CHAPTER III

THEORETICAL CONSIDERATIONS

Most of the chemical reactions in industry are catalytic, and many chemical engineers work to understand and apply catalysis. Catalysis is the phenomenon of a catalyst in action. The basic definition of catalyst is a substance that increases the rate at which a chemical system approaches equilibrium, without being comsumed in the process [29]. Catalysts are the keys to the efficiency of most industrial chemical processes. Hence, almost researches in catalytic field try to find the proper catalyst and to determine the structure of those catalysts that can give the good catalytic performance in each process.

Oxidation is the process which catalysts are widely used in the reaction. Oxidation is categorized as selective and non-selective oxidation [29]. Non-selective oxidation or deep oxidation is the combustion of hydrocarbon (HC) and oxygen to the combustion products, CO_2 and H_2O. Selective oxidation is the reaction between HC and oxygen to produce oxygenates (such as alcohols, aldehydes, carboxylic acids which are produced from partial oxidation processes) or unsaturated hydrocarbons (such as ethene and propene which can be produced from oxidative dehydrogenation processes).

Oxidative dehydrogenation is a petrochemical process that is still only in a period of research and development in laboratory. It will take sometimes before it can beome the real practical process in the petrochemical industry. Because of its relatively new alternative in this field, there is no much information available about this process. There are many conjectures and presumptions that are still not clear and waiting to be exactly demonstrated such as confusion of the true situation

about which kind or source of oxygen that is active and selective for oxidative dehydrogenation. Nevertheless, oxidative dehydrogenation is one part of oxidation, then theoretical considerations in this chapter are substantially based on oxidation catalysis data. This chapter will include the explanation about the oxidative dehydrogenation, surface properties and surface species of oxide catalyst.

3.1. Oxidative Dehydrogenation

One of the selective oxidation is the oxidative dehydrogenation (or sometimes called oxydehydrogenation, ODH) which is the functionalization of alkanes in the presence of oxygen [13]. Selective oxidation is the most widely exploited of all the reactions used to convert alkanes into more useful and valuable products [29]. Great effort have been expended on discovering and developing catalysts that can convert alkanes by reaction with air in a single step into partially oxidized products which are of great demand. Aromatic hydrocarbons and some saturated hydrocarbons, can also be selectively oxidized to more valuable products.

It has been mentioned [29] that the pure oxide catalysts were of little practical interest in hydrocarbon oxidation since they only catalysed 'deep' oxidation to carbon dioxide and water; this was especially true of p-type oxides (see the detail in appendix C). Simple reactions of non-selective oxidation reaction were, of course, of interest in the control of environmental pollution by catalytic means, but selective oxidation often required catalysts of a more complex nature.

Table 3.1 Classification of catalysed reactions of hydrocarbons with oxygen.[29]

CLASS I	OXIDATIVE DEHYDROGENATION
	1. Dimerization of propene to hexadiene or benzene
	2. Dehydrogenation of butane or butene to butadiene
	3. Dehydrocyclization of hexane to cyclohexane
CLASS II	FORMATION OF OXYGENATED PRODUCTS WITHOUT CARBON-CARBON BOND FISSION
	1. Oxirane from ethene
	2. Acetaldehyde from ethene
	3. Acrolein and acetone from propene
	4. Allyl alcohol from propene
	5. Acrylic acid from propene
	6. Maleic anhydride from butadiene
	7. Phthalic anhydride from o-xylene
CLASS III	FORMATION OF OXYGENATED PRODUCTS WITH CARBON-CARBON BOND FISSION
	1. Acetaldehyde and acetic acid from propene
	2. Maleic anhydride from benzene
	3. Phthalic anhydride from naphthalene
CLASS IV	DEEP OXIDATION

Table 3.1 listed the main classes of selective hydrocarbon oxidations, with illustrative examples of each. In reactions of Class I, the hydrocarbon was oxidized by dehydrogenation, either intramolecularly to give a diene or a cyclic molecule, or intermolecularly to give a dimer. Theoretically it was possible to use a metal catalyst for dehydrogenation, but high temperatures were needed to obtain an adequate equilibrium concentration of product, and at these temperatures the hydrocarbon was often unstable and decomposed completely and gave a deposit of

carbon on the catalyst. A successful process could only be obtained if the thermodynamics allowed the use of a somewhat low temperature: the dehydrogenation of cyclohexane (C_6H_{12}) to benzene (C_6H_6) was one of the few reactions where a metal catalyst was satisfactory. However, the reaction of a hydrocarbon with oxygen to give a more unsaturated molecule plus water, e.g.

$$2C_3H_8 + O_2 \rightarrow 2C_3H_6 + 2H_2O$$
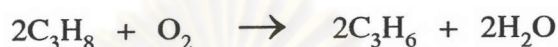
was more thermodynamically favoured because of the high enthalpy of formation of water. Provided a catalyst could be found to conduct this reaction selectively, i.e. without giving deep oxidation at the same time, good yields of propene were obtainable at a lower temperature than would be possible in a direct dehydrogenation. The term *oxidative dehydrogenation* was applied to such reactions.

3.1.1 Oxydehydrogenation of Ethane [26]

Some of the catalysts developed for the reaction of methane (CH_4) coupling were also active in the ethane (C_2H_6) oxydehydrogenation. In other cases, entirely new catalytic systems had been developed. The performances of catalysts reported in literature were summarized in Figure 3.1 which reported the highest achieved yields in a selectivity vs. conversion plot, and the levels of maximum productivity obtained at the average operative temperature for each system.

Generally, the catalysts could be classified into:

a) Catalysts based on ions and oxides of Group IA and IIA metals, which were also active for methane coupling [30-37]; these activate ethane at temperatures usually higher than $600\,^{\circ}C$ to form ethyl radicals, which then further react in the gas phase. The most successful of these catalysts was the Li-Mg-O.
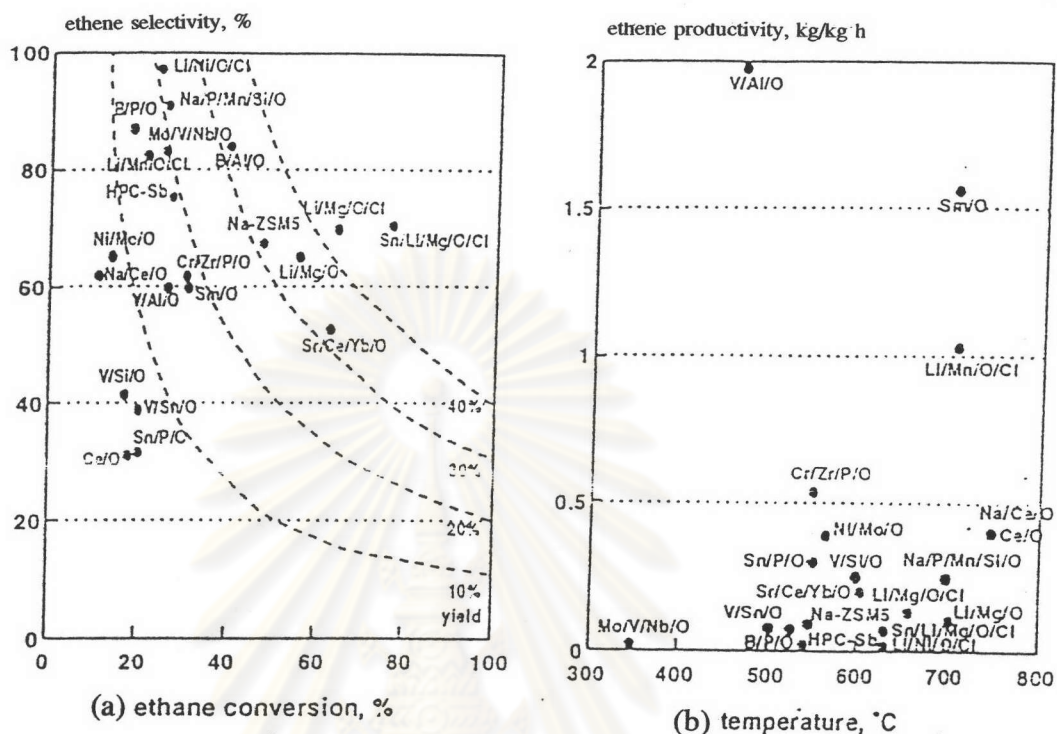
Figure 3.1 Best yields of ethene reported in literature (a) and ethene productivity (b) on the various catalytic systems [26].

This mechanism did not involve a classical redox-type cycle; thus, no furnishing of bulk oxygen occurred, and the catalyst only involved in C-H heterolytic scission with radical formation, analogously to that occurring with methane. The role of the generation of Li^+-O^- centers was its capability to abstract a $H^{\cdot}$ and form the ethyl radical. However, a progressive loss of Li occurred at temperatures higher than 700 $^{\circ}$C. Such catalysts could be employed after a methane coupling reactor in order to increase the yield to ethene (C_2H_4) through oxydehydrogenation of formed ethane. Catalysts for coupling operate at 700-800°C, and the hot outlet stream could be fed to a downstream catalytic or thermal oxydehydrogenation reactor.

High selectivities and yields to ethene could be achieved with this catalytic system, above all when chlorine-containing compounds were also fed to the reactor, or when the catalyst was doped with halides [32,37]. The promoter effect was maintained by continuous feeding of the chlorine, which modified catalyst surface [38]. Chlorine radicals were thought to favour the homogeneous decomposition of ethyl radicals to ethene. Yields as high as 34% to ethene could be achieved [31,37]. However, the use of chlorine was limited by problems related to equipment corrosion.

The selectivity to ethene was increased with temperature; this was due to the fact that the formed ethyl radical at high temperature (600-700°C; above 700°C homogeneous overoxidation of ethene decreased the selectivity) desorbed and formed ethene in the gas phase via reaction with molecular oxygen. The high stability of ethene and the contribution of the heterogeneously-initiated homogeneous reactions led to the observed high selectivity. At lower temperatures the formation of a surface ethoxy species, precursor of CO_x formation, was preferred.

A further aspect of this system was the formation of H_2 under oxidative conditions [35,39]. H_2 could be formed either via thermal or catalyzed dehydrogenation. Also, a contribution was proposed due to water gas shift equilibrium (over rare earth oxides) or of intermediate ethoxy species decomposition into CO, C and H_2. Recently [40], it was found that catalysts like Ca-Ni-K-O and Li-Mg-O were active in the water gas shift at the temperatures at which ethane oxydehydrogenation occurred.

Other systems that were active at temperatures higher than 600°C were Li_2O/TiO_2, $LiCl/NiO$, $LiCl/MnO_2$ and $LiCl/Sm_2O_3$. Dopants other than Li^+ had been reported: SnO_2, Na_2O, lanthanides (mainly CiO_2) [41].

b) Catalysts based on transition metal oxides [5,42-49]. Rare earth oxides were remarkably active [39,42], and yielded ethene with high productivity and good selectivity. In addition, they exhibited a very high stability even at high temperature. Doping Sm_2O_3 with alkali metals gave the best performances. These systems were believed to operate with a mechanism similar to that of Li-Mg-O catalysts.

Also $Na_4P_2O_7/MnO_x/SiO_2$ catalyst operated at very high temperature. Such system was claimed for cyclic operation with ARCO [43] or Phillips [44] technology in circulating-bed applications, where higher selectivities were achieved by dividing the reaction into two stages; i.e.) oxydehydrogenation of the paraffin in the absence of molecular oxygen and ii) regeneration of the catalyst by treatment with air.

In vanadium oxide-based systems the catalyst was reduced by interaction with the hydrocarbon, through a classical redox cycle [5,45-49]. These systems could activate ethane at temperature as low as $400\,^{\circ}C$, and the entire reaction was heterogeneous, hence controlled by the catalyst. The contribution of homogeneous reactions only occurred at the highest temperatures. Mixed oxides of Mo-V-Nb were shown to be active in ethane oxidation at temperatures as low as $250\,^{\circ}C$, with selectivity to ethene higher than 80%. However, the reported experimental conditions led to an ethene productivity which appeared to be too low to have practical application. Mo-V-Nb-O also formed considerable amounts of acetic acid. Alumina-supported vanadium oxide exhibited an high activity in ethane conversion, with fairly high productivity.

Figure 3.2 summarized the mechanisms proposed in the literature for the two classes of catalysts, operating at low and high temperature.
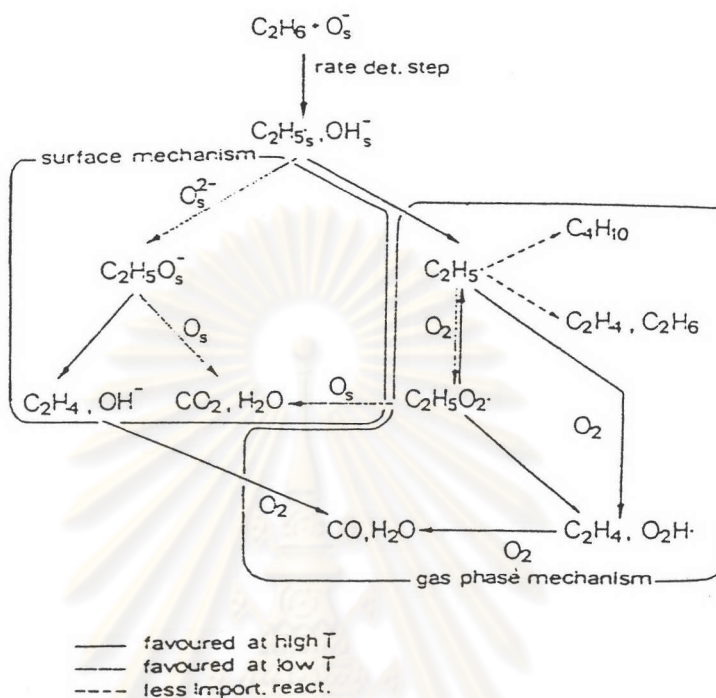
Figure 3.2 Summary of the mechanisms proposed in the literature [26].

3.1.2 Oxydehydrogenation of Propane [26]

Most catalysts described in the literature were based on vanadium oxides as the main component [2,8,14,24,50-60]. Particular attention had been given to the magnesium vanadates. A summary of the catalytic performance described in literature was given in Figure 3.3.
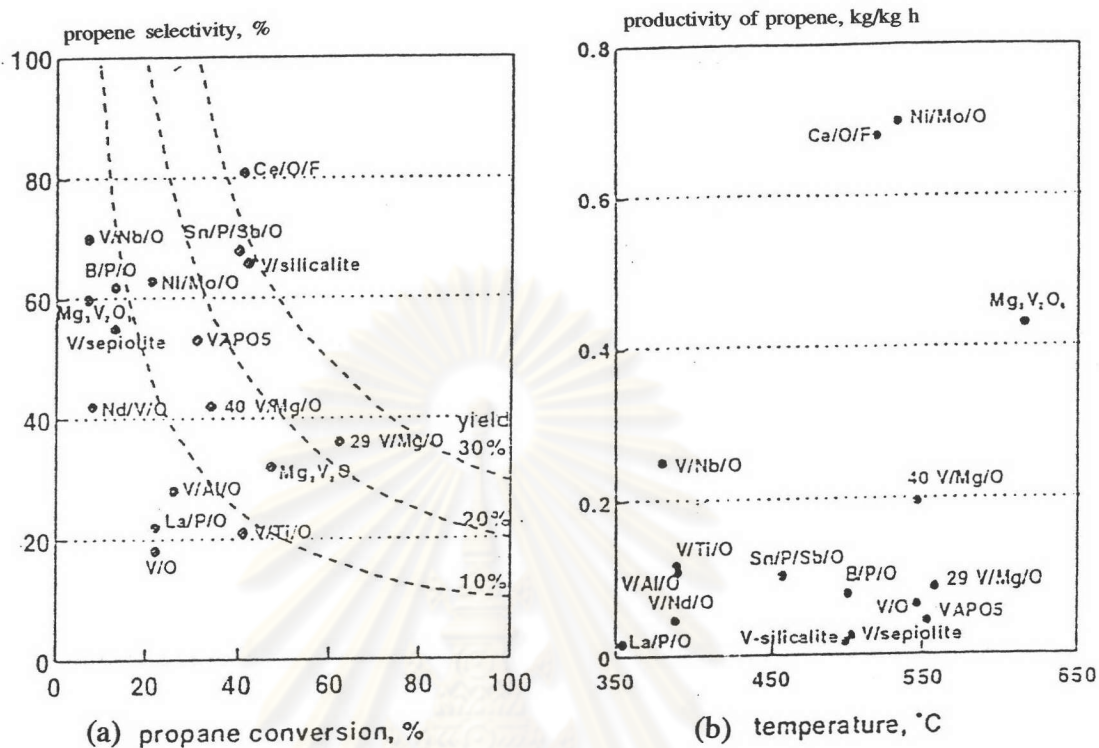
Figure 3.3 Best yields of propene reported in literature (a) and propene

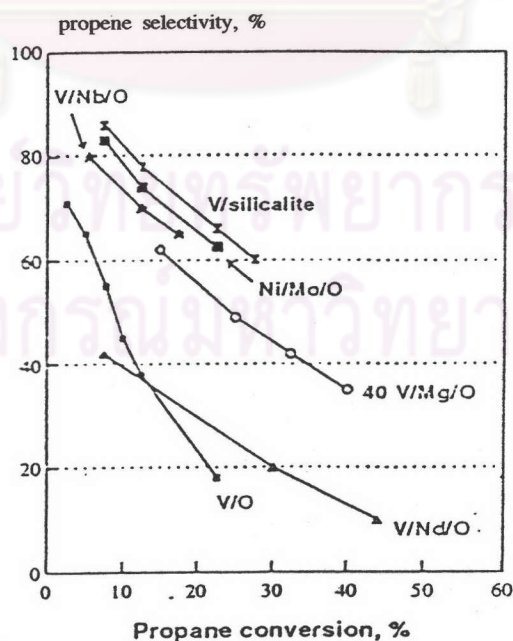productivity (b) on the various catalytic systems [26].

Figure 3.4 Selectivity vs. conversion plot for various catalysts [26].

A general feature of most catalytic systems was that the selectivity to propene was decreased on increasing the propane conversion (Figure 3.4). This was likely due to the presence of labile allylic hydrogen atoms in the formed propene which acted as a center for consecutive oxidative attacks. This conversion/ selectivity trade-off was one of the main differences between ethane and propane (as well as other higher paraffins).

Recently, Burch and Crabb [56] had been pointed out that the non-catalyzed thermal oxidative pyrolysis of propane gave an overall yield to olefins (ethene and propene, approximately 1/1) in a quartz apparatus higher than that achieved by whichever catalytic system and at temperature only 50-100 degrees higher than that usually employed for the catalyzed reaction. This made doubtful whether it was really advantageous to develop a catalyst for this reaction. However, it had to be pointed out that in the Burch and Crabb' apparatus the operating mechanism was a surface-initiated homogeneous reaction. Other authors had pointed out that higher yields to propene could be achieved with a post-catalytic homogeneous reaction [58].

The following was a summary of the catalytic performances of the various systems.

a) V_2O_5 was not a good catalytic system for the paraffins oxydehydrogenation, but the spreading of the oxide onto a support with basic features (such as sepiolite) or over alumina, with the formation of centers with peculiar chemical-physical features and reactivity led to a more selective catalyst [51,54]. Oxygenated compounds were not formed. These catalysts were active at relatively low temperature (in the 350-450°C range, however, selectivity not higher than 40% were obtained, and only at low levels of conversion, with low overall productivity and yields (not higher than 8-9%).

The effect of oxide structure and cation reduction potential of vanadates on the selective oxidative dehydrogenation of butane and propane had been reported by Owen et al.[11] . From the report, the oxidative dehydrogenation of butane over a series of orthovanadate of cations of different reduction potential showed a correlation that the selectivity for dehydrogenation decreased with increasing ease of reduction of the cation. The observed correlation implies that the easier it was to reduce the oxide, that was, to remove a lattice oxygen, the more likely it was for the oxide to react with the surface hydrocarbon intermediates to result in carbon oxides. This phenomenon perhaps was due to a higher tendency of oxide to attack C-C and C-H bonds indiscriminately. Moreover, they suggested that Mg pyrovanadate was nonselective for butane oxidation but was as selective as Mg orthovanadate in propane oxidation. In testing of ODH of propane on vanadium aluminophosphate catalysts [14], it was suggested that the catalyst containing V^{5+} species with a tetrahedral coordination presented the higher yield of propane in the oxidative dehydrogenation of propane.

b) V-Mg-O catalysts had been the object of several investigations in recent years. These systems were active in the 500-600°C temperature range, and with respect to V_2O_5 were characterized by improved basicity and surface area [2,24,52,53,55,56]. This catalyst also led to the formation of oxygenated by-products. Selectivity to propene as high as 60% could be reached, with yields of 20% and fairly high productivity. The selectivity generally decreased with conversion.

Some disagreement existed in literature about the nature of the preferred structure, exhibiting the best catalytic performance. The published results could be summarized as follow:

- $Mg_3(VO_4)_2$ (Mg orthovanadate) spread over MgO was considered by some authors to be the most active and selective composition in n-butane oxydehydrogenation (propane was instead much less sensitive to the catalyst structure), due to the presence of isolated VO_4 units which were not active in oxygen insertion onto activated hydrocarbon (oxygenated hydrocarbons were precursors of CO_x formation) [2,52,53,57].

- $Mg_2V_2O_7$ (Mg pyrovanadate) was reported to exhibit a superior catalytic performance in terms of selectivity; the scale of selectivity was consistent with the vanadates redox properties: the highest the cation reducibility (the redox couple V^{4+}/V^{5+} was supposed to be the one catalytically operating), the highest the selectivity [24,55].

Indeed, it was likely that factors other than the crystalline structure of the vanadates could contribute in affecting the catalytic performance i.e.: i) the presence of small undetected amounts of V_2O_5 (the preparation of pure reference phases was indeed a hard task); ii) the presence of alkali metals impurities coming from the raw materials employed for the preparation; iii) the surface enrichment in either magnesium or vanadium; iv) particle size and morphology, which could be affected by the thermal treatment; v) the method of preparation employed.

c) V-Nb-O catalysts operated at 380-450°C; they exhibited good productivity to propene and apparently no formation of oxygenates [8,59,60]. Nb_2O_5 itself was a selective catalysts, and the addition of vanadium improved the activity while maintaining the high selectivity. The active sites were assumed to be vanadium ions in the form of small clusters, and neighboring surface Nb ions improved the selectivity. Selectivities as high as 90% could be reached at low propane conversion in samples prepared by 'melt method' (solid state reaction between NH_4VO_3 and hydrated niobia).

d)   Metal-zeolites [14,61]; isolation of oxidizing sites was realized by dispersion of vanadium ions inside matrixes catalytically inert, such as zeolites or zeolitic-like compounds.   V-silicalite exhibited relatively high yields, but low productivity.   In VAPO-5 isolated VO_4 tetrahedron structures had been proposed to be the active and selective sites in paraffins oxydehydrogenation.

e)   Molybdates, bismuth molybdates and vanadomolybdates were known to successfully operated in the oxidation and ammoxidation of propane to acrolein, acrylonitrile [62].   Nickel molybdates exhibited a very high activity, with 60% selectivity to propene; oxygenated products also formed [7].   Magnesium molybdates were claimed for butane oxidative dehydrogenation in two steps, with 80% overall yield to butadiene plus butenes [63].

The problem of propene stability towards consecutive unselective oxidative attack made the finding of a suitable catalyst for propane oxidative dehydrogenation a hard task: several systems had been found that could activate the paraffin, but not one able to save the formed olefin.   It was likely that best conditions might come from the coupling of i) an heterogeneous system able to activate propane at (relatively) high temperature, and ii) an homogeneous decomposition of desorbed radical species to propene, in fact, low temperatures favoured the surface-catalyzed further oxidation of propene.   This happened because the activation energy for the gas-phase dehydrogenation was higher than that one for the heterogeneous combustion.

3.1.3 Principle of Process and Its Thermodynamics

Oxidative dehydrogenation takes place in the presence of an hydrogen acceptor such as molecular oxygen in the reaction medium, for example, the following propane oxidative dehydrogenation equation,

$$2C_3H_8 + O_2 \rightarrow 2C_3H_6 + 2H_2O$$

The comparison of the thermodynamical equilibrium constant value between two reactions of oxidative dehydrogenation and dehydrogenation in Table 3.2, showed clearly that this process had the potential to overcome the major technical problems associated with pure dehydrogenation. However, other problems such as the removal of the heat of reaction, control of selectivity due to the formation of undesired oxygenated by-products and carbon oxides, the flammability of the reaction mixtures and the possibility of run-away of the reaction arised [26]. Hence no commercial plants for the oxidative dehydrogenation of light paraffins were believed to be currently operational, although pilot or demonstration plants had been built and operated [26].

Table 3.2 Equilibrium constants for each temperatures of dehydrogenation vs. oxidation reaction.

T(K)	equilibrium constant, K_{eq}	
	dehydrogenation	ODH
298	$7.82*10^{-16}$	$6.45*10^{17}$
500	$6.15*10^{-7}$	$6.53*10^{8}$
1000	3.14	155.35

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3.1.4 Catalysts

A great variety of catalysts have been formulated and tested and almost of them are oxide catalysts [1-27].
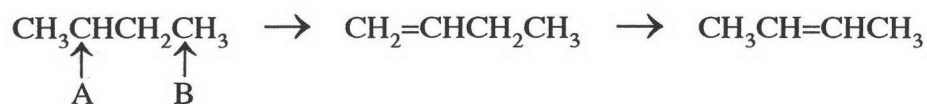
Because of still having major problem concerning the oxidation control, it is difficult to control the consecutive reaction of alkene since alkene is much more reactive than alkane [1,2,13]. The proper catalyst should have the following properties:

1. It must be able to give the type of oxygen that can react with alkane better than alkene or can excite alkane reactivity.

2. It should be able to reduce the residence time on the catalyst surface in order to avoid alkene to be reacted to be the other undesired products (CO and CO_2). For example, it should be basic because alkene is basic, so it can adsorp on the catalyst surface in a short time.

3.2 Important Reactions

### 3.2.1 Oxidative Dehydrogenation of Butane

According to the reaction mechanism of butane in oxidative dehydrogenation reaction over V-Mg-O catalysts, as reported in the literature [1], it was proposed that butane was activated by the catalyst that abstracted a H atom from the molecule to form an adsorbed butyl radical and a surface OH group. Butane first reacted by the dissociation of a methylene C-H bond to form a secondary butyl radical, confirmed by the deuterium isotope effect on V-P-O catalyst. The butyl radical formed was very reactive. It formed butenes by losing another hydrogen from the carbon atoms adjacent to the first carbon site:

$$CH_3CHCH_2CH_3 \rightarrow CH_2=CHCH_2CH_3 \rightarrow CH_3CH=CHCH_3$$

$$\begin{array}{cc} \uparrow & \uparrow \\ A & B \end{array}$$

Loss of any one of the three hydrogens at position A led to 1-butene. Loss of one of the hydrogens at position B led to *cis*-2-butene, and loss of the other hydrogen at position B led to *trans*-2-butene.

3.2.2 Oxidative Dehydrogenation of Propane

The oxidative dehydrogenation of propane over V-Mg-O catalysts had also been investigated [2]. The conclusion about its reaction mechanism was as followed. The two reactions of butane and propane proceeded with a similar reaction mechanism. It appeared that propane first reacted primarily by breaking a methylene C-H bond to form an adsorbed alkyl radical. Rapid breaking of a second C-H bond at an end carbon then formed propene:
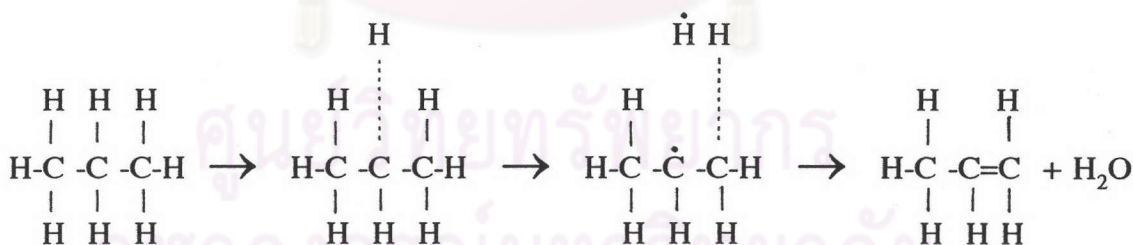
A methylene C-H bond was first broken instead of a methyl C-H bond because it was weaker by 15 kJ/mol. This suggestion was consistent with the fact that under similar reaction conditions and at low conversions, butane reacted about 1.5 times faster than propane. This could be interpreted by the fact that butane has more methylene C-H bonds than propene.

It was known that in oxidative dehydrogenation reaction, these substances (alkane, alkene or diene) reacted with highly reactive surface oxygen species of the oxide catalyst [1-3,5-9,11-17,19-27]. The catalyst which was reduced by these substances could oxidize oxygen from the gas phase subsequently [3-5,12,23].

3.3 Characterization of Oxide Catalyst [64]

Surface Oxide Species

It was theoretically possible for many different forms of oxygen to exist on a reacting catalyst surface and to participate in the reaction [65]. Since the detection of a particular species on a surface did not necessarily imply that it was significant in catalysis, the identification of the actual reactive oxygen species was of major importance in uncovering reaction mechanism. As before, results would be discussed as though a single phase was present although this was rarely so and each phase might have its own chemistry.

a. Lattice Oxygen

In the case of BiMo, much of the evidence for the participation of lattice oxygen depended on $^{18}O_2$ tracer studies. The original experiments [66,67] showed clearly that in the oxidation of propene with $^{18}O_2$, the acrolein and CO_2 produced contained largely ^{16}O which must have originated from the catalyst lattice and this had been confirmed in subsequent work [68-71]. From the very low ^{18}O content of the products, it was also clear that oxygen introduced into the catalyst from dioxygen equilibrated rapidly with the bulk on the time scale of propene oxidation [67,69-71]. These facts were usually interpreted by a direct participation of surface

lattice oxygen mobility. A former paper [72], however, had suggested that they were also consistent with mechanisms in which water exchanged rapidly with the catalyst and was also the source of oxygen appearing in the products. This implied either direct involvement of water in the reaction, which was unlikely [73], or rapid oxygen exchanged between water and both the reaction products and the BiMo bulk. Available experimental results [74] showed, however, that these reactions were too slow for this explanation to be correct and the direct incorporation of lattice oxygen could therefore be considered as established.

Experiments on the propene-$^{18}O_2$ reaction over BiMo, carried out at lower temperatures than usual, had revealed that the ratio of ^{18}O to ^{16}O acrolien was temperature dependent, with somewhat greater ^{18}O incorporation at lower temperatures. Here the restricted lattice mobility allowed a higher $^{18}O_2$ lattice oxygen concentration on the surface that would occur if scrambling with bulk oxygen were complete [68]. Detailed interpretation was in terms of a rapid reversible dissociative adsorption of dioxygen to give an uncharged monotomic species which could exchange with the surface lattice oxygen. Although evidence for this analysis was circumstantial and other schemes were, no doubt, possible. The analysis presented, however, suggested that the uncharged species, if present, did not react significantly with propene and was only important in lattice reoxidation. More importantly, the observation of the temperature effect showed that oxide removal and replacement on the same crystal face was possible [68] and that the postulate that different faces were involved was unnecessary [75]. Russian workers [71], also using $^{18}O_2$, claimed that CO_2 produced from propene over BiMo by a parallel route contained larger quantities of ^{18}O than that produced by consecutive oxidation of acrolein. They suggested that acrolein formation and combustion involved lattice oxygen but that CO_2 was produced directly from propene by a different mechanism. More evidence would be required before this

could be accepted particularly since experiments at low conversion in a flow reactor showed no difference in the ^{18}O content of acrolein and CO_2 suggesting no distinction could be made as to the oxygen source in the two products [69]. This latter work also found γ-BiMo to have higher activity and greater oxygen mobility ($\approx$250 monolayers) than α ($\approx$100 monolayers). A correlation between activity and bulk oxygen mobility was suggested and quantitative correlation, using Fick's law to calculate relative diffusion constants, was attempted. A good line was obtained, the treatment was questionable and probably showed only that rates of propene oxidation were correlated with rates of reaction with hydrogen, values of the latter being used to calculate a bulk-surface concentration gradient.

An interesting approach [75], which might reveal much about the processes occurring both at the surface and in the bulk in BiMo catalysts, arised from the observation that γ-Bi_2MoO_6, which was produced from a solid state reaction between $Bi_2{}^{18}O_3$ and $Mo{}^{16}O_3$ at 550°C, differed from that made from $Bi_2{}^{16}O_3$ and $Mo{}^{18}O_3$ in the composition of water produced on reduction by hydrogen. For γ-Bi_2O_3, $Mo{}^{18}O_3$, the water was initially low in ^{18}O content but increased as reaction proceed. For γ-$Bi_2{}^{18}O_3$, MoO_3, the ^{18}O content was initially high and fell with reduction. Thus a non-uniform isotopic distribution was maintained in the γ-phases even after 20h in vacuum at 550°C and, on reduction with H_2, initially, the oxygen in the water was preferentially supplied by the Bi_2O_2 layer of the koechlinite structure. In a further experiment, a partially reduced sample of γ-$Bi_2Mo{}^{16}O_6$ was reoxidized with $^{18}O_2$ to give a sample designated γ-$Bi_2Mo{}^{18}O_6$ which on reduction with H_2 showed behavior similar to γ-Bi_2O_3, $Mo{}^{18}O_3$ implying that reoxidation had occurred preferentially at the Mo layers. It was therefore suggested that oxide was most easily removed from the Bi layers but replaced into Mo layers and that interlayer transfer occurred only on reduction.

b. Other Forms of Oxygen

Many forms of oxygen including the excited singlet state of dioxygen [65,77] had been proposed as reactive species. Other suggestions included the activation of dioxygen invariably leading to total combustion [78], that O_2 was a selective oxidant while O^- was unselective [65] and that O^-, formed from surface lattice oxygen by electron transfer, was the active species giving selective chemistry [79,80]. These suggestions were clearly incompatible and emphasized the impossibility of assigning selectivity to a particular reactive species out of its context in the total reaction path leading to products [64].