a higher conversion and selectivity was obtained for aromatic and cyclic alkenes than aliphatic alkenes, while the reduction of aldehyde in the presence of the catalyst gave 56-100% conversion for most aldehydes.

A new heterogeneous catalyst for selective oxidation of dibenzothiophene (DBT) was synthesized by immobilizing the VO-Schiff base complex on modified GO nanosheets. However, the catalyst was efficient and recyclable up to 6 times without loss of catalytic activity.<sup>95</sup> Similarly, Zhang *et al.*<sup>96</sup> reported VO-MONFs heterogeneous catalysts (MONFs-supported vanadium catalyst) as one of the catalysts with the highest values and excellent for the catalytic oxidation of thiols because of their high porosity, good distribution and easy access to the active sites.. The heterogeneous catalyst is synthesized by incorporating oxo-vanadium (IV) onto functionalized microporous organic nanotube frameworks. Also the metal species (vanadium (IV)) is dispersed within the nanotube walls. Therefore, the catalytic oxidation of thiols with MONFs-supported vanadium catalysts (VO-MONFs) in the presence of urea hydrogen peroxide (UHP) oxidant gave a 98% yield.

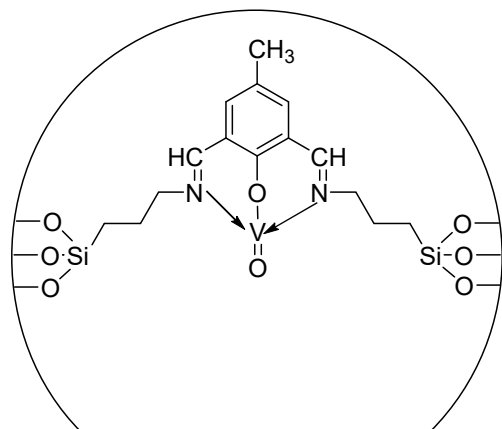
Polymer anchored complexes PS-im-[VO<sub>2</sub>(hynd-ap)] and PS-im-[VO<sub>2</sub>(hynd-ae)], were synthesized to catalyse the oxidation of primary aliphatic alcohols. An increase in the carbon chain of the aliphatic alcohol reduces its reactivity, more so aliphatic alcohol (straight-chain) has lower reactivity than the aromatic alcohol, thereby making its oxidation harder with a lower substrate conversion rate. However, a 65% conversion rate was observed for oxidation of 1-hexanol while 95% substrate conversion was obtained for 1-butanol. In addition, the PS-im-[VO<sub>2</sub>(hynd-ap)] complex exhibits better reactivity than the PS-im-[VO<sub>2</sub>(hynd-ae)] complex. The complexes were synthesized by grafting modified chloromethylated polystyrene with dioxidovanadium(V) complexes.<sup>97</sup> Paul *et al.*<sup>98</sup> synthesize polystyrene anchored oxovanadium(IV) catalyst **24** shown in **Fig. 13** for oxidation of alkane and alkenes, the catalyst is recycled 6 times without a change in the catalytic properties, more importantly, alkanes with the electron-donating group gave a high percentage conversion selectivity compared to the electron-withdrawing group. However, a maximum of 96% conversion and 95% selectivity was observed for the oxidation of ethyl benzene, while styrene gave 97% conversion and 88% selectivity.



**Fig. 13.** Polystyrene anchored oxovanadium(IV) catalyst (PS-VO-naph)

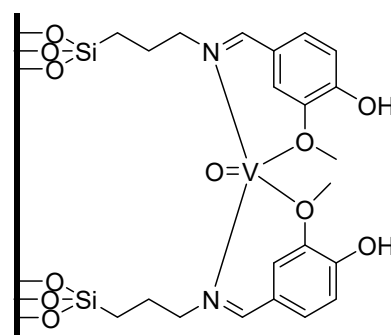
More importantly, in the oxidation of alkenes with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)], tert-butyl hydroperoxide (TBHP) shows to be a suitable oxidant which gave 82-95% yield for aromatic alkenes while a lower yield is obtained in aliphatic alkenes. The small yield in the oxidation of aliphatic alkenes is because of the low reactivity of aliphatic alkenes because of their less electron density and mobility to the active catalytic site. Also, the heterogeneous catalyst is synthesized by immobilizing the oxidovanadium(IV) Schiff base complex on the magnetic nanoparticles ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>)<sup>99</sup>.

In addition, Verma *et al.*<sup>100</sup> findings on oxidation of alcohols, vanadium metal in silica-supported oxo-vanadium complex **25** (**Fig. 14**) is an active species responsible for the oxidation reaction. The reaction without a catalyst or the presence of only silica-supported Schiff base did not give any oxidized products even when the time was prolonged. However, in this reaction, secondary aromatic alcohols and alcohols with electron-donating are more reactive than alicyclic and alcohols with an electron-withdrawing group. Most importantly, a small amount of the catalyst shows moderate catalyst activity. In addition, VO-NH<sub>2</sub>-GO catalyst was synthesized for epoxidation of fatty acid and esters in the presence of TBHP (*t*-butyl hydroperoxide) as an oxidant. The concentration of the oxidant does not affect the reaction, while the temperature affects the selectivity of the epoxide produced; an increase in temperature reduces the selectivity of the epoxides. Also, the heterogeneous catalyst shows excellent catalytic activity compared to the homogeneous vanadyl acetylacetonate. In the oxidation of oleic acid, 99% selectivity, 98% conversion and 97.4% yield was obtained, the findings ascertain the scalability of the process.<sup>101</sup>



25

**Fig. 14.** Silica immobilized oxo-vanadium Schiff base complexes (V-LHMS-1).



26

**Fig. 15.** Structural formula of VO–vanillin-MCM-41.

The simple process of recovering nanomagnetic heterogeneous catalysts by an external magnetic field increases the recovery rate, catalytic activity and reusability of the catalyst.<sup>102</sup> Hussin et al. reported cyclohexene's epoxidation, catalysed by vanadium complex supported on montmorillonite K10 (MMT-K10). In this study, the catalyst shows increased catalytic activity with an increase in the amount of VO(acac)<sub>2</sub>.<sup>103</sup> Maurya Mannar reported using chloromethylated polystyrene immobilized on vanadium complexes as polymer-supported catalysts; the study shows that introducing a functional group improves the reactivity of polymer-supported catalysts.<sup>104</sup>

The oxidation of cyclopentanone catalysed by Vanadium Schiff base complexes (VO(L)H<sub>2</sub>O]-Y) undergoes the following mechanism (i) V(IV) species is activated through electrophilic by H<sub>2</sub>O<sub>2</sub> (ii) The active intermediate species activate the ketone substrate. The results show 80.22% conversion, 84–85% yields and 83.56% selectivity towards  $\delta$ -valerolactone.<sup>105</sup> Another study by Modi et al, used zeolite-Y entrapped on vanadium Schiff base complexes to catalyse the oxidation of olefins (cyclohexene,  $\alpha$ -pinene, limonene, styrene). Therefore, the catalyst [VO(L):H<sub>2</sub>O]-Y proves to be potent for the oxidation of olefins with an excellent conversion rate (87.44%: limonene, 90.01%: cyclohexene, 82.01%: styrene, and 85.44%:  $\alpha$ -pinene).<sup>106</sup> Nikoorazm et al.<sup>107</sup> synthesize vanillin complex immobilized onto MCM-41 (**Fig. 15**) for oxidative coupling of thiols. The oxidative coupling of thiols with catalyst (VO-vanillin-MCM-41) **26** gave an excellent yield between 92-98%. Also, a shorter reaction time and high reactivity with aromatic thiols were reported.

Heterogeneous nanocatalyst (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CPTMS-L-VO(OEt)) synthesized to oxidize various olefins (cyclohexene, norbornene, cyclooctene,  $\alpha$ -methyl styrene, and styrene), a short reaction time and high turn-over number was obtained compared to homogeneous complexes [VOL(H<sub>2</sub>O), oxovanadium hydrazone complex]. In this study, the oxidation of norbornene with heterogeneous nanocatalyst gave a 99% conversion rate and 84% selectivity for norbornene epoxide.<sup>108</sup> Vanadium(V) complexes supported on a porous MIL-100(Fe) were obtained for oxidation of toluene. In this study, low catalytic activity and yield were observed for the heterogeneous catalyst compared to the homogenous complexes [VO(OMe)L and [VO<sub>2</sub>L]]. The addition of diphenylamine inhibits the oxidation of toluene.<sup>109</sup>

Veisi et al. synthesized oxo-vanadium Schiff base complex immobilized on coated chitosan magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles [VO(CS)@Fe<sub>3</sub>O<sub>4</sub>] for chemoselective oxidation of sulfides<sup>110</sup>. There is an improvement in the catalytic activity and an easy separation because of the magnetic core and oxo-vanadium presence.<sup>110</sup> Epoxidation reactions were reported to give a low selectivity and a high conversion, but with vanadyl Schiff base complex supported on graphene oxide (VO-f-GO), epoxidation of styrene gave 99.2% conversion and 98.7% selectivity, and a sole product was obtained<sup>111</sup>

Finally, the epoxidation of 2-naphthol and styrene was catalysed with an effective heterogeneous and homogeneous dinuclear and mononuclear oxido vanadium Schiff base complexes, the catalyst demonstrates excellent activity in yield and enantioselectivity towards epoxidation of styrene. Also, a change in the structural variation of a metal complex brings about differences in the catalytic activity of the metal Schiff base complexes. The catalyst quantity, oxygen flow and temperature affect the catalytic activity of the complexes. However, low oxidation potential gives higher catalytic activity. Therefore encapsulated complexes with Zeolite-Y show a better catalytic activity than the dinuclear and mononuclear homogeneous catalyst.<sup>112</sup>

## 5. Conclusion

The application of heterogeneous vanadium Schiff base complexes in different catalytic oxidation of alkane, alcohol, sulfide and epoxides has been explored widely in recent years. The review describes the synthesis and application of heterogeneous vanadium Schiff base complexes. Vanadium Schiff base complexes exhibit effective catalytic activity and selectivity because of the imine bond and the electron-donating substituents. However, vanadium Schiff base immobilized on a solid support such as graphene oxide, alumina ( $\text{Al}_2\text{O}_3$ ), silica, zeolites, carbon materials and polymer have high catalytic activity, can be recycled several times with no loss of catalytic activity, is chemically stable at room temperature. Conclusively, conversion rate and reactivity in the oxidation of alcohols are dependent on the substituent on the substrate, high electronegative substituent on the substrate gives a low conversion rate. Also, electron-rich Schiff base ligands are more efficient than electron-deficient ligands. The title reviewed has industrial significance and is promising in catalysis with an interdisciplinary approach. The presence of pyrazinecarboxylic acid (PCA) as a co-catalyst or a stabilizer increases the catalytic activity of vanadium Schiff base complexes toward oxidation of alcohol and alkanes. As discussed in this review more development has been accomplished with vanadium Schiff base complexes in oxidation catalysis. However, some challenges should be solved by developing greener processes, heterogeneous catalysts, economical procedures, or using unconventional microwave heat with vanadium Schiff base complexes in oxidation catalysis.

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Department of Chemistry, University of the Western Cape, Prof Salam Titinchi

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