# CHAPTER III

THEORY

Heterogeneous catalytic oxidation on oxide catalysts is one of the most important fields of catalysts which have been actively developed in recent years [Sokolovskii (1990)]. It widely employed for the functionalization of alkenes and aromatics, the most important raw materials for the petrochemical industry. In future, however, the petrochemical industry will probably directly use alkanes, which are more economical than the corresponding olefins, comprising readily available raw materials with low toxicity as compared to aromatics. Moreover, the demand for olefins is increasing, and the existing capacity (principally from steam-cracking of naphtha and FCC in oil refining) may well become insufficient to meet this demand. Consequently, the increased future demand for olefins is likely to be satisfied mainly by direct production in plants dedicated to individual olefins [Cavani et al. (1997)].

In studies on oxidative catalysis, commonly great attention is attached to the state of oxygen on the catalyst surface. A relatively inert oxygen molecule is activated by interacting with the surface of oxide catalyst. The main parameter determining oxygen reactivity on the catalyst is energy of oxygen binding with the catalyst as a thermochemical characteristic [Golodets (1983)]. Correlation between rates of catalytic oxidation and oxygen binding energy on oxide catalysts have been established : The weaker the oxygen biding with the catalyst surface, the more efficient is complete oxidation with this catalyst [Sokolovskii (1990)].

According to the nature of the surface oxygen species, it may favor electrophilic or nucleophilic attack. It corresponds to O^-, O_2^-, superoxo ($M-O-O^\circ$), peroxo (O-O electrophilic), or oxo (M=O necleophilic) species related to the metal oxygen bond nature and to the heat of meal oxygen formation [Vedrine et al. (1996)]. Such surface oxygen species including hydroxyls are usually negatively charged, i.e. should exhibit basic character.

Depending on the nature, on the oxidation state of the cation and on its environment, the metal oxygen bonds may be more or less polarized and then the oxygen will exhibit electrophilic or nucleophilic properties [Vedrine et al. (1996)].

$$\overset{\delta^+}{M} = \overset{\delta^-}{O} \qquad \overset{\delta^-}{M} = \overset{\delta^+}{O} \qquad M = O$$

nucleophilic   electrophilic
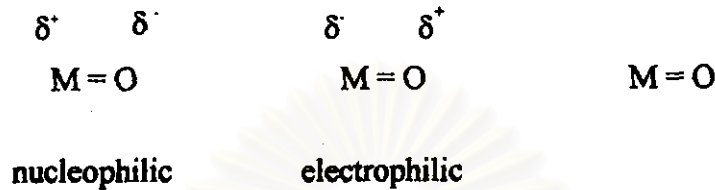
The first case will favor deprotonation according to $M=O + H^+ \longrightarrow M^+-OH$.

The second case (weak polarization) will favor homolytic concerted reactions as allylic dehydrogenation of olefins.

The third case with electrophilic character will favor direct attack of a double bond or of an aromatic ring, i.e., acetone from an aromatic ring.

In all of oxidation reactions, it usually necessitate H atom(s) abstraction, and O atom(s) insertion from the surface into the hydrocarbon molecule and several electrons transfer [Vedrine et al. (1996)]. In the well accepted Mars and Van Krevelen mechanism, lattice oxygen anions are assumed to be inserted in the substrate molecule or to facilitate its dehydrogenation by forming H_2O while the metallic cations insured the redox mechanism to occur by changing their oxidation state. This was postulated that the catalytic reaction comprises two steps [Satterfield (1980)].

1) Reaction between catalyst in an oxidized form, Cat-O and the hydrocarbon, R, in which the oxide becomes reduced.

$$Cat - O + R \longrightarrow R - O + Cat.$$

2) The reduced catalyst, Cat., becomes oxidized again by oxygen from the gas phase.

$$2\,Cat. + O_2 \longrightarrow 2\,Cat. - O$$
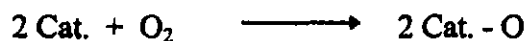
Under steady-state conditions the rates of the two steps must be the same.

Catalytic oxidation can be categorized as complete oxidation and selective oxidation [Sokolovskii (1990)]. Complete oxidation is a practicable method for elimination of organic pollutants in gaseous streams. On the other hand, complete oxidation is the combustion of hydrocarbon and oxygen to the combustion products; CO_2 and H_2O [Thammanonkul (1996)]. Selective oxidation is the reaction between hydrocarbon 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) [Abello et al. (1996), Thammanonkul (1996)]. Many examples of catalysts, active in the selective oxidation and oxydehydrogenation of paraffins, have been reported in patents and in scientific literature [Cavani et al. (1992), Landau et al. (1996)]. However, low yields in the final product were frequently observed and, in almost all cases, the productivity of these processes was far from that of industrial interest. Indeed, many problems in the oxidation of paraffins, concerning the activation of the saturated organic substrate and its selective transformation to the desired product, remain to be solved. For example, one of the main problems concerns the reactivity of the product of partial oxidation, which is higher than that of the reactant itself. This made it difficult to step the reaction at the desired product and avoid its further nonselective oxidation under the condition at which the reactant was activated [Cavani et al. (1997)]. Table 3.1 summarizes the reactions of oxidation of alkanes which are actually employed it the petrochemical industry, as well as those that are under study and development (for the synthesis of intermediates and of base building blocks, i.e., olefins) [Cavani et al. (1997)].

In most cases, which are still at the research stage, the main problem is the development of a catalyst with good catalytic performance, in terms of both activity and selectivity to the desired product, in order to obtain acceptable levels of productivity and reduce the operating costs associated with the purification of the product and possible recycling of the unconverted reactant. The second problem associated with the catalyst lifetime, which is sometimes limited by the presence of the irreversible phenomena of deactivation [Cavani et al. (1997)].

On the other hand, in some cases, the greatest opposition to the development of new oxidative processes arose on account of the loss of valuable coproducts, as in the case of oxydehydrogenation as an alternative to dehydrogenation. The increasing demand for hydrogen for refinery applications is a convincing reason for improving existing dehydrogenation technologies rather than developing alternative ones which do not yield hydrogen [Cavani et al. (1997)]. Therefore, oxidative dehydrogenation is still in a period of research and development in laboratory, although, it has the potential to overcome the thermodynamic limitations of pure dehydrogenation operating at low temperature with an exothermic reaction and avoiding frequent catalyst regeneration. From these advantages, there are several researchers aim to develop the oxidative dehydrogenation of paraffins for production of olefins.

Table 3.1 Industrial processes and processes under study or development for the oxifunctionalization of light paraffins (C_1 -C_6) in the petrochemical industry. [Cavani et al. (1997)]

No.	Raw material	Product	Phase	Stage of development
1	Cyclohexane	Cyclohexanol, one	Liquid, hom [a]	Industrial
2	n-Butane	Acetic acid	Liquid, hom	Industrial
3	n-Butane	Maleic anhydride	Gas, het [b]	Industrial
4	Methane	Chloromethanes	Gas, het	Industrial
5	Methane	Methanol	Gas, het/hom [c]	Pilot plant
6	Methane	Syngas	Gas, het/hom	Research
7	Methane	Ethylene	Gas, het/hom	Pilot plant
8	Ethane	1,2 - Dichloro-ethane, vinyl chloride	Gas, het	Research
9	Ethane	Acetic acid	Gas, het	Research
10	Ethane	Ethylene	Gas, het/hom	Research
11	Propane	Acrylic acid	Gas or liquid	Research
12	Propane	Propyl alcohol	Liquid, het or hom	Research
13	Propane	Acrylonitrile	Gas, het	Demonstration plant
14	Propane	Propylene	Gas, het	Research
15	n-Butane	Butadiene	Gas, het	Industrial, abandoned
16	Isobutane	Methacrylic acid	Gas, het	Pilot plant
17	Isobutane	Isobutene	Gas, het	Research
18	Isobutane	t-Butyl alcohol	Liquid, het or hom	Research
19	n-Pentane	Phthalic anhydride	Gas, het	Research
20	Cyclohexane	Cyclohexanone	Liquid, het or hom	Research

[a] hom - homogeneous.

[b] het - heterogeneous.

[c] het/hom - the likely presence of a mechanism initiated on the catalyst surface and transferred in the gas phase.

3.1 Oxidative Dehydrogenation [Cavani et al. (1995)]

One type of the selective oxidation is the oxidative dehydrogenation (or sometimes called oxydehydrogenation, ODH) which is the functionalization of alkanes in the presence of oxygen [Corma et al. (1993b)], but without oxygen atom in the structure of product.

Theoretically it is possible to use a metal catalyst for dehydrogenation, but high temperatures is needed to obtain an adequate equilibrium concentration of product, and at these high temperatures the hydrocarbon is often unstable and decomposed completely and give a deposit of carbon on the catalyst. A successful process can only result if the thermodynamics allow the use of a somewhat low temperature: the dehydrogenation of cyclohexane to benzene is one of the few reactions where a metal catalyst is satisfactory. However the reaction of a hydrocarbon with oxygen to give a more unsaturated molecule plus water, e.g.

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

is more thermodynamically favored because of the high enthalpy of formation of water. Provided a catalyst can be found to conduct this reaction selectively, i.e. without giving deep oxidation at the same time, good yields of propene are obtainable at a lower temperature than would be possible in a direct dehydrogenation. The term *oxidative dehydrogenation* is applied to such reactions:

3.1.1 Oxydehydrogenation of ethane [Cavani et al. (1995)]

Some of the catalysts developed for the reaction of methane coupling are also active in the ethane oxydehydrogenation. In other cases, entirely new catalytic systems have been developed. The performances of catalysts reported in literature is summarized in figure 3.1 [Cavani et al. (1995)], which reports 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, it can be classified the catalysts into:

a) Catalysts based on ions and oxides of Group IA and IIA metals, which are also active for methane coupling [Burch et al. (1990), Conway et al. (1991), Cavani et al. (1995)];these activate ethane at temperatures usually higher than 600°C to form ethyl radicals, which then further react in the gas phase. The most successful of these catalysts is the Li/Mg/O one.
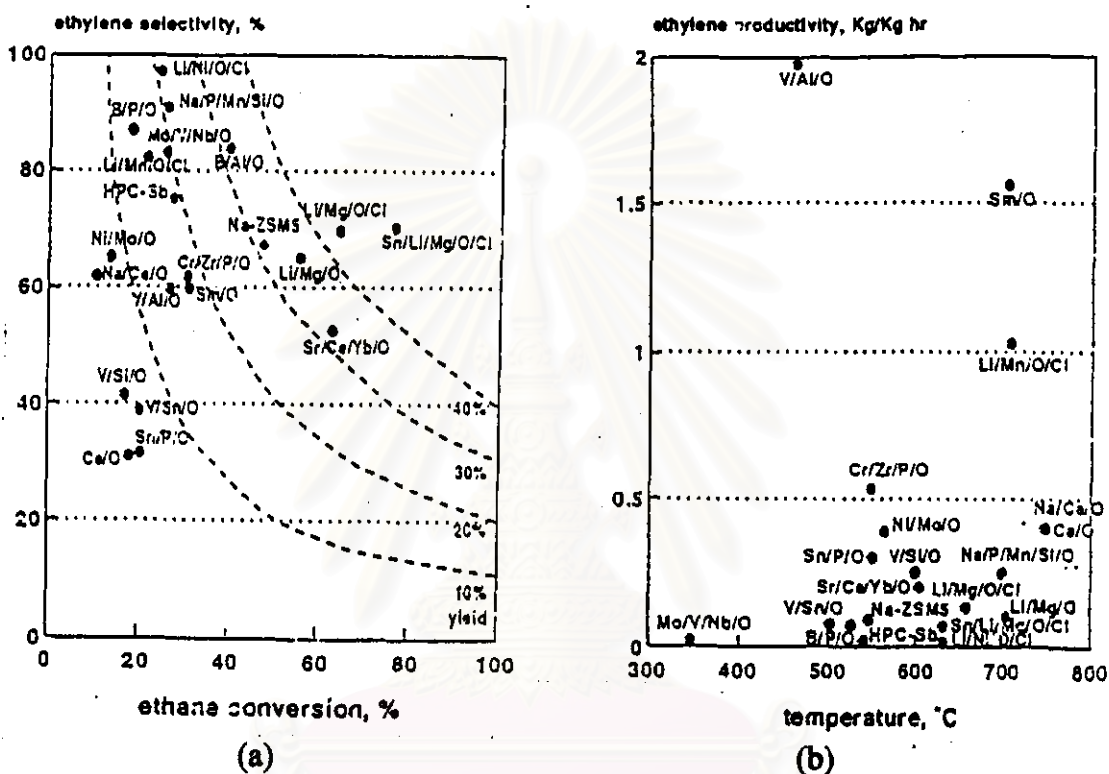

Figure 3.1 Best yields of ethene reported in literature (a) and ethene productivity (b) on the various catalytic systems [Cavani et al. (1995)]

This mechanism does not involve a classical redox-type cycle; thus, no furnishing of bulk oxygen occurs, 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 capable of abstracting a H. and forming the ethyl radical. However, a progressive loss of Li occurs at temperatures higher than 700 °C. Such catalysts could be employed after a methane coupling reactor, in order to increase the yield to ethene 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 can be achieved with this catalytic system, above all when chlorine-containing compounds are also fed to the reactor, or when the catalyst is doped with halides [Burch et al. (1990), Conway et al. (1991)]; the promoter effect is maintained by continuous feeding of the chlorine, which modified catalyst surface ; chlorine radicals are thought to favor the homogeneous decomposition of ethyl radicals to ethene. Yields as high as 34% to ethene could be achieved [Burch et al. (1993), Ducarme et al. (1994)]; however, the use of chlorine is limited by problems related to equipment corrosion.

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

Other systems that are active at temperatures higher than 600°C are Li_2O/TiO_2, $LiCl/NiO$, $LiCl/MnO_2$ and $LiCl/Sm_2O_3$. Dopants other than Li^+ have been reported: SnO_2, Na_2O, lanthanides (mainly CiO_2) [Conway et al. (1991)].

b) Catalysts based on transition metal oxides [Burch et al. (1991)]. Rare earth oxides are remarkably active [Choudary et al. (1992)], and yield ethene with high productivity and good selectivity. In addition, they exhibit a very high stability even at high temperature. Doping Sm_2O_3 with alkali metals gives the best performances. These systems are believed to operate with a mechanism similar to that of Li/Mg/O catalysts.

Also $Na_4P_2O_7/MnO_x/SiO_2$ catalyst operates at very high temperature. Such system is claimed for cyclic operation with ARCO [Jones et al. (1998)]or Phillips [Eastman et al. (1983)] technology in circulating-bed applications, where higher selectivities can be 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 is reduced by interaction with the hydrocarbon, through a classical redox cycle [Burch et al. (1991),Oyama et al. (1990)]. These systems can activate ethane at temperature as low as 400°C, and the entire reaction is heterogeneous, hence controlled by the catalyst; the contribution of homogeneous reactions only occurs at the highest temperatures. Mixed oxides of Mo/V/Nb were shown to be active in ethane oxidation at temperatures as low as 250 °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 forms considerable amounts of acetic acid. Alumina-supported vanadium oxide exhibits an high activity in ethane conversion, with fairly high productivity. Figure 3.2 summarizes the mechanisms proposed in the literature for the two classes of catalysts, operating at low and high temperature.
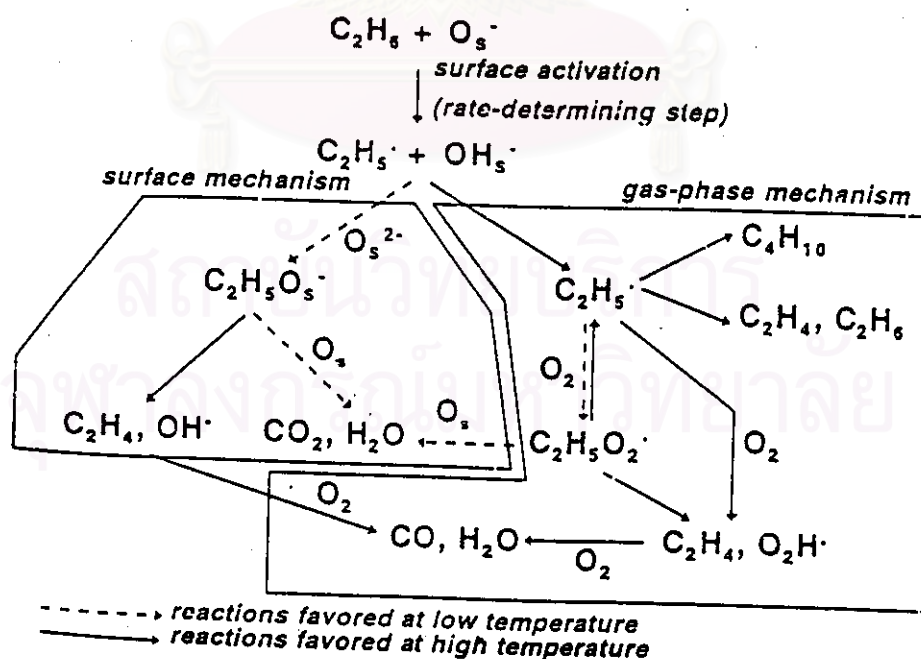

Figure 3.2 Summary of the mechanisms proposed in the literature [Thammanonkul (1996)]

3.1.2 Oxydehydrogenation of propane

Among the catalysts that have recently been receiving much attention for the oxidative dehydrogenation of propane are supported vanadium oxide [Bhattacharyya et al. (1992), Boisdron et al. (1995), Burch et al. (1991), Chaar et al. (1988), Creaser et al. (1996), Gao et al. (1994), Lars et al. 1994), Pantazidis et al. (1996a), Okuhara et al. (1993), Vuurman et al. (1996)]. Vanadium oxide is not a good catalytic system for the paraffins oxydehydrogenation, but the spreading of the oxide onto a support with basic features (such as sepiolite, MgO, etc.) or over alumina, with the formation of centers with peculiar chemical-physical features and reactivity lead to a more selective catalyst[Bhattacharyya et al. (1992), Chaar et al. (1987-1988), Corma et al. (1993a)]. Oxygenated compounds are not formed. These catalysts are active at relatively low temperature (in the temperature range of 350-450°C). Here, the V-Mg-O catalyst system is mainly discussed, due to this system gave the best performance (typically 60% of propane selectivity at 15% of propane conversion).

3.1.2.1 Active phases and active sites

The nature of the active phase in this system is still discussed. According to Kung et al. (1991) both magnesium orthovanadate ($Mg_3V_2O_8$) and α-pyrovanadate (α - $Mg_2V_2O_7$) phases are selective in the partial oxidation of propane. For Volta et al. (1990)only the latter phase is responsible for the high propylene selectivities observed whereas the former is responsible for total oxidation. Reducibly and electrical conductivity measurements [Guerrero-Ruiz et al. (1992)] have shown that the $Mg_2V_2O_7$ phase was more easily reduced than the other two while anionic vacancies were created according to :

$$C_3H_8 + O^{2-}_{surf} \longrightarrow C_3H_6(g) + H_2O + \square + 2e^-$$

It seems that the differences of interpretation results from the presence or not of potassium impurities introduced during the catalyst preparation and which may modify the selectivities of the considered reaction [Owen et al. (1992)]. In the same way, a recent study of Delmon's group (1994a) showed that the method of

preparation of V-Mg-O catalysts may also modify their performance due to formation of mixed phases which probably interact synergetically [Gao et al. (1994a)].

The nature of the active sites of the V-Mg-O catalysts is also still under debate [Chaar et al. (1987), Guerrero-Ruiz et al. (1992), Sam et al. (1990)]. According to Volta et al. (1990, 1992), the vanadium occupies isolated tetrahedral VO_4 sites in $Mg_3V_2O_8$, VO_6 octahedral linked through edges in MgV_2O_6 and V_2O_7 units consisting of pairs of corner-sharing VO_4 tetrahedral in α-$Mg_2V_2O_7$. The obtained order of reactivity and selectivity for three phases were α-$Mg_2V_2O_7$ > MgV_2O_6 > $Mg_3V_2O_8$. From this result it was concluded that the active site included V-O-V bridge and short V=O bond simultaneously present in the V_2O_7 units of the α-$Mg_2V_2O_7$ phase [Sam et al. (1990)]. The short V=O bond is proposed to initiate the H abstraction step whereas the V-O-V bridge participates in the subsequent steps where water is formed. The V^{4+} ions generated by water desorption should be stabilized in association with oxygen vacancies leading to structural changes from V_2O_7 units to two edge sharing square based VO_3 units [Sam et al. (1990)]. This proposal is supported by the easier reducibility of the corresponding pyrovanadate phase [Gao et al. (1994a), Guerrero-Ruiz et al. (1992)]. Due to the different reactivity orders obtained, Kung et al. (1992) proposed the bridged oxygen atoms as selective sites for propylene and the terminal vanadyl species as responsible for total oxidation.

It could be noted that in the case of supported vanadium oxides the obtained reactivity results allowed Corma et al. [Corma et al. (1993b, 1993c] to conclude that V-O bonds with vanadium in tetrahedral or octahedral coordination are responsible for selective oxidation to propylene whereas the presence of V-O bond near a V=O bond leads to more oxygenate product amounts.

3.1.2.2 Surface reducibility and basicity

A general agreement is that the reducibility of the catalyst plays an important role in the reaction course on the activation of propane [Gao et al. 1994a), Guerrero-Ruiz et al. (1992), Owen et al. 1990), Sam et al. (1990)]. In V-Mg-O catalysts, where one V atom is replaced by one Mg atom , the involved lattice V-O-M oxygen atom is
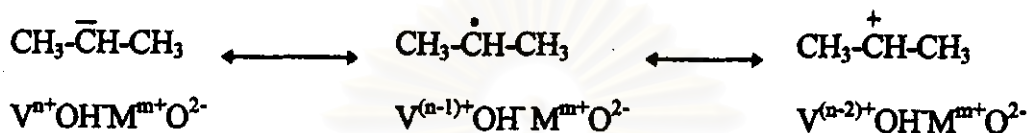
less mobile and thus the catalyst surface is less reducible : these catalysts led to dominant propylene selectivity [Corma et al. (1993b), Sam et al. (1990)]. The basic catalyst surface has also been claimed [Bhattacharyya et al. (1992), Corma et al. (1993c), Owen et al. (1992)] to increase the alkene selectivity during the ODH of alkanes. Thus, on supported vanadium or molybdenum oxides, it was shown that incorporating alkaline metals decreased both the conversion of propane and the yields of products but increased the selectivity of propylene at the expense of the selectivity of the CO_x [Grabowski et al. (1995)]. The reason should be that basic surfaces facilitate the desorption of alkenes, more basic compounds than the corresponding alkanes, thus preventing them from further oxidation to carbon oxides. It could be the case of the V-Mg-O catalysts where the magnesia phase plays the role of basic centers during the propane partial oxidation to propylene [Chaar et al. (1987), Guerrero-Ruiz et al. (1992), Kung et al, (1992), Nguyen et al. (1991), Sam et al. (1990)].

However, the effect of the acid-base properties on selective oxidation of hydrocarbons is more complex since it should depend on the nature of the catalyst (and therefore on its oxidizing properties) and even, on the nature of the hydrocarbon molecules [Chaar et al. (1987), Concepcion et al. 1994)]. In addition, in the case of the propane molecule, the selective oxidation to propylene probably also needs BrØn sted acid sites as shown recently by Moro-oka and Ueda [Yoon et al. (1994)] for the MoMgO catalysts. The different steps of the routes to propylene and CO_x, respectively, are probably differently sensitive to the acid-base nature and strength of the used catalyst.

3.1.2.3 Reaction mechanisms and reaction intermediates

Concerning the reaction mechanism, a general agreement in literature is that the rate determining step of the reaction is the breaking of the first C-H bond, leading to a propyl species [Patel et al. (1988), Sulikowski et al. (1994)]. Moreover, Michalakos et al. (1993) suggested the existence of a selectivity determining step which was related to of propylene produced should also be considered as selectivity

determining [Michalakos et al. (1993)]. The selective route to propylene should then be the breaking of the second C-H bond of the propyl species whereas the oxygenates (organic products or CO_x) route should involve the insertion of the surface oxygen atom in the alkyl intermediate [Michalakos et al. (1993)].

In the mean time, the C-H bond breaking is believed to be homolytic and the propyl species thus produced should be a propyl radical [Burch et al. (1991), Michalokos et al. (1993), Nguyen et al. (1990)]. This radical species is then able to give propylene either after desorbing in the gas phase and reacting with gaseous oxygen or by a surface reaction [Chang et al. (1993), Michalakos et al. (1993), Morales et al. (1989)]. Then the reaction course depends both on the reaction temperature and the nature of the catalyst [Burch et al. (1991), Nguyen et al. (1990)]. High temperature favors the alkyl desorption route [Burch et al. (1991), Nguyen et al. (1990)] whereas low reaction temperatures and reducible catalysts promote surface reaction route [Burch et al. (1991), Corma et al. (1993c)]. Thus, propane oxidation over V containing catalysts is considered to be initiated in the gas phase and completed on the catalyst surface. Figure 3.3 resumes these assumptions.

$$V^{n+}O^{2-}V^{n+}O^{2-}$$
$$\downarrow C_3H_8$$
$$CH_3 - CH - CH_3 \qquad\qquad CH_3\text{-}CH\text{-}CH_3$$
$$V^{(n-1)+}OH^-V^{n+}O^{2-} \longrightarrow V^{(n-2)+}O^-V^{n+}OH^-$$
$$-C_3H_6 \qquad \downarrow -H_2O$$
$$+ 1/2\ O_2 \quad CH2{=}CH\text{-}CH_3 \qquad [O] \qquad \text{Organic products}$$
$$V^{(n-2)+}\square V^{n+}O^{2-} \longrightarrow +CO_x$$

Figure 3.3 Mechanism of the oxydehydrogenation reaction of propane to propylene on V-Mg-O catalysts. [Bettahar et al. (1996)]

It must be mentioned that heterolytic splitting of the C-H bond was also proposed in the ODH of propane. This breaking should lead either to the formation a

cation by hydride abstraction [Matsuura et al. (1994)] or to the formation of a carbanion by proton abstraction [Sokolovskii (1990), Wang et al. (1994)]. The former process should be expected to occur on acidic catalysts whereas the latter supposes rather basic catalysts. In fact, it should be considered that redox equilibria coexist at the catalyst surface whatever the initial mode (homolytic or heterolytic) of activation as shown below :

$$CH_3\text{-}\overline{C}H\text{-}CH_3 \quad \longleftrightarrow \quad CH_3\text{-}\overset{\bullet}{C}H\text{-}CH_3 \quad \longleftrightarrow \quad CH_3\text{-}\overset{+}{C}H\text{-}CH_3$$

$$V^{n+}OH^-M^{m+}O^{2-} \qquad V^{(n-1)+}OH^-M^{m+}O^{2-} \qquad V^{(n-2)+}OH^-M^{m+}O^{2-}$$

(V is a surface vanadium atom and M a surface metallic promoter or a second surface vanadium atom). The position of these equilibria depends on the redox and acid-base properties of the catalyst and on the reactive atmosphere.

Other mechanistic schemes can be envisaged. A concerted mechanism (figure 3.4) should be thus considered : the transition state in this case is probably of lower energy since it involves simultaneous breaking and forming of chemical bonds. In this mechanism the acid- base and redox properties of the catalyst play a role as a whole in only one step.

Another mode of activation of propane should be its adsorption as alkoxy species, this is, the occurrence of the direct insertion of a lattice oxygen atom into a C-H bond (see also figure 3.4) :

$$C_3H_8 \quad \xrightarrow{[O]} \quad [C_3H_7OH] \quad \xrightarrow{H^+} \quad C_3H_6 + H_2O$$

The alkoxy species then decomposes to propylene. This decomposition needs the presence of Brønsted acid sites as can be deduced from the finding of Moro-oka and Ueda (1994) of the correlation between the propylene formation from propane and the number of the Brønsted acid sites in the case of the MoMgO catalysts. The alkoxy route here proposed is also supported by the in-situ FT-IR studies of Finnochio et al. (1996b) showing the formation of propyloxy surface species as intermediate to propylene during the oxidation of propane over CrMoO catalysts.

In conclusion for the ODH of propane to propylene, the most studied catalytic formulation V-Mg-O system consists of a vanadia phase which provides the oxidizing properties needed and a magnesia phase which provides the base properties decreasing the propylene consecutive oxidation. It is proposed that high propylene selectivity needs both V=O and V-O-V isolated sites and the overall process is probably initiated in the gas phase and completed on the catalyst surface.

A)

B)

Figure 3.4 Concerted mechanism in the oxidative dehydrogenation of propane on vanadium based catalysts. [Bettahar et al. (1996)]

3.2 Nature of Surface Oxide Species [Kemball (1977)]

It is theoretically possible for many different forms of oxygen to exist on a reacting catalyst surface and to participate in the reaction [Kryrov (1973)]. Since the detection of a particular species on a surface does not necessarily imply that it is significant in catalysis, the identification of the actual reactive oxygen species is of major importance in uncovering reaction mechanism. As before, results will be discussed as though a single phase is present although this is rarely so and each phase may have its own chemistry.

a. Lattice Oxygen

In the case of BiMo, much of the evidence for the participation of lattice oxygen depends on $^{18}O_2$ tracer studies. The original experiments [Blanchard et al. (1973), Wragg et al. (1973, 1996)] showed clearly that in the oxidation of propene with $^{18}O_2$, the acrolein and CO_2 produced contain largely ^{16}O which must have originated from the catalyst lattice and this has been confirmed in subsequent work [Gelbshtein et sl. (1974)Pendleton et al. (1976), Sancier et al. (1975)]. From the very low ^{18}O content of the products, it was also clear that oxygen introduced to the catalyst from dioxygen equilibrated rapidly with the bulk on the time scale of propene oxidation [Gelbshtein et al. (1974), Pendleton et al. (1976)Sancier et al. (1975)]. These facts are usually interpreted by a direct participation of surface lattice oxygen mobility. A former paper [Otsubo et al. (1975)], however, has 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 implies either direct involvement of water in the reaction, which was unlikely [Watling et al. (1996)], or rapid oxygen exchange between water and both the reaction products and the BiMo bulk. Available experimental results [Moro-oka et al. (1972)] showed, however, that these reactions were too slow for this explanation to be correct and the direct incorporation of lattice oxygen can therefore be considered as established.

Experiments on the propene-$^{18}O_2$ reaction over BiMo, carried out at lower temperatures than usual, have 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 [Sancier et al. (1975)]. Detailed interpretation was in terms of a rapid reversible dissociate 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 are, 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 [Sancier et al. (1975)] and that the postulate [Matsuura et al. (1994)] that different faces were involved was unnecessary. Russian workers [Gelbshtein et al. (1974)], also using $^{18}O_2$, claim 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 will be required before this can 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 can be made as to the oxygen source in the two products [Keulks et al. (1976)]. 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 calcine a bulk-surface concentration gradient.

An interesting approach [Matsuura et al. (1994)], which may reveal much about the processes occurring both at the surface and in the bulk in BiMo catalysts, arises from the observation that γ-Bi_2MoO_6, produced from a solid state reaction between $Bi_2^{18}O_3$ and $Mo_{16}O_3$ at 550°C, differs 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 in ^{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 occurs only on reduction.

b. Other Forms of Oxygen.

Many forms of oxygen including the excited singlet state of dioxygen [Kryrov (1973), Schulz et al. (1975)], have been proposed as reactive species. Other suggestions include the activation of dioxygen invariably leading to total combustion, that O_2 was a selective oxidant while O^- was unselective [Kryrov (1973)] and that O^-, formed from surface lattice oxygen by electron transfer, was the active species giving selective chemistry [Kazanskii (1973)]. These suggestions were clearly incompatible and emphasize the impossibility of assigning selectivity to a particular reactive species out of its context in the total reaction path leading to products [Kemball (1977)].