CHAPTER II
LITERATURE REVIEWS

Oxidation is an oxyfunctionalization which is the functionalization of alkanes in presence of oxygen such as deep oxidation, partial oxidation and oxidative dehydrogenation (ODH) [13]. Deep oxidation, or sometimes called total oxidation, is a combustion reaction of hydrocarbon (HC) with oxygen to convert hydrocarbon into CO_2 and H_2O, such as in catalytic converter. Partial oxidation is the reaction that converts hydrocarbon into oxygenates by substracting hydrogen atoms from and introducing oxygen atoms into the reactant structure. Oxidative dehydrogenation is a reaction of alkane and oxygen to produce unsaturated hydrocarbon (alkene or diene).

When compares the equilibrium constants of dehydrogenation and ODH reaction, it can be clearly seen that ODH can overcome the problems which occur in dehydrogenation process. However, ODH still has a problem about the control of the consecutive reactions of alkene up to carbon oxides. Therefore, the proper catalyst should has the properties that can overcome this major problem. In the past, several researchers try to find catalyst and catalyst structure that suitable for ODH reaction.

Despite the fact that vanadium oxides have been widely used in oxidation processes for a long time, their application in oxidative dehydrogenation reaction is relatively new. This review, therefore, is concentrated on the works on ODH reaction using vanadium oxides and some related compounds.

2.1 Review of Works on ODH Reaction

Chaar et al. [1], in 1987, studied the oxidative dehydrogenation of butane (C_4H_{10}) over V-Mg-O catalysts. Vanadium contents were varied between 0-54 wt% (as V_2O_5). The reaction temperature was 480 to $600^{\circ}C$. The feed contained 4 vol% butane and 4-8 vol% oxygen and the balance argon. A selectivity, which is defined as the percentage of the consumed reactant that formed the desired product, of up to 60% was obtained. The catalysts were characterized by Infrared Spectroscopy (IR), Scanning Electron Microscopy (SEM), Auger Electron Spectroscopy (AES) and X-ray diffractrometer (XRD).

Because they could not observe the characteristic V=O stretching band in the spectrum of all their V-Mg-O catalysts, they concluded that vanadium oxide in V-Mg-O did not form a layer structure on the MgO substrate. Auger spectroscopy also showed the presence of substantial amounts of Mg on the catalysts even with high vanadium loading. These results combined with their XRD study drew them to the conclusion that the active component was the compound magnesium orthovanadate.

The reaction study showed that unsupported vanadium oxide showed low activity and low dehydrogenation selectivity even at low conversions, and the dehydrogenation products was 1-butene ($CH_2=CHCH_2CH_3$) but a much higher selectivity to C_3 products was observed at a low conversion than at high conversion. For MgO, the activity and the dehydrogenation selectivity were also low, and the main dehydrogenation products were also butenes (C_4H_8). For mixed oxide catalysts, the selectivity for oxidative dehydrogenation increased markedly with increasing vanadium content. At 3.5 wt% vanadium, there was only a small increase in the selectivity compared with MgO. More significantly, there was a distinct increase in the selectivity for butadiene, and substantial increase in the

activity of the catalyst. As vanadium content increased to 19 wt%, the selectivity for dehydrogenation increased to about 50% at the expense of all other reaction products. The activity and the selectivity stayed at these high levels for catalysts of higher vanadium content. No oxygenated product was observed. The high selectivity for oxidative dehydrogenation instead of oxygenated production was attributed to two factors: the basic surface which facilitated the desorption of basic butene (C_4H_8) and butadiene (C_4H_6), and the absence of V=O which lowered the oxidation activity of the surface.

Chaar et al. [2], in 1988, investigated the selective oxidative dehydrogenation of propane over V-Mg-O catalysts. Vanadium content was varied between 0-40 wt%. The reaction was carried out in a quartz U-tube reactor at close to atmospheric pressure. The standard feed composition was 4 vol% propane (C_3H_8)and 8 vol% oxygen and the balance argon. The conversion of propane for an empty reactor increased with increasing temperature, but was negligible (i.e. less than 0.5%) even at 540°C. Under the same conditions, a reactor with quartz wool and silica gel showed lower conversion than an empty reactor.

Their results showed that the propene (C_3H_6) selectivity decreased with increasing conversions. However, for all V-Mg-O catalysts at the same operating conditions, the selectivity was quite independent from vanadium content. A selectivity of up to 65% was obtained at 10% conversion. In addition, no oxygenates were observed. The reaction order were reported as 0.6±0.15 order in propane and 0.85±1.15 order in butane and zeroth order in oxygen. The reaction was believed to proceed primarily with breaking of a methylene C-H bond to form an adsorbed alkyl species.

Qiu et al. [3], in 1989, demonstrated that the ferrite $ZnFe_2O_4$ was an active and selective catalyst for the oxidative dehydrogenation of butene to butadiene. However, it was deactivated at high temperatures owning to the segregation of the

phase which is presumably triggered by some reduction. They also reported that an external phase, such as Sb_2O_4 and $BiPO_4$, was able to stabilize the structure of $ZnFe_2O_4$ causing by its capability of producing oxygen species (O^{2-}).

Giamello et al. [4], in 1989, suggested the model of the O_2^-....H species which was the hyperfine interaction between a surface superoxide species on MgO and a neigbouring hydroxylic proton. They generated superoxide O_2^- radical ion by two different methods both involving the formation of surface hydroxyls. This O_2^- acted as an intermediate in the oxidation of the HX molecule when X is hydrocarbon chain.

Burch and Swarnakar [5], in 1991, investigated the ODH of ethane (C_2H_6) on a range of Mo-V-Nb oxide catalysts. The reaction was carried out in the temperature range 300-550°C. For Mo/V oxide catalysts, the maximum activity was obtained when Mo content was between 60-70 wt%. The addition of Nb to Mo/V oxide catalysts increased both the activity and the selectivity. Furthermore, temperature-programmed reduction (TPR) revealed that the catalysts containing Nb could be reduced at lower temperature than the catalyst without Nb. They also observed that the alumina-supported catalyst was more active than the unsupported catalyst, but the supported catalyst had a lower selectivity to ethene (C_2H_4). In addition, they also reported that the selectivity was essentially independent of temperature in the range 350-410°C. Their results also showed that the selectivity to ethene was quite sensitive to variation in oxygen partial pressure especially at lower oxygen partial pressures.

Kim et al. [6], in 1991, studied the catalytic properties of multicomponent metal oxide catalysts. The reaction studied was the oxidation of propane to acrolein ($CH_2=CHCHO$). The standard feed composition was 32 mol% of propane, 59 mol% of oxygen and the remainder being nitrogen. The reaction temperature was varied in the range 380-520°C. From their study they noticed that a catalyst

containing no molybdenum, $BiVO_4$, showed very low selectivity to acrolein, but propene was formed in large amount on this catalyst. With increasing concentration of Mo, the selectivity to acrolein increased markedly. For bismuth vanadomolybdate catalysts, the doping of small amount of K, Ru and Tl resulted in a rather large decrease in catalytic activity in the formation of acrolein. These catalysts gave propene with high selectivity. Improvements in the activity in the formation of acrolein were obtained by the addition of Li, Na and Ag.

They also observed that when the reaction of propane was conducted in the presence of a catalyst by using a reactor in which the volume of the pre-catalyst zone was minimized, no reaction occurred at all. From this result they suggested that, first, propyl radical might form from propane in the gas phase at high temperature. If the propyl radical formed in the pre-catalyst zone was not directed to undesirable reactions, such as C-C bond fission and quenching by the action of oxide catalysts, the reaction of the propyl radical might go forward to give propene. If the catalysts showed a poor ability to oxidize propene to acrolein, then propene was a major product.

Mazzocchia et al. [7], in 1991, investigated α- and β-phase of $NiMoO_4$ with X-ray diffraction, electrical conductivity and IR spectroscopy techniques in order to tentatively rationalize the different catalytic activities observed in the ODH of propane to propene. They found that α-phase was converted completely to β-phase at $700\,^{\circ}C$. From the presence of anionic vacancies, it was proposed that propene was formed by the reaction of propane with surface O^{2-} anions. Furthermore, they found that β-phase was almost twice more selective in propene formation than the α-phase that may be due to the different oxygen environments on the active catalytic site.

Smits et al. [8], in 1991, studied the ODH of propane over niobium pentoxide. They investigated the effect of calcination temperature with unsupported niobia samples by varying temperatures between 300 and 850°C. It was found that niobium pentoxide, calcined at temperatures between 500-700°C, exhibited a high selectivity for the ODH of propane, although conversion was low. However, the conversion could be improved by increasing the partial pressure of oxygen without decreasing the selectivity. But unlike propene selectivity, the proportion of CO_x decreased with an increase in the calcination temperature. These results may be due to the presence on the sample calcined at this low temperature of acidic OH groups originating from the hydrated starting material used for the preparation (it is known that Bronsted acidity is the main form of acidity on niobia calcined below 500°C). Furthermore, they investigated the activity of niobium pentoxide by depositing them on a high surface area α-alumina support. This result showed that the addition of niobia gave a significant improvement in selectivity when compared to unmodified α-alumina (conversion 1.6%, selectivity 31%). They noted that compared to vanadia, niobia was very difficult to reduce. Also niobia was known to play an important role in the reoxidation of the surface when present in a multicomponent oxide catalyst. The relatively inert surface behavior, combined with a unique type of interaction with oxygen, was probably responsible for the very selective behavior of niobia in the ODH of propane.

Armendariz et al. [9], in 1992, studied the oxidative dehydrogenation of n-butane on iron-zinc oxide catalysts. They found that the presence of a zinc ferrite ($ZnFe_2O_4$) phase with a spinel structure yield high selectivity to butenes. This phenomenon was explained by the loss of mobility of the lattice oxygen as a consequence of crystallographic structure change, from corundum in α-Fe_2O_3 to spinel in $ZnFe_2O_4$. When ZnO was present, the n-butane oxidative dehydrogenation reaction was observed to proceed to butadiene formation.

Hayakawa et al. [10], in 1992, tested the catalytic activity of a series of perovskite catalysts for the oxidative dehydrogenation of ethane. The composition of the catalysts covered $CaTi_{1-x}Fe_xO_{3-\delta}$, with $0 \leq X \leq 0.4$, $SrTi_{1-x}Fe_xO_{3-\delta}$, with $0 \leq X \leq 1.0$. They found that the catalyst containing more basic Sr metal showed higher selectivity to ethene than the catalysts containing less basic Ca.

Owen et al. [11], in 1992, reported their study on the effect of oxide structure and cation reduction potential of vanadates on the selective oxidative dehydrogenation of butane and propane. Magnesium orthovanadate $[Mg_3(VO_4)_2]$ was found to be a rather selective catalyst for the oxidative dehydrogenation of butane than magnesium pyrovanadate $[Mg_2V_2O_7]$. For the reaction of propane, however, both catalysts were found to have similar selectivities. They explained that in $Mg_3(VO_4)_2$ the isolate VO_4 units resulted in a condition that the adsorbed molecule could only interact with one VO_4 unit. In $Mg_2V_2O_7$, on the other hand, the V_2O_7 could provide the opportunity for a surface species to react with two VO_4 units simultaneously, provided that the size of the molecule was sufficiently large enough. Propane could interact with one VO_4 unit and could not distinguish between $Mg_3(VO_4)_2$ and $Mg_2V_2O_7$. Butane, due to its sufficiently large size, was able to interact with two VO_4 units in the V_2O_7 group simultaneously. This led to the combustion of butane on $Mg_2V_2O_7$ catalyst.

Desponds et al. [12], in 1993, reported the study of the role of catalyst composition of molybdenum-vanadium-niobium oxide catalysts on the oxidative dehydrogenation of ethane. The studies were performed under atmospheric pressure at temperatures varying from 350 to $450^\circ C$. They reported that below $350^\circ C$ the rate was too low and could not be measured reliably. At temperatures higher than $450^\circ C$, the sintering of the catalysts occurred with a significant reduction on the surface area. This lost of surface area by sintering prevented operation at

temperature higher than $450^{\circ}C$. The rates of formation of ethene and carbon dioxide were found to vary slowly with the reaction temperature and yielded activation energies at 18-20 kcal/mol for ethene and 16-17 kcal/mol for carbondioxide. The product distribution was found to be slightly affected by the change in the ethane to oxygen ratio. Although water was formed during the reaction, the effect of the water vapour could not be observed. The reaction order with respect to oxygen partial pressure was observed to have a complex pattern. For oxygen partial pressure below 7 kPa the reaction was almost independent of the oxygen partial pressure but became half order at high temperature. In a pressure range of 7.5-15 kPa, the reaction was again almost independent of the oxygen at high temperatures. The dependence of the oxygen reaction order on the temperature was explained in terms of lability of the lattice oxygen and speed of reoxidation of the catalysts. At low temperature, the reoxidation of the catalysts was so fast that it was not a rate limiting process, but at high temperature it became the rate limiting step. The reactivity of ethene was founded to be lower than that of ethane. With this result they proposed that during the ODH of ethane, carbon oxides were being formed by the direct oxidation of ethane and to a lesser extent by the secondary oxidation of ethene.

They also founded that the presence of the three transition metal oxides was necessary to obtain an active and selective catalyst. An oxide mixture having the atomic proportions of 19:5:1 for Mo:V:Nb was founded to yield the best results. The role of niobium oxide was suggested to inhibit the total oxidation of ethane, thus, improving the selectivity for ethene.

The study of the stabilities with time of the Mo:V:Nb with the atomic ratios of 6:3:1, 8:2:1 and 19:5:1 showed an interesting result. They observed that the Mo6:V3:Nb1 catalyst deactivated at the beginning of the run. The surface area measured before was less than the surface area after the reaction which can be

attributed to the deactivation by sintering. The surface compositions of the fresh and the used catalysts determined by X-ray photoelectron spectroscopy (XPS) did not show any significant variation in the composition. However, they observed from their XPS data that a significant amount of carbonaceous species existed on the surfaces of all the three catalysts after use. Thus, they suggested that the reason why only one catalyst was deactivated, though all had carbon deposition, was probably due to a difference in sensitivity towards carbon deposition, which could depend on the catalyst composition.

Centi [13], in 1993, reviewed the works on the selective heterogeneous oxidation of light alkanes, especially on V-P-O catalysts. The paper reported that the deep oxidation products (i.e. oxygenates and carbon oxides) starting from an alkane and its respective alkene could be different. This phenomenon was due to the difference between the strength of adsorption of alkane, alkene and oxygen. In the direct oxidation of alkane, both alkane and oxygen could adsorb on the catalyst surface, hence, the surface concentration of alkene was limited. In the direct oxidation of alkene, on the contrary, almost all the active sites were covered by alkene and therefore inhibited the adsorption of oxygen.

Concepcion et al. [14], in 1993, tested the catalytic properties of vanadium aluminophosphate catalysts on the selective oxidative dehydrogenation of propane to propene. The reaction was carried out in an isothermal flow reactor at atmospheric pressure in the temperature range 500-540°C. They have reported that, depending on the vanadium contents and the preparation procedure, different vanadium species and different catalytic behavior were observed. Vanadium species with a tetrahedral coordination present in vanadium aluminophosphate catalysts were proposed to be the active and selective species in the oxidative dehydrogenation of propane.

Burch and Crabb [15], in 1993, studied the oxidative dehydrogenation of ethane to ethene in a quartz reactor in the absence and in the presence of range of MgO-based catalysts and/or inert packing. Their experiment on thermal pyrolysis of ethane with no oxygen present using an empty reactor showed that the non-oxidative pyrolysis of ethane was not really significant until reaction temperatures were of at least 700°C. When air was added, they could observe that the oxidative route became important at temperatures at least 100°C lower than for the thermal pyrolysis reaction. Using ethane/air ratio of 1:2 at a temperature of 600°C, a conversion of 45% was achieved at a selectivity of 73.7%. However, when the reactor filled with quartz wool was used, the gas-phase radical reactions were greatly inhibited. They suggested that the packing material inhibited the gas-phase radical reaction by reducing the residence time in the hot zone and possibly by trapping radicals.

When a MgO catalyst was used, they found that the conversion increased sharply with temperature. The selectivity to ethene increased to a plateau at a value of 60% at temperature about 630°C. Addition of Li resulted in a decrease in the conversion of ethane, but the selectivity to ethene was found to be greatly enhanced. Addition of Sn to MgO initially resulted in a substantial decrease in activity. However, further addition resulted in a more active catalyst, but selectivity to ethene was lower.

In addition, by comparison with published results on the catalytic oxidative dehydrogenation of ethane on various catalysts, they suggested that the non-catalysed gas-phase reaction was competitive with the best available catalysts.

Corma et al. [16], in 1993, studied the oxidative dehydrogenation of propane on sepiolite supported catalysts. The reaction was carried out in a fixed-bed microreactor. Silica carbide (SiC) was used as diluent. They found that at low vanadium content, isolated tetrahedral species was formed and both activity and

selectivity to propene increased when increasing the vanadium content. At medium or high vanadium content the appearance of associated vanadium species could be observed and, while the activity still increased when total vanadium content was increased, the selectivity to propene remained constant. MgV_2O_6 and V_2O_5 crystallites which were suggested to be formed at vanadium in a tetrahedral position was less active than the vanadium in octahedral position, the yield to propene was higher.

Okuhara et al. [17], in 1993, studied the structure and dehydrogenation activities of vanadium oxide overlayers on supports (MgO, Al_2O_3 and SiO_2) by X-ray absorption (EXAFS) and temperature programmed decomposition of ethanol adsorbed respectively. On MgO, the result indicated that vanadium on MgO formed new phases such as $Mg_3V_2O_8$ and $Mg_2V_2O_7$. $Mg_3V_2O_8$ consists of V ions in tetrahedral sites (V-O) and Mg ions in octahedral sites, and $Mg_2V_2O_7$ has V_2O_7 groups (V=O, V-O). EXAFS spectra revealed that the structure of V_2O_5 was very sensitive to the supports and the preparation method (impregnation or chemical vapor deposition (CVD)). They indicated that preparation by CVD brought about thin films which had high thermal stabilities and catalytic activities for dehydrogenation.

Yoon et al. [18], in 1993, studied the oxidative dehydrogenation reaction of propane to propene over cobalt molybdate catalysts. The catalysts were prepared from aqueous solution of cobalt nitrate and ammonium paramolybdate. The reaction was carried out at temperatures around $450^{\circ}C$. The reactant gas contained 18 mol% propane, 7 mol% oxygen and the remainder being nitrogen. They reported that cobalt molybdate showed high catalytic activity for the oxidative dehydrogenation of propane to propene. In addition, they also reported that composition of the catalyst strongly affected catalytic properties. For the oxidation

of propane, $Co_{0.95}MoO_4$ showed 4 times higher in activity than $CoMoO_4$. Furthermore, the Na-added catalyst, $Co_{0.95}Na_{0.05}MoO_4$ was completely inactive.

Lindbald et al. [19], in 1994, characterized vanadia supported on amorphous $AlPO_4$ catalyst and its properties for oxidative dehydrogenation of propane. Activity tests were carried out in a conventional flow micro reactor at atmospheric pressure. The gas flow rate was 7-12 dm^3hr^{-1} containing 0.25-8 vol% propane, 3-32 vol% oxygen and balance of nitrogen. The result showed that the activity for oxidation of propane increased with the vanadium loading. The reaction was best performed at 6 wt% V which was suggested to be associated with the presence of tetrahedral vanadium species. A low selectivity at higher vanadium loading was suggested to be associated with more active and less selective sites on V_2O_5.

Andersson [20], in 1994, studied the kinetic of the oxidative dehydrogenation of propane over vanadium supported on amorphous $AlPO_4$. The operating conditions were the same as in the former work [19]. The main products observed at low conversion were propene and ethene, while carbon oxides were dominating at high conversion. No oxygenates could be detected. The initial rate of oxidation of propene on the catalyst with various compositions was found to be first order with respect to both oxygen and propane at low partial pressure. At higher partial pressure, however, a deviation from linearity was obtained and in some cases an almost zeroth-order dependence was obtained for oxygen.

Concepcion et al. [21], in 1994, studied the oxidative dehydrogenation of ethane on magnesium-vanadium-aluminophosphate (Mg-V-$AlPO_4$) catalysts. The reaction was studied in the temperature range 500-600°C using ethane/oxygen/helium molar ratio in the feed of 4/8/88. From their experimental results they could conclude that activity and selectivity to ethene decrease in the trend Mg-V/$AlPO_4$ > V/$AlPO_4$ > Mg/$AlPO_4$ > $AlPO_4$. The catalytic activity for the conversion of ethane was reported to decrease in the order V/$AlPO_4$ $\geq$ Mg-V/$AlPO_4$

$\gg$ Mg/AlPO$_4$ $\approx$ AlPO$_4$. They have proposed that the presence of Mg^{2+} ions, which increased the acidity of the catalyst, increased the selectivity to ethene although the activity was not influenced. The presence of vanadium species, which increased the redox character of the catalyst, increased both the activity and selectivity for the oxidative dehydrogenation of ethane. Another role of Mg^{2+} was suggested to stabilize isolated VO$_4$ tetrahedron site which was proposed as selective sites for the oxidative dehydrogenation of ethane, propane and n-butane.

Zhang et al. [22], in 1994, studied the oxidative dehydrogenation of propane over fluoride promoted rare-earth based catalysts. The catalysts studied were CeO$_2$/2CeF$_2$, Sm$_2$O$_3$/4CeF$_3$, Nd$_2$O$_3$/4CeF$_3$ and Y$_2$O$_3$/4CeF$_3$. They found that CeO$_2$/2CeF$_2$ was the most active and selective. At 500$^{\text{o}}$C the conversion of propane was 42.3% and selectivity to propene reached 81.1%. Their XRD results indicated that after CeF$_3$ addition to the catalysts, the F$^-$ and O^{2-} were exchanged in the lattice. This kind of exchange would form anion.

Wang et al. [23], in 1994, investigated catalytic and electrocatalytic oxidation of propane on V-Mg-O and V-Mg-O(Ag) catalysts. This reaction occurred in two different methods in their study, first was the conventional heterogeneous catalytic reaction which obtained 79% selectivity at 10% conversion (813K) from vanadium magnesium oxide. The later occurred under electrochemical pumping of oxygen (EOP) towards the catalysts. With oxygen present in the feed gas, both conversion and selectivity were found to increase slightly, indicating the effect of electrical current can be exhibited by an oxide catalyst. But in the absence of oxygen in the feed gas, EOP could lead to an even higher selectivity at 84 and 86.9%, respectively, with V-Mg-O(Ag) catalyst. In the case of V-Mg-O(Ag) catalyst, the role of Ag was found to be "non-chemical"; it simply increased the three-phase (gas/catalyst/Ag electron) interfacial area. They noted that for both catalytic and the electrocatalytic processes, a surface oxygen ion (or vacancy) was

suggested to be involved. Whereas the rate determining step involved heterolytic splitting of the C_3H_8 molecule leading to the formation of a surface bonded C_3H_7 ion and a surface hydroxyl ion. The higher selectivity towards C_3H_6 in the case of EOP was attributed to the relatively weaker surface bond between C_3H_7 and the vanadium ion and thereby less vulnerable towards deep oxidation.

Gao et al. [24], in 1994, prepared and characterized three pure magnesium vanadate phases of MgV_2O_6, α-$Mg_2V_2O_7$ and $Mg_3V_2O_8$. These three phases were prepared by the citrate method with Mg/V atomic ratios equal to 1/2, 1/1 and 3/2. From characterization of these vanadate phases (using Fourier-transform IR, Raman, XRD and SEM techniques), it was found that the particle size and morphology of the MgV_2O_6 phase, which was a function of calcination temperature, appeared to have a strong effect on the infrared spectra. A significant change was observed in the position, relative intensity and width of the infrared bonds as a function of calcination temperature. Furthermore, the catalytic properties of the three phases were examined in the oxidative dehydrogenation of propane. The propene selectivity followed the order: α-$Mg_2V_2O_7$ > $Mg_3V_2O_8$ > MgV_2O_6, which was consistent with their redox properties. This fact suggested that there was some correlation between the catalytic and redox properties of these magnesium vanadate phases. They noted that if the catalytic reaction mechanism was as suggested through the redox cycle between V^{5+} and V^{4+}, the good redox behavior under reaction conditions might be favorable for the selective oxidation of propane.

Deo et al. [25], in 1994, investigated the molecular structural and reactivity properties of supported vanadium oxide catalysts (MgO, γ-Al$_2$O$_3$, TiO$_2$, ZnO$_2$, Nb$_2$O$_5$ and SiO$_2$) by using various characterization techniques (e.g. XPS, Raman, IR, X-ray absorption). They suggested that in all the supported vanadium oxide samples (exception of V$_2$O$_5$/MgO), the vanadium ion presented as an aqueous solution on the surface of the oxide support under ambient condition. Under dehydrated condition, the surface vanadium oxide species bonded directly with the oxide support surface. In the case of V$_2$O$_5$/MgO, no drastic change occurred in Raman spectra between under ambient and dehydrated conditions. This result could be explained that vanadium oxide predominantly forms compounds with MgO on MgO surface. Moreover, they found that the net surface pH at point of zero charge (pzc) of the surface moisture depended on the specific oxide support and the vanadium oxide loading. This pH value controlled the structure of the hydrated surface vanadium oxide species. Hence, more vanadium oxide loading and lower pH value, the surface vanadium oxide structures became more polymer. The model of aqueous solution and the samples of vanadium oxide species are shown in Figures 2.1 and 2.2 respectively.
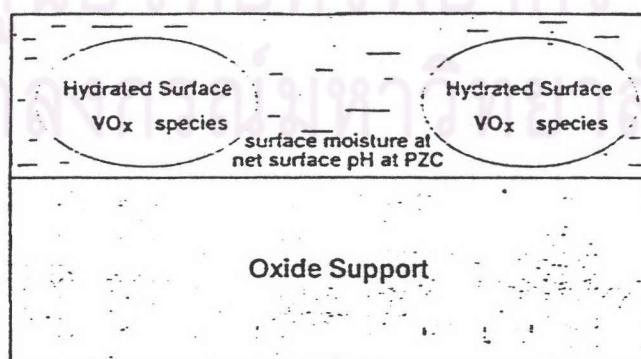

Figure 2.1 The model of aqueous solution on the surface of the oxide support under ambient condition.
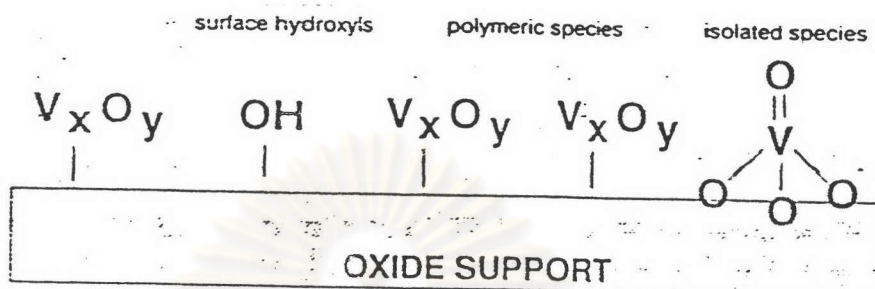
Figure 2.2 The vanadium oxide species on supported vanadium oxide surface.

Cavani and Trifiro [26], in 1995, compared the performance of various catalysts described in the literature and used in oxidative dehydrogenation of ethane and propane. They indicated that vanadium oxide was not a good catalyst for the paraffins ODH, but the spreading of the oxide onto a support with basic features led to a more selective catalyst. Mg orthovanadate and Mg pyrovanadate were reported to exhibit the best catalytic performance of V-Mg-O in ODH. Moreover, they discussed the main aspects of ethane and propane oxidative dehydrogenation also (see more detail in sections 3.1.1 and 3.1.2).

Matyshak and Krylov [27], in 1995, used *in situ* IR spectroscopy to investigate intermediates in heterogeneous oxidative catalysis. The objective of their study was to determine the mechanism that occurred in oxidation reaction. Many kinds of oxidation reaction were studied in the work, i.e. partial olefin oxidation. In partial oxidation of ethene (C_2H_4), Fourier-transform IR spectroscopy (FT-IR), diffuse reflectance spectroscopy, together with transient response kinetic measurements revealed the presence of weakly and strongly bound acetaldehyde (CH_3CHO) and also CH_3CHO_{ads} in the oxidation of C_2H_4 to C_2H_4O on Ag/α-

Al_2O_3. Similar investigations over $Ag/\gamma-Al_2O_3$, which had a lower selectivity, showed that adsorbed ethene, carbonates and Ag-CO, which possibly were precursors of total oxidation were present on the surface. In the case of Gleave and coworkers' work [28], oxygen which reacted with ethene over Ag powder did not act in the same way. CO_2 was formed quicker than C_2H_4O mainly at the expense of the weakly bonded surface oxygen O^*, due to that the intermediate charge state of silver ($Ag^{\delta+}$) is possibly Ag^{3+}. It have been suggested for this phenomenon that there were two forms of oxygen, the one (electrophilic oxygen, $O^{\delta+}$), formed a complex, giving rise to ethene oxide
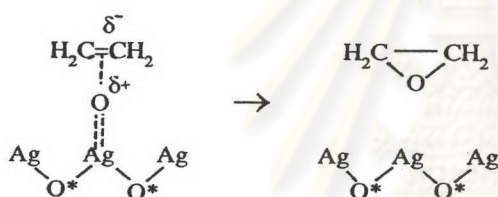
and another (nucleophilic oxgen, $O^{\delta-}$), formed a complex, giving rise to total oxidation.
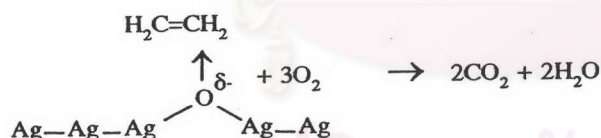
Further studying of this process indicated that ethene was oxidized by subsurface oxygen, then this subsurface oxygen was exchanged quickly with $O^{\delta-}$. FT-IR revealed the presence of a π-complex (the intermediate complex) of C_2H_4, adsorbed acetaldehyde and also some weakly bound enol complexes.

The results of temporal analysis of products (TAP) experiments [28] showed that weakly bound forms of adsorbed propene did take part in its oxidation to acrolein over $Bi_2O_3-MoO_3$. These experiments also found the existence of two

forms of adsorbed oxygen. One of them taked part in partial oxidation, the other did not, but could easily be exchanged with oxygen from the gas phase.

The sites, at the oxide surface where olefin complex can be adsorbed as π-allyl, were not only metal ions but also the surface acid Bronsted sites.

2.2 Comments on Previous Work

It can be seen that there is no general agreement on the relationship between catalyst structure and its reactivity. Moreover, the investigation of the effect of alkali doping is not clear and evident in term of basic surface improvement. Basic surface oxide is believed to prefer selective oxidation. Alkali metal basic catalysts are known to be effective and selective catalysts for the oxidative coupling of methane. Hence, it is interesting to study such effects in this work.