CHAPTER III

THEORY

The basic knowledge of the spinel structure, zinc gallate and zinc aluminate are described in the first section this chapter and in the next section explanation on the oxidative dehydrogenation of alkane.

3.1 Spinel [18, 19, 20, 21]

3.1.1 The spinel group of mineral

The spinel group of oxides that have a very similar structure. The spinel group contains over twenty members, but only a few are considered common. Named after their sole gemstone representative, spinel, this is an important group of minerals. It includes one of the most important ores of iron, magnetite; an important ores of chromium, chromites; an important ores of lead, minium; a once important ores of manganese, iron and zinc; franklinite and many other interesting members. The general formula of the spinel group is **AB_2O_4**. The **A** represents a divalent metal ion such as magnesium, iron, nickel, manganese and/or zinc. The quad valent lead ion can also occupy this site. The **B** represents trivalent metal ions such as aluminum, iron, chromium and/or manganese, titanium may be also occupy this site with a +4 charge and lead at +2 can occupy this site.

3.1.2 Spinel structure

Several commercially important magnetic oxides have the spinel structure. The parent spinel is $MgAl_2O_4$. It has cubic close pack oxides ions with Mg^{2+}, Al^{3+} in tetrahedral and octahedral interstices, respectively. Many oxides, sulphides and halides have the spinel structure and different charge combinations are possible, namely:

2, 3	as in	$MgAl_2O_4$
2, 4	as in	Mg_2TiO_4
1, 3, 4	as in	$LiAlTiO_4$
1, 3	as in	$Li_{0.5}Al_{2.5}O_4$
1, 2, 5	as in	$LiNiVO_4$
1, 6	as in	Na_2WO_4

Similar cation combination occur with sulphides, e.g. 2, 3: $ZnAl_2S_4$ and 2, 4: Cu_2SnS_4 with helides, cations are limited to charges of 1 and 2, in order to give an overall cation: anion ratio of 3:4, e.g. Li_2NiF_4.

Naturally occurring spinel minerals are found as minor constituents of both igneous and metamorphic rocks. The prototypic mineral after which the structure is named has the idealized formula $MgAl_2O_4$. In nature, other element in varying amounts will substitute for Mg^{2+} and Al^{3+}. The most renowned member of the spinel group is doubtless magnetite, Fe_3O_4, the lodestone, man's first useful magnet. The general formula for spinel is AB_2X_4, where A and B are metallic cations in the +2 and +3 oxidation states, respectively, and can equally well be written as $(AX)(B_2X_3)$. Most spinels are oxides, although a much smaller number of sulfides, selinides, and tellurides also exist. Stability decreases with decreasing electronegativity, making the oxides the most stable

The spinel crystal structure is frequently described by saying that it is a close packed face-centered cubic configuration of X^{2-} ions with the cations filling one-eighth of the octahedral interstices.

An expanded view of two of the eight cubic units that make up the unit cell is shown in Figure 3.1

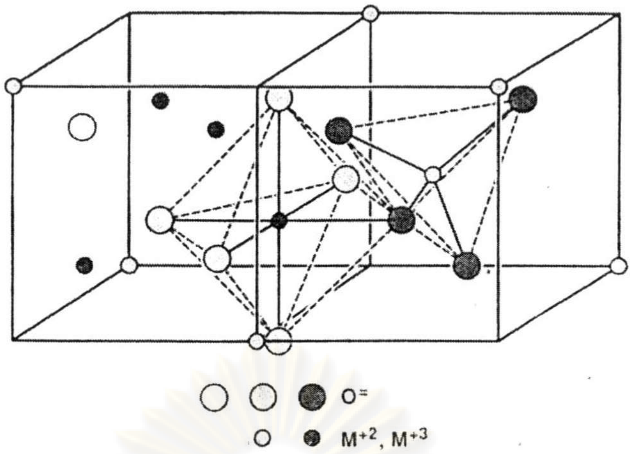

Figure 3.1 Two octants o the spinel structure. Note that the octahedrally coordinated cation has one O^{2-} ligand in common with the tetrahedrally coordination ion.

When the tetrahedrally coordinated A sites are occupied by M^{2+}, and the octahedral B sites by M^{3+} the structure are called a normal spinel. If the A sites are occupied by M^{3+} and the B by randomly disposed mixture of M^{2+} and M^{3+}, the structure is known as an inverse spinel. The oxidation states of the cations are not restricted necessarily to +2 and +3. They can also be formed of M^{4+}, M^{3+}, and even M^{+}, where the quadrivalent ion occupies the smaller a site and the lower oxidation state the B site.

3.1.3 Zinc gallate ($ZnGa_2O_4$)

$ZnGa_2O_4$ is a binary oxides consisting of ZnO an Ga_2O_3 that crystallizes in spinel structure. The unit cell of spinels is represented by formula of AB_2O_4. The Zn^{2+} ions occupy the tetrahedrally coordinated A site and Ga^{3+} ions occupy the octahedrally coordinated B sites. The structure of zinc gallate is shown in figure 3.2.

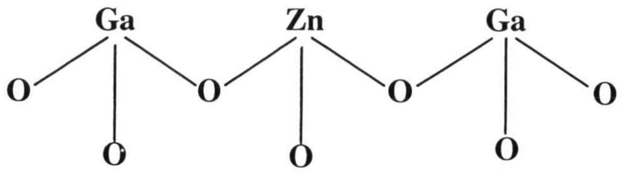

Figure 3.2 Structure of zinc gallate

3.1.4 Zinc aluminate ($ZnAl_2O_4$)

$ZnAl_2O_4$ is a binary oxides consisting of ZnO an Al_2O_3 that crystallizes in spinel structure. The unit cell of spinels is represented by formula of AB_2O_4. The Zn^{2+} ions occupy the tetrahedrally coordinated A site and Al^{3+} ions occupy the octahedrally coordinated B sites. The structure of zinc gallate is shown in figure 3.2

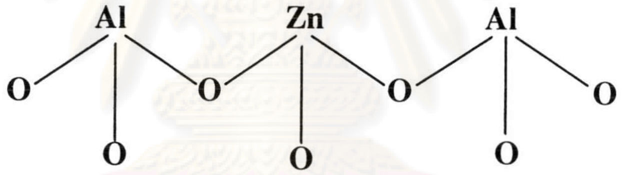

Figure 3.3 Structure of zinc aluminate

3.2 Oxidative dehydrogenation of alkane [17, 24,30]

3.2.1 Dehydrogenation versus oxidative dehydrogenation

The recent global demand for alkanes and their shortage as a consequence of both an increase in their primary used as monmers/comonomers and relative decrease in their production because of changes in operating condition in steam and catalytic cracking units-have engendered new interest in producing them from alkanes. There are several commercial or near-commercial dehydrogenation processes, including: steam active reforming, Catofin, UOP Oleflex, Linde-BAFS, and Snamprogetti-Yarsintez processes, which differ from one another mainly in terms of reactor technology and type of catalyst. Two principal classes of catalysts are used: supported platinum catalysts and chromium oxide catalysts usually supported over alumina.

These catalytic dehydrogenation processes suffer from several limitations:

1. Thermodynamic restrictions on conversion and selectivity.
2. Side reaction such as thermal cracking.
3. Difficulty in separating the alkene from the alkane and by products.
4. Strong endothermic main reaction and the necessity to supply the heat at high temperature.
5. Rapid formation of coke and thus continuous necessity for catalyst regeneration as well as the loss of hydrocarbon in this side reaction.
6. Irreversible catalyst deactivation owing to the severe reaction condition.

The severity of reaction conditions increase with decreasing carbon chain length and thus dehydrogenation of ethane by far the least thermodynamically favored reaction. At present there are no commercial ethane dehydrogenation processes. Propane dehydrogenation is technically feasible, but costly because of the severe condition. n-butane dehydrogenation required less severe condition, but gives rise to several product. In the dehydrogenation of isobutene, n-butane and butane are undesired by-product formed by skeletal isomerization that accumulate in the recycle loop and give rise to butadiene formation leading to severe deactivation by coke.

There are various lines of research in place to overcome these limitation: (i) development of improved catalysts that limit some of the drawbacks especially in term of selectivity and resistance by deactivation, (ii) coupling of dehydrogenation (endothermic reaction) with hydrogen oxidation (strong exothermic reaction; H_2 is a main by-product of dehydrogenation) to directly supply the heat of reaction required and ship the equilibrium toward the alkene (H_2, however, is a very valuable coproduct and it combustion weakens the economic of processes), and (iii) use of catalytic membrane to shift the equilibrium allowing the operation at low temperatures (current membrane, however, are very costly so this is still a remote possibility). A fourth option being researched is the oxidative dehydrogenation of alkanes, which overcomes the thermodynamic limitations, allows operation under relatively mild conditions, and avoids the necessity of continuous catalyst regeneration, but has a major drawback in the difficulty of controlling the consecutive oxidation to carbon oxides. Other secondary problems are the removal of the heat of reaction, the flammability of the reaction mixture, and possibility of reaction runaway.

In contrast to alkane dehydrogenation processes, most critical problems in oxidative dehydrogenation are related to finding a catalyst and reactor technology that allow control of consecutive oxidation to carbon oxides. Therefore, although considerable research and development remains to be done to improve the technically the technical and economic performance of oxidative dehydrogenation before it can complete commercially with established technologies [steam cracking of either naphtha or liquefied petroleum gas (LPG)], the outlook for the development on industrial-scale oxidative dehydrogenation process still remains good, especially for light alkane such as ethane.

The major challenge is to improve the selectivity, both in regard to reducing carbon oxide formation at high conversion and minimize (elimination) condensable oxygenate hydrocarbons. This requires not only the better catalyst design, but also a reactor technology that can maximize catalyst effectiveness in alkene formation.

The basic concept of oxidative dehydrogenation is that reaction take place in the presence of a hydrogen acceptor (oxygen), which give a rise to an exothermic reaction so avoiding the thermodynamic limitations of reversible endothermic reaction (pure dehydrogenation) an at the same time avoids formation of heavier products with high C/H ratios (carbonaceous-type species) leading to fast catalyst deactivation. This concept makes it possible to distinguish between a system formed by a pure dehydrogenation catalyst coupled to a catalysts for H_2 oxidation to H_2O (only the first of the characteristic is present) and an oxidative dehydrogenation catalyst in which both operate. In the approach a main difficulty is to find a catalyst selective only for hydrogen oxidation and not toward oxidation of the regents and products.

In the UOP process for propane dehydrogenation coupled with a second stage of hydrogen oxidation supported noble metals doped with alkali and alkaline earth metals and/or tin are used as H_2 selective oxidation catalysts, and similar types have also been proposed by other companies. These are basically dehydrogenation-type catalysts modified to moderate activity and neutralize acidity (negative with respect to side reactions on the alkene products). This coupled dehydrogenation $+H_2$ oxidation approach makes it possible to compile the advantages of high selectivity (characteristic of pure dehydrogenation), internal heat supply necessary for the endothermic dehydrogenation reaction, and shift of equilibrium by consuming H_2 (Considering recycling a recycling process-the $H_2+1/2O_2 \rightarrow H_2O$ reaction-physically separate from the dehydrogenation reaction although it takes place in the same reactor; in oxidative dehydrogenation H_2O is formed as part of the catalytic reaction cycles of alkane formation). However, the oxidative dehydrogenation approach has the potential additional advantages of avoiding catalyst deactivation and not requiring high operating temperature, thus considerably simplifying the process and improving process economic. In addition, the effective combination of dehydrogenation and H_2 oxidation catalysts requires specific reaction condition. In fact, while the concept has been shown to be effective in the case of styrene production from ethylbenzene (SMART process by Lummus and Monsanto), the indications are less clear for light alkane dehydrogenation.

Membrane –assisted dehydrogenation also has the potential of avoiding some of limitations of the dehydrogenation process. Its main advancetages are that: (i) the hydrogen is removed continuously, and thus the equilibrium is shifted; and (ii) an autothermic process can be obtained when the dehydrogenation id done on one side of the membrane and an exothermic reaction (such as hydrogenation or hydrogen oxidation) occurs on the other side of the membrane. Two basics types of membrane have been proposed for use in dehydrogenation. : (i) non porous membranes consisting of metals (such as Pd) or alloy (such as Pd/Ag); and (ii) porous membranes, consisting, e.g., Vycor glass, aluminium ceramics, and SiC. However, due to membrane cost, low productivity, coke formation, heat-exchange problems, low chemical and thermal resistance, and problems of irreproducibility in large-scale operation (difficulty in obtaining uniform microporosity and absent of coke), it is not likely that membranes will be used in dehydrogenation processes of light alkanes in the near future.

3.2.2 Constrains in Oxidative Dehydrogenation

The flammability of the reaction mixture in light alkane oxidative dehydrogenation is a major constrain in the reaction because operation under safe conditions is not optimal for productivity. The general flammability diagram for the system of alkane/oxygen/inert is shown in Figure 3.3. The diagram is the function of the alkane, temperature, and pressure, but although these parameters influence the numerical values, the general features remain the sane so the graph in Figure 3.3 can be considered a representative model for discussing the constrains in oxidative dehydrogenation of light alkane due to flammability and explosion limits.

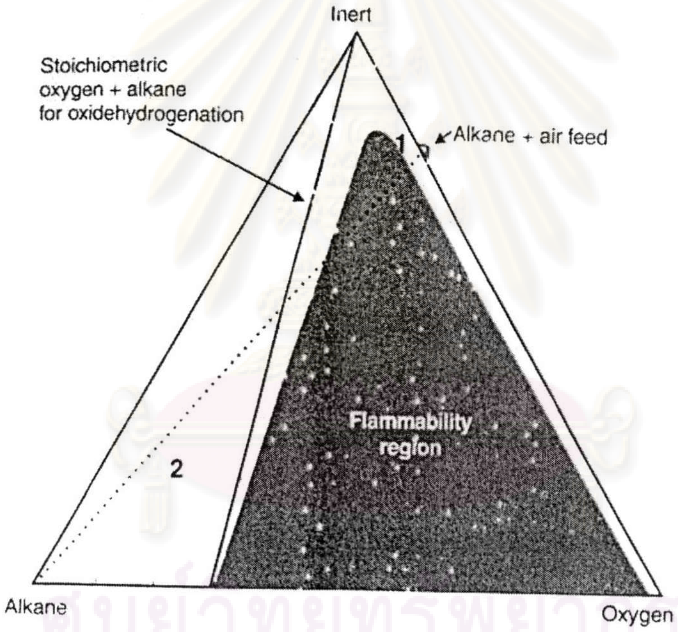

Figure 3.4 General flammability diagram for the system alkane/oxygen/inert. The dashed line shows the curve for the stoichiometric oxygen/alkane oxidehydrogenation.

Operation inside the flammability bell is possible using special reactor configurations such as the fluidized-bed reactor (FIBR), where the continuous movement of catalyst mass efficiently inhibits radical chain propagation, but it is necessary that; (i) outside the catalyst bed the mixture composition is outside the flammability bell, and (ii) the fluidization of the catalyst s is completely homogeneous to avoid gas pockets where explosion can start. Control of these parameters is very difficult, especially in the case of the occasional malfunction. Thus, for reasons of safety, it is preferable to operate the process outside the flammability bell.

Different zone of operation outside the flammability bell can be distinguished: (i) low alkane-to-oxygen ratio, i.e., the right side of the flammability bell; (ii) near the stoichiometric ratio of alkane to oxygen, i.e., the left side of the flammability bell, and (iii) high alkaane to oxygen ratio.

In the first case, the composition must be close to the alkane/air mixture, because otherwise pure oxygen must be added to feed, which usually renders the process unprofitable. The conversion path in the case of complete alkane conversion is indicated in Figure 3.3 by line No. 1. Under this condition, recycling of unreacted alkane is not possible and thus a high hydrocarbon conversion per pass is required. Major disadvantages are the low productivity; high oxygen-to-alkane ratios, which favor complete combustion; and the cost of separating alkane from large volumes of gas owing to the large quantity of the inert gas(nitrogen). As high alkane conversions and high oxygen-to-alkane ratios are uneconomical for selectivity for the alkane, operation with feedstock compositions corresponding to this first operation (low alkane-to-oxgen ratio) may be less suitable for alkane selective oxidation. However, when the alkane produced can be converted directly to condensable products without a preliminary separation stage (e.g., an ethane to ethane oxidative dehydrogenation unit followed directly by an ethane oxychlorination unit), operation with alkane/air mixture can be economically advtageous, as the cost operation with pure oxygen feedstocks (as required in the two other options discussed below) is avoided.

Therefore, the choice of feed composition for operation has constrains that derive not only from the flammability limits but also from the advantages/cost of using air versus oxygen and from the use of the reaction products. It is worthwhile noting as well that the choice of optimal catalyst and type of reactor is influenced by the choice of the feed composition, because, e.g., with low alkane-to -oxygen ratios the key catalyst parameter is selectivity at high conversion, whereas with feedstock compositions from the left side of the flammability bell the hey feature must be selectivity at low conversion and productivity at low conversion and productivity.

The choice of the optimal reactor configuration is also determined by the type of feedstock and in turn the catalyst characteristics (e.g., thermal and mechanical resistance, porosity, particle dimensions) must be optimized with respect to the reactor characteristics. Consequently studies of catalyst performance must proceed with an awareness of the intended application and the constrain that derive from it in terms of feedstock composition, reactor design, and catalyst properties. Most of the studies that have been published leave these considerations aside and thus may not address relevant problems. It is clear that future research must involve an integrated approach taking catalyst, reactor, and process design into account.

A second possible operating zone is at the left of the flammability bell near the stoichiometric alkane-to-oxygen ratio for oxidehydrogenation. In this zone one possibility to operate directly with alkane and oxygen in feedstock without an inert (in figure 3.3 Operating path No. 2). The alkane in this case is in excess when oxygen is also consumed in other side reactions (i.e., in combustion) and thus, theoretically, complete oxygen conversion could be achieved. The main advantages of this operating zone are: (i) the theoretical possibility of obtaining the highest alkene productivity; (ii) the low oxygen-to-alkane ratio, which favors high selectivities; and (iii) reduce dimensions of the reactor per mass of alkane produced, but disadvantages are: (i) great amont of heat of released; (ii)high alkane loss, if it is not convenient to recycle it;(iii) difficulty in achieving high conversion of alkane; and (iv) difficulty in controlling catalyst deactivation and reactor operation in general.

Most of the patent and scientific papers on light alkane oxidative dehydrogenation report catalytic results obtained using a feed composition close to the stoichiometric alkane-to-oxygen ratio, but in the presence of large quantities of an inert gas, which would correspond (in the hypothesis of translating the feed composition to a process situation) to a process in which large volumes of an inert are added to the feed. This is clearly an unrealistic process option. From a practical point of view the only possibility is to add steam as the inert component, but steam considerably modifies catalyst reactivity and thus cannot be considered as equivalent to nitrogen as inert. Catalyst performances in the case of light alkane oxidative dehydrogenation are very sensitive to feed composition and thus wrong indications can be obtained when the right feed composition is not used, even at the stage of preliminary screening of catalyst behavior.

Indeed, when the operation is carried out with recycling of the unconverted reactant, inert components are present in the reactor inlet that are either generated in the reactor (typically, carbon monoxide, which is difficult and expensive to separate from light hydrocarbons) or present as impurities in the make up feed (typically, argon in pure oxygen, or less reactive molecules in the hydrocarbon feed). Therefore, the true operating region lies above the alkane-oxygen line (zone 2 in figure 3.3). Sometimes an additional inert component is added, which can be easly separated from other components in plants selections downstream of the reactor, with the aim of (i) improving heat condition properties of the fluid, (ii) diluting the components, or (iii) operating in the safer region (i.e., in the upper part of the diagram in figure 3.3). The preferred inert is steam; in other cases a part of off-gas is added to the hydrocarbon recycle stream. With almost all catalysts for light alkane oxidative dehydrogenation the selectivity for alkene decreases considerably with increasing alkane conversion. In addition the increase in carbon oxide formation make control of the reaction temperature to increase conversion even more difficult (alkane combustion is a much more exothermic reaction than alkane-to-alkene conversion). Generally conversion per pass must not exceed 10-20% further to be reasonable selectivity for alkanes. Although the cost of alkane feedstock is very near to that of fuel and thus unreacted hydrocarbon can be used economically to produce high-pressure steam, a hypothetical process based on state-of-the-art oxidative dehydrogenation catalysts would probably require alkane recycling and thus the use of an oxygen/steam combination to reach the required combustion. The observation again illustrates the necessity of studying the reaction of light alkane oxidative dehydrogenation in the presence of steam.

The reactor configuration also puts constrains on the catalyst requirement, not only in term of size, shape, and thermomechanical characteristics and porosity, but also in regard to activity-selectivity properties in the relation to the type of feedstock used and the optimal feedstock for the reactor type. There are three main options for reactor configuration to address the general problem of maximizing selectivity for the alkane (with respect to carbon dioxide), and minimizing formation of carbon monoxide and condensable oxygenated products. The latter products (e.g., acetic cid) are often corrosive and thus, even in traces, imply the use of expensive materials for reactor and separation units and make separation of the alkane and recycle of the alkane more expensive. Carbon monoxide formation should be also be minimized, because its presence makes separation of the hydrocarbons more expensive. The three possible options are circulating-bed (CBR), mutitubular fixed-bed (MFBR), and fluidized-bed (FIBR) reactors.

3.2.3 Class of catalyst active in oxidative dehydrogenation

Different types of catalysts have been reported in the literature to be selective in light alkane oxidative dehydrogenation

1. Catalysts based on alkali and alkaline earth ions and oxides. The catalysts (e.g., the Li/MgO system) are basically active in methane oxidative coupling. But also show selectivity behavior in ethane oxidative dehydrogenation at temperature above about 600 °C. The mechanism usually involves the formation of an ethyl radical on the surface, with then reacts further, mainly in gas phase. The catalysts can be further promoted by adding halides and/or rare earth oxides.

2. Catalysts bases on reducible transition metal oxides, which activate the paraffin at much lower temperatures than the first class of catalysts. The reaction in this case is almost completely heterogeneous. Examples of such catalysts includes: (i) vanadium-based catalysts such as magnesium vanadate, supported vanadium oxide, vanadium-containing microporous materials, V/Nb oxide and V/P oxide catalysts, (ii) molybdenum-based catalysts (supported molybdenum oxides and metal molybdates),(iii)heteropolyacids (molybdophosphoric acid containing or not vanadium, and tungstophosphoric acids with the Wells-Dawson structure), and (iv) supported chromia catalysts.

3. Other catalysts such as Sn/P oxides and B/P oxides, LaF_3/CeO_2 or LaF_3/SmO_3, Ga/zeolites, and boron oxide supported on yttria-stabilized zirconia (this last catalyst operates in an electrochemical apparatus.

3.2.4 Role of nature of the alkane

Kung et al. explained this and similar results obtained over V/P oxide catalysts on the basis of the idea of a selectivity-determining step that id different from the rate-determining step. They suggested that an adsorbed alkyl forms as the first intermediate and that, depending on the number of surface VO_x units that effectively interact with the adsorbed alkyl (a function of the size of adsorbed hydrocarbon, rate of reoxidation of the vanadium active center, and type of catalyst), the reaction can be selective or proceed to carbon oxides. Thus, for magnesium orthovanadate, where VO_4 units are isolated from each other, adsorbed ethyl, propyl, or butyl species can interact with one surface VO_4 unit. If one assume that each VO_4 unit supplies a certain number of oxygen atom to react with an adsorbed hydrocarbon molecule, then the reaction of these alkanes would show the same average oxygen stiochiometry (the average number of oxygen molecules that react with each hydrocarbon molecule).

A geometrical model should determine the nature of adsorbed intermediate by common quantum-mechanical methods and then estimate the number of lattice oxygen that could really interact with the adsorbed intermediate, with is not proportional to the dimension of molecule. In fact, the surface potential of catalyst is clearly not uniform, and there are no energetic reasons why an intermediate is simply adsorbed flat on the surface. In the absence of interactions with the surface site, the top-on configuration is the energetically favorable, but interactions usually occur, so configuration of the adsorbed intermediate may change considerably as a function of: (i) the local structure of the neighboring active site, (ii) the nature of the adsorbed molecule, and (iii) the nature of the surface-hydrocarbon bond. From this last point it is clear that an alkyl radical intermediate unlike an alkoxy species would have a very weak interaction with the surface.

There are two critical aspects in the geometrical model discus above: (i) the effect of electronic surface modification (and surface relaxation) by extraction of a second (or more) lattice oxygen near a first oxygen vacancy (created by oxygen incorporation in the hydrocarbon), and (ii) the role of the stabilization and reactivity of intermediate species. The geometrical model discussed above has with in the implicit assumption that is no difference when one lattice oxygen is released from the active site (due to regeneration of water after extraction of two hydrogen atoms) or when two or more lattice oxygen are incorporated into a hydrocarbon as a first step leading finally to carbon oxides. Clearly, the local creation of more than one oxygen vacancy is an energetically unfavorable process, unless surface reconstruction rapidly. This process is even less favorable if the electrons given by the hydrocarbon to the surface are considered. In a material that is not highly conductive, such as magnesium vanadate, such electrons are not transported away from the active site quickly. In fact, although the mechanism of oxidative dehydrogenation of carbon is not well understood, it is quite well accepted that the first step is the formation of carboxylate adsorbed species (thus without extraction of lattice oxygen) and then, depending on the relativity of the carboxylate , carbon oxide may from rather than other oxygen containing species. It also much be taken into account that carboxylate species are often quite stable and unreactive (especially on basic catalysts such as magnesium vanadate) and can cause self-inhibition of the reactivity with respect to this partway, thus blocking nonselective site. There for, the formation of carbon oxides clearly cannot be associated simply with the presence of two or more labile oxygens near an adsorption site.

Furthermore, after abstraction of the first hydrogen from alkane and generation of a surface OH group there should be an electronic relaxation of the surface site (its geometry changes), but also the nature of the repulsive interaction between active site and hydrocarbon changes. It is also important to consider the nature of the possible interaction between the catalyst and the product after intermediate transformation. Clearly, this type of stabilization of the consecutive products of transformation varies, again depending on the nature of the hydrocarbon, the presence of reactive hydrogens, and the possibility of multiple attack. Other basic differences are also important, such as the fact that there is twice the probability of abstracting a second hydrogen in propane than in ethane.

The acid-base properties of the catalyst also influence the selectivity in alkane oxidative dehydrogenation, while influencing the selectivity in various ways depending on the nature of the alkane.

Oxidative dehydrogenation takes place in the presence of an hydrogen acceptor such as molecular oxygen in the reaction medium, for example, 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 to reaction of oxidative dehydrogenation and dehydrogenation in table 3.1, show clearly that this process had the potential to overcome the major technical problems associated with pure dehydrogenation. However, other problem such as the removal of heat of reaction, control of selectivity due to the formation of undesired oxygenate by-product and carbon oxide, the flammability of the reaction mixtures and the possibility of run-away of the reaction arised.

Table 3.1 Equilibrium constants for each temperatures of dehydrogenation vs. oxidation reaction.

Temperature (K)	Equilibrium constants, K_{eq}	
	dehydrogenation	Oxidative dehydrogenation
298	7.82×10^{-16}	6.45×10^{17}
500	6.15×10^{-7}	6.53×10^{8}
1000	3.14	155.35