

## CHAPTER II

### LITERATURE REVIEW

Oxidative dehydrogenation (ODH), a kind of exothermic reaction, is an oxidation of alkane with oxygen to convert alkane into unsaturated hydrocarbon (alkene or diene) and water, which are the main products. To compare with dehydrogenation reaction, oxidative dehydrogenation can overcome the problem of deactivation of catalysts due to the coke formation covered on the surface of catalyst. Furthermore, oxidative dehydrogenation has no equilibrium limitation on thermodynamic at low temperature. Consequently, it can save energy consumption and cost needed in the conventional process. However, the oxidative dehydrogenation still has a problem about the control of the consecutive reactions of alkene up to carbonoxides. Besides,  $H_2$  gas which is an important product using in the further reaction is also lost. Thus, there are several researchers trying to search the proper catalysts for oxidative dehydrogenation to provide alkene as main product. It was found that for the oxidative dehydrogenation, V-Mg-O catalyst is a suitable catalyst in which high alkene selectivity is obtained. However, the attempt to study the structure and the nature of V-Mg-O catalyst for improving catalytic performance is still being undertaken.

#### 2.1 Reviewed literature

There are many papers that emphasize V-Mg-O catalyst in oxidative dehydrogenation as follows.

Chaar et al. (1987) suggested that the V-Mg-O catalysts are quite selective for the oxidative dehydrogenation of butane to butenes and butadiene. The active and selective component of V-Mg-O catalyst was the compound magnesium orthovanadate,  $Mg_3(VO_4)_2$ . No oxygenate product was formed over V-Mg-O catalyst. They could not observe characteristic V=O stretching in the V-Mg-O. Thus they suggested that the vanadium oxide in V-Mg-O did not form a layer structure of  $V_2O_5$  on the MgO substrate. They also reported that the selectivity for the oxidative

dehydrogenation increased with decreasing oxygen-to-butane ratio, decreasing conversion and decreasing temperature. A selectivity of up to 60 % was obtained. The high selectivity for the oxidative dehydrogenation instead of oxygenate production was attributed to two factors: the basic surface which facilitated desorption of basic butenes and butadiene, and the absence of V=O which lowered the oxidation activity of the surface.

Chaar et al. (1988) have studied the selective oxidative dehydrogenation of propane over V-Mg-O catalysts. They found that the active and selective catalysts for the oxidative dehydrogenation were vanadium-magnesium oxides. A selectivity of up to 65% was obtained at 10% conversion, but decreased with increasing conversion. The major products were propene, CO and CO<sub>2</sub>. No oxygenates were detected. The reaction rate was found to be  $0.6 \pm 0.15$  order in propane and zeroth order in oxygen. For comparison, the rate for butane oxidation dehydrogenation was  $0.85 \pm 0.15$  in butane and zeroth order in oxygen. Both reactions were believed to proceed primarily with the breaking of a methylene C-H bond to form an adsorbed alkyl radical species.

Qiu et al. (1989) reported the effect of Sb<sub>2</sub>O<sub>4</sub>, BiPO<sub>4</sub> or SnO<sub>2</sub> on the catalytic properties of ZnFe<sub>2</sub>O<sub>4</sub> in the oxidative dehydrogenation of butene to butadiene. ZnFe<sub>2</sub>O<sub>4</sub> was found to be a moderately active and selective catalyst but could be deactivated at high temperature (>380°C), probably due to segregation of the phase. The properties of ZnFe<sub>2</sub>O<sub>4</sub> could be modified by mechanically mixing Sb<sub>2</sub>O<sub>4</sub>, BiPO<sub>4</sub> and SnO<sub>2</sub> to ZnFe<sub>2</sub>O<sub>4</sub>. It was observed that for pure ZnFe<sub>2</sub>O<sub>4</sub>, an increase in reaction temperature would favor the activity of lattice oxygen. After a certain temperature had been reached, however, the lattice oxygen was so active that its disappearance to oxidation products was much more rapid than the reoxidation rate of the catalyst by gaseous oxygen, resulting in a reduction of the catalyst. The role of Sb<sub>2</sub>O<sub>4</sub>, BiPO<sub>4</sub> and SnO<sub>2</sub> was to transform oxygen species adsorbed on these compounds (which were mainly electrophilic species : O<sub>2</sub><sup>-</sup>, O<sup>-</sup>) to nucleophilic species (O<sup>2-</sup>) which were more suitable than the electrophilic one for the reoxidation of the catalyst.

Sam et al. (1990) studied the oxidative dehydrogenation of propane at 500-550 °C over V-Mg-O catalysts and over the reference phases orthovanadate, pyrovanadate, and metavanadate of magnesium. The active phase for this reaction of propane to propene was magnesium pyrovanadate,  $Mg_2V_2O_7$ . The unique feature of  $\alpha$ - $Mg_2V_2O_7$  was the presence of the  $V_1=O$  short bond which could initiate a H abstraction. The bridging O of the  $V_1-O-V_{11}$  bond could participate in the oxidative dehydrogenation mechanism for the formation of water. All these steps could take place simultaneously giving rise to a dynamic model in which the local structure should change from the  $V_2O_7^{4-}$  unit to two square-based  $MgVO_3$  units.

The oxidative dehydrogenation of ethane has been investigated on a range of mixed Mo-V-Nb oxide catalysts by Burch and Swarnakar (1991). The maximum activity of Mo-V oxide catalysts was at 70 wt.% Mo. Addition of niobium oxide to this mixed oxide enhanced both activity and selectivity. They found that the orders of reaction was close to first order in ethane pressure but almost independent of oxygen pressure, except at higher temperatures and lower oxygen pressures. Besides, they also found a correlation between the ease of reduction of the catalyst and the activity and selectivity, with the most easily reduced catalyst being the most active and selective for the formation of ethene.

Kim et al. (1991) studied the catalytic properties of multicomponent metal oxide catalysts in the oxidation of propane to acrolein. They noted that a catalyst containing no molybdenum,  $BiVO_4$ , showed very low selectivity to acrolein, but propene was formed in large amounts on this catalyst. With increasing concentration of Mo, the selectivity to acrolein increased markedly. For bismuth vanadomolybdate catalysts, the doping of small amount of K, Ru and Tl resulted in a rather large decrease in catalytic activity in the formation of acrolein. These catalysts gave propene with high selectivity. Improvements in the activity in the formation of acrolein were obtained by the addition of Li, Na and Ag.

They also suggested that, first, propyl radical might form from propane in the gas phase at high temperature. If the propyl radical formed in the pre-catalyst zone

was not directed to undesirable reactions, such as C-C bond fission and quenching by the action of oxide catalysts, the reaction of the propyl radical may go forward to give propene. After propene was formed in the gas phase, it could be further catalytically converted to acrolein over the metal oxides. If the catalyst showed a poor ability to oxidized propene to acrolein, the propene was a major product.

The oxidative dehydrogenation of cyclohexane was studied at 440 and 484°C over  $\text{NdVO}_4$ ,  $\text{Mg}_3(\text{VO}_4)_2$ , and a mixed V-Mg-O catalyst by Kung and Kung (1991). Cyclohexane was the major initial product which was further dehydrogenated to benzene. Thus, benzene, carbon oxides, and a trace of cyclohexadiene were also observed. The catalytic behavior of the mixed V-Mg-O catalyst in this reaction was very similar to its behavior in the oxidation of butane. However, the behavior of  $\text{NdVO}_4$  was quite different from that of V-Mg-O catalysts in number of aspects. First, its benzene yield reached a steady state much faster than that on the V-Mg-O catalysts. Second, it showed a much higher selectivity for benzene and carbon oxides, and benzene was a substantial initial product. Third, the reaction was nearly zeroth order in  $\text{O}_2$  and first order in cyclohexane on V-Mg-O catalyst at 440°C over the range of 3.7 to 7.5%  $\text{O}_2$  or cyclohexane, but it was 0.63 order in  $\text{O}_2$  and 0.82 order in cyclohexane.

Mazzocchia et al. (1991) have studied the  $\alpha$ - and  $\beta$ - phases of  $\text{NiMoO}_4$  with different techniques (X-ray diffraction, electrical conductivity, IR spectroscopy) in order to tentatively rationalize the different catalytic activities observed in the oxidative dehydrogenation of propane to propene. The  $\alpha$ -phase was converted completely to  $\beta$ -phase at 700°C. From the presence of anionic vacancies, they proposed that propene was formed by the reaction of propane with surface  $\text{O}^{2-}$  anions. Moreover, the  $\beta$ -phase was almost twice more selective in propene formation than the  $\alpha$ -phase due to the different oxygen environments on the active catalytic site.

Nguyen and Kung (1991) have investigated the nature of the desorbed species that caused surface-initiated gas-phase reactions on a V-Mg-O catalyst during the oxidation of propane. They used the model of reactions in the postcatalytic reactor

(reactor volume downstream of the catalyst) with elementary reactions of the oxidative pyrolysis of propane to explain these reactions. In the catalytic oxidation of propane, propyl radicals were found to be the likely species that desorbed from the catalyst surface, although the desorption of OH radicals could not be excluded. The desorption of  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$  radicals was found to be unlikely. The rate of propyl radicals desorbing from a V-Mg-O catalyst was estimated to be 23% of the reaction rate of propane on the catalyst surface at 570 °C and 5% at 556 °C

Smits et al. (1991) found that niobium pentoxide, calcined at temperatures between 500 and 700 °C, exhibited a high selectivity for the oxidative dehydrogenation of propane. At temperature above about 480 °C, the conversion increased steadily while the selectivity dropped with increasing temperature. They noted that increasing the partial pressure of oxygen gave a significant increase in the conversion without decreasing the selectivity.

Armendariz et al. (1992) studied the oxidative dehydrogenation of n-butane on iron-zinc oxide catalysts. They found that the presence of a zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ ) phase with a spinel structure yielded high selectivity to butenes. This phenomenon was explained by the loss of mobility of the lattice oxygen as a consequence of crystallographic structure change, from corundum in  $\alpha\text{-Fe}_2\text{O}_3$  to spinel in  $\text{ZnFe}_2\text{O}_4$ . When ZnO was present, the n-butane oxidative dehydrogenation reaction was observed to proceed to butadiene formation.

Bhattacharyya et al. (1992) have investigated the effects of different promoters ( $\text{Cr}_2\text{O}_3$ ,  $\text{MoO}_3$  and  $\text{TiO}_2$ ) added to V-Mg-O catalyst for the selective oxidation of n-butane to butadiene. The detailed experimental investigation of these catalysts with respect to variables :- the reaction temperature, contact time and n-butane feed concentration indicated the order of activity as follows : 24 V-Mg-O, $\text{Cr}_2\text{O}_3$  > 24 V-Mg-O, $\text{MoO}_3$  > 24 V-Mg-O > 24 V-Mg-O,  $\text{TiO}_2$  and the order of selectivity was 24 V-Mg-O,  $\text{TiO}_2$  > 24 V-Mg-O, $\text{Cr}_2\text{O}_3$  > 24 V-Mg-O > 24 V-Mg-O, $\text{MoO}_3$ . It was likely that butenes and butadiene, being basic in nature, interacted more strongly with acidic catalysts than with relatively basic catalysts. Besides, they proposed that the

catalyst 24 V-Mg-O incorporating both  $\text{Cr}_2\text{O}_3$  and  $\text{TiO}_2$  provided not only higher activity but also better selectivity. A maximum yield of 35.6 mol.% was obtained with this catalyst. They suggested a very low chance of the operation of  $\text{V}^{4+} \leftrightarrow \text{V}^{3+}$  redox cycle for this oxidation reaction.

Cherrak et al. (1992) have investigated the oxidative coupling of methane (OCM) and the oxidative dehydrogenation of propane (ODHP) on new mixed Bi-V oxides having a  $\gamma\text{-Bi}_2\text{MoO}_6$  - like structure. They found that solid ionic conductors had an OCM activity which depended on the diffusivity of lattice oxygen. This diffusivity was possible at high temperature with  $\text{Bi}_4\text{V}_2\text{O}_{11}$  which had a layered structure similar to  $\gamma\text{-Bi}_2\text{MoO}_6$ , but also with  $\text{BiVO}_4$  which presented some similarities. The introduction of copper, iron and strontium (10 mol.% with respect to vanadium) improved the  $\text{C}_2$  selectivity. For ODHP, it needed a much lower reaction temperature. The propane yield increased with the temperature, the CO remained the dominant product as on  $\text{V}_2\text{O}_5/\text{TiO}_2$  or  $\text{V}_2\text{O}_5/\text{MgO}$  catalyst. This can be explained by the easy abstraction of hydrogen (the first step in ODHP mechanism) in an allylic position in alkene, owing to the stable  $\pi$  complex intermediate.

Hayakawa et al. (1992) tested the catalytic activity on a series of perovskite catalysts for the oxidative dehydrogenation of ethane. The composition of the investigated catalysts covered  $\text{CaTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ , with  $0 \leq x \leq 0.4$ ,  $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ , with  $0 \leq x \leq 1.0$ . They found that the catalyst containing more basic Sr metal showed higher selectivity to ethene than the catalysts containing less basic Ca.

The effect of potassium in the preparation of magnesium orthovanadate and pyrovanadate on the oxidative dehydrogenation of propane and butane was studied by Kung and colleagues (1992). The mixed oxides prepared by two different methods, with or without the use of potassium, were compared. For samples without potassium, magnesium orthovanadate was quite selective for the oxidative dehydrogenation of both propane and butane, whereas magnesium pyrovanadate was selective only for propane. However, the presence of residual potassium in the oxide lowered the selectivity, especially in the butane reaction. Moreover, they observed that the

presence of potassium increases the thermal stability of magnesium pyrovanadate against reaction with MgO to form magnesium orthovanadate.

Owen et al. (1992) reported their study on the effect of oxide structure and cation reduction potential of vanadates on the selective oxidative dehydrogenation of butane and propane. They supposed that the selectivity for oxidative dehydrogenation on these compounds could be correlated with the aqueous reduction potential of the cation in the compound : the more easily reducible the cation, the lower the selectivity. This correlation could be explained by the effect of the ease of removal of lattice oxygen on the selectivity. They also found that magnesium orthovanadate ( $\text{Mg}_3(\text{VO}_4)_2$ ) was a rather selective catalyst for butane oxidation than magnesium pyrovanadate ( $\text{Mg}_2\text{V}_2\text{O}_7$ ), but was as selective as magnesium pyrovanadate in propane oxidation. These results were interpreted by the different structures of the two magnesium vanadates. In magnesium orthovanadate, the isolated  $\text{VO}_4$  units resulted in a condition that the adsorbed molecule could only interact with one  $\text{VO}_4$  unit. In magnesium pyrovanadate, on the other hand, the  $\text{V}_2\text{O}_7$  units, which consisted of two corner-shared  $\text{VO}_4$  units, provided the opportunity for a surface species to react with two  $\text{VO}_4$  units simultaneously, provided that the size of the molecule was sufficiently large to do so. Propane interacted with only one  $\text{VO}_4$  unit and did not distinguish between orthovanadate and pyrovanadate. Butane was sufficiently large that its two end carbons could interact with the two  $\text{VO}_4$  units in the  $\text{V}_2\text{O}_7$  group. Thus, in the case of magnesium pyrovanadate, this interaction led to combustion of the molecule.

Peng and Barteau (1992) carried out acid-base reactions of three MgO surfaces of different structures (annealed MgO (100), ion-bombarded MgO(100) and MgO thin film). The adsorption of acid molecules was used to characterize the acid-base properties of MgO surfaces. They found that all the acids used in their study, including  $\text{HCOOH}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_2$ , underwent heterolytic dissociation on all the model surfaces to form the corresponding conjugate base anions, except that the dissociation of weaker acids on the MgO (100) surface required low temperature adsorption or surface modification by bombardment

In 1993, Castiglioni et al. suggested the oxidative dehydrogenation of propane in presence of rare earth vanadates such as CeVO<sub>4</sub>, PrVO<sub>4</sub>, NdVO<sub>4</sub>, TbVO<sub>4</sub>, CrVO<sub>4</sub> and YbVO<sub>4</sub>. They observed three main reactions involved :



They noted that the rare earth vanadates in which only the 3+ state was stable show a higher propene selectivity for a given conversion. The oxygen/propane ratio in the feed influenced the conversion and the selectivity. At low conversion.(10 %), the selectivity decreased slightly whereas the activity increased if O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> was passing from 0.5 to 2. In same conditions, at high conversion (30%) they observed a sharp decrease of the propene selectivity and an increase of the conversion whereas the olefin yield remains relatively stable. In the mechanistic study, the reduction of V<sup>5+</sup> to V<sup>4+</sup> was explained in accordance with the participation of the lattice oxygen in a Mars and Van Krevelen mechanism.

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

In 1993, vanadium aluminophosphate catalysts have been tested for the oxidative dehydrogenation of propane by Concepcion et al.(1993). They found that the catalyst containing V<sup>5+</sup> species with a tetrahedral coordination present in



vanadium aluminophosphate are also the more active and selective species in the selective oxidative dehydrogenation of propane. The higher the vanadium content in vanadium aluminophosphate catalysts the higher the activity is. In addition, the same yields of  $\text{CO}_2$  are observed on all vanadium aluminophosphate catalysts, while the higher the yield of propene the lower the yield of CO is.

Corma et al. (1993a) have studied the oxidative dehydrogenation of propane on sepiolite supported catalysts. They found that at low vanadium content, isolated tetrahedral species were formed and both activity and selectivity to propene increased with the vanadium content. At medium or high vanadium content the appearance of associated vanadium species could be observed and, while the activity still increased when total vanadium content was increased, the selectivity to propene remained constant.  $\text{MgV}_2\text{O}_5$  and  $\text{V}_2\text{O}_5$  crystallites which were suggested to be formed at vanadium in a tetrahedral position was less active than the vanadium in octahedral position, the yield to propene was higher.

In the same year, Corma et al. (1993c) interested in preparing of V-Mg-O catalysts by using MgO or magnesium oxalate and aqueous solutions of vanadyl-oxalate or ammonium metavanadate as vanadium sources. After calcination, large differences in the V/Mg surface atomic ratios were observed on the different catalysts, indicating differences in the V-Mg interaction, which were related to the preparation method of catalysts. By X-ray diffraction, IR, UV-VIS and X-ray photoelectron spectroscopic characterization of samples before and after the calcination step, different Mg- and V-compounds have been observed. Before the calcination step,  $\text{Mg}(\text{OH})_2$  and/or magnesium-oxalate, as well as  $\text{V}^{5+}$  and/or  $\text{V}^{4+}$  species, depending on vanadium sources and vanadium content, were observed. After the calcination step, the formation of magnesium vanadates depended only on the vanadium content of the catalysts.  $\text{Mg}_3\text{V}_2\text{O}_8$  formed at low vanadium content of the catalyst and  $\text{Mg}_3\text{V}_2\text{O}_8 + \alpha\text{-Mg}_2\text{V}_2\text{O}_7$  at high vanadium content.

In 1993, the catalytic oxidation of ethane, propane, 2-methylpropane, butane, pentane and cyclohexane has been studied over three vanadate catalysts ( $\text{Mg}_3\text{V}_2\text{O}_8$ -

MgO,  $\text{Mg}_2\text{V}_2\text{O}_7$  and  $(\text{VO})_2\text{P}_2\text{O}_7$  ) by Michalakos et al. These reactions produced a wide range of products ranging from alkenes, dienes, anhydrides, acids and carbon oxides. They classified the sets of products into two groups by using the average oxygen stoichiometry (AOS). First group in which dehydrogenation products were dominant and for which the initial AOS values were about two, and the second group in which oxygen - containing products are dominant and for which the initial AOS values were about four. In addition, they explained the selectivity patterns in terms of the formation of dehydrogenation products versus oxygen - containing products including carbon oxides by assuming that there existed a selectivity - determining step, which could be the reaction of the surface alkyl species or the adsorbed alkene before its desorption. The formation of oxygen-containing products would be facilitated if the surface alkyl or adsorbed alkene could interact with the vanadium ions in two adjacent  $\text{VO}_x$  units such that it could easily react with the reactive oxygen in the V-O-V bridge.

Okuhara et al. (1993) studied the structures and dehydrogenation activities of vanadium oxide overlayers on supports ( $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ ). On  $\text{MgO}$ , the vanadium was not in the form of  $\text{V}_2\text{O}_5$ . They reported that vanadium oxides reacted readily with the surface of  $\text{MgO}$  to form new phases such as  $\text{Mg}_3\text{V}_2\text{O}_8$  and  $\text{Mg}_2\text{V}_2\text{O}_7$ ,  $\text{Mg}_3\text{V}_2\text{O}_8$  consisted of V ions in tetrahedral sites (V-O) and Mg ions in octahedral sites, and  $\text{Mg}_2\text{V}_2\text{O}_7$  had  $\text{V}_2\text{O}_7$  groups (V=O, V-O). EXAFS spectra revealed that the structure of  $\text{V}_2\text{O}_5$  was very sensitive to the supports and the preparation method (impregnation or chemical vapor deposition, CVD). They indicated that the preparation by CVD led to be thin films which had high thermal stabilities and catalytic activities for dehydrogenation.

Concepcion et al. (1994) have studied the oxidative dehydrogenation of ethane on a magnesium vanadium aluminophosphate ( $\text{MgVAPO-5}$ ) catalyst which is prepared by hydrothermal synthesis. They noted that  $\text{AlPO}_4-5$  had a low activity and low selectivity for the ODH of ethane. The presence of  $\text{Mg}^{2+}$  ions in  $\text{MgAPO-5}$ , which increased the acidity of the catalyst, increased the selectivity to ethene although

the activity was not influenced. On the other hand, the presence of vanadium species in VAPO-5, which increased the redox character of the catalyst, increased both the activity and selectivity for the ODH of ethane. The presence of  $Mg^{2+}$  and  $V^{5+}$  species in the vanadium-magnesium aluminophosphate (MgVAPO-5) resulted in a more selective catalysts for the ethane ODH. The behavior of MgVAPO-5 could be attributed to the presence of acid sites ( $Mg^{2+}$  near to the redox sites ( $V^{5+}$ ) in the molecular sieve framework.

Ducarme and Martin (1994) have studied Ni/SiO<sub>2</sub> catalysts in the oxidative dehydrogenation of ethane. The products over this catalysts were ethylene, CO<sub>2</sub>, CH<sub>4</sub> and CO. At 450°C ethylene selectivity as high as 80 % are obtained and decreased with increasing temperature. They also found the effect of potassium adding to Ni/SiO<sub>2</sub> catalysts on this reaction. For K-Ni/SiO<sub>2</sub> catalysts, the selectivity to ethylene was small at 500°C, while it increased with increasing temperatures. This behavior was in contrast to that achieved by Ni/SiO<sub>2</sub> catalyst where the reverse situation occurred. They noted that K-Ni/SiO<sub>2</sub> and K/SiO<sub>2</sub> in contrast to Ni/SiO<sub>2</sub> did not produce any CO at temperature over 900 K. This could result from an inhibition by potassium compounds of the gas phase oxidation of hydrocarbons which led to CO.

Gao et al. (1994a) prepared and characterized three pure magnesium vanadate phases of MgV<sub>2</sub>O<sub>6</sub>,  $\alpha$ -Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Mg<sub>3</sub>V<sub>2</sub>O<sub>8</sub> for selective oxidation of propane to propene. These three phases were prepared by the citrate method with Mg/V atomic ratios equal to 1/2, 1/1, and 3/2. From characterization of these vanadate phases (using FT-IR, LRS, XRD and SEM techniques), they found that the particle size and morphology of the MgV<sub>2</sub>O<sub>6</sub> phase, which was a function of calcination temperature, appeared to have a strong effect on the infrared spectra. Furthermore, the catalytic properties of the three phases were examined in the oxidative dehydrogenation of propane. The propane selectivity followed the order :  $\alpha$ -Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub> > Mg<sub>3</sub>V<sub>2</sub>O<sub>8</sub> > MgV<sub>2</sub>O<sub>6</sub> which was consistent with their redox properties. They suggested that there was some correlation between the catalytic reaction mechanism and the redox cycle.

between  $V^{5+}$  and  $V^{4+}$ . The good redox behavior under reaction conditions might be favorable for the selective oxidation of propane.

In the same year, they have also investigated the effect of coexistence of magnesium vanadate phases in the selective oxidation of propane to propene (1994b). They found that among the three pure magnesium vanadate phases ( $Mg_2V_2O_7$ ,  $Mg_3V_2O_8$ ,  $MgV_2O_6$ ), the magnesium pyrovanadate ( $Mg_2V_2O_7$ ) was the most selective for propene, while magnesium metavanadate ( $MgV_2O_6$ ) was the worst one. However, the presence of more than one phase was found to be able to promote the selectivity to propene. They noted that the highest selectivity at a given conversion was observed on the biphasic catalysts. For example, the selectivity of the magnesium orthovanadate ( $Mg_3V_2O_8$ ) phase could be improved by the coexisting pyrovanadate phase or excess magnesium and magnesium oxide phases.

Lars and Andersson (1994) interested in the kinetic of the oxidative dehydrogenation of propane over vanadia supported on amorphous  $AlPO_4$ . Vanadium concentrations supported on  $AlPO_4$  were varied in the range of 0.2-15 wt.%. Main products at low conversion were propene and ethene, while carbonoxides dominated at high conversion. No oxygenates could be detected. At low vanadium concentrations, 0.2-2 wt.%, the selectivity for propene and ethene increased with reaction temperature, while at high vanadium concentrations, 6-15 wt.%, it decreased with increasing temperature. An increase in the propane partial pressure or a decrease in the oxygen partial pressure favors propene and ethene formation. The kinetic analysis of the partial pressure dependencies of propane oxidation showed that for each an expression like  $k'P/(1+KP)$ , where  $k'$  is rate constant and  $K$  is adsorption constant, was adequate. Both the propane and the oxygen adsorption constants varied with the vanadium concentration. In addition, they noted that the initial rate of oxidation of propane over the various catalysts was of first order with respect to both oxygen and propane at low partial pressures. At high partial pressures, however, a deviation from linearity was obtained and in some cases an almost zero-order dependence was obtained for oxygen.

Lindblad et al. (1994) characterized vanadia supported on amorphous  $\text{AlPO}_4$  and its properties for oxidative dehydrogenation of propane. At low vanadium concentrations,  $\leq 2$  wt.% V, formation of highly dispersed vanadyl species was observed. At 6 wt.% V, the amount of highly dispersed vanadyl species was lower and tetrahedral vanadium species and crystalline  $\text{V}_2\text{O}_5$  were formed. FT-IR results indicated that vanadium species had reacted with aluminium and phosphorus surface hydroxyl groups, forming Al-O bonded and P-O bonded species. They proposed that the best performance of catalysts was at 6 wt.% V which was suggested to be associated with the presence of tetrahedral vanadium species. A low selectivity at higher vanadium loading was suggested to be associated with more active and less selective sites on  $\text{V}_2\text{O}_5$ .

Oganowski et al. (1994) investigated the chemical, catalytic and spectroscopic properties of vanadate catalysts which was added by modifiers such as Cr(III), Mo (VI) and Co(II). They noted that the orthovanadate was both more active and more selective in the oxidative dehydrogenation of ethylbenzene. The modifier was added to suppress the origin of by-products. The combustion activity, very high for Co/MgO and Cr/MgO, decreased by 5-6 times due to Mo addition. The cracking and dealkylation was also lowered. Moreover, they proposed that the synergistic effect should be considered, being probably caused by the quantitative increase of the mixed valence  $\text{M}_1^{n+}\text{-O-M}_2^{m+}\text{-O}$  active centers. Also some additional mixed centers of the type V-O-Cr, Cr-O-Mo, Co-O-Mo and others were created, being responsible for the increased catalytic activity. The increase of the catalytic selectivity in Mo containing systems was probably caused by the change of the electronic structure of the respective active centers leading to the bond strength change of the active oxygen and/or adsorbed alkane molecule.

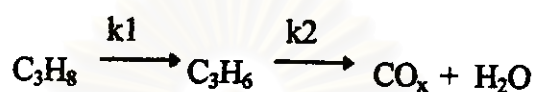
Wang et al. (1994) worked on catalytic and electrocatalytic oxidation of propane on V-Mg-O and V-Mg-O (Ag) catalysts. They compared two different methods for this reaction. The first method was the conventional heterogeneous catalytic reaction which obtained 79% selectivity at 10% conversion at reaction

temperature 440°C. No oxygenated or C<sub>2</sub> products were detected. The latter occurred under electrochemical pumping of oxygen (EOP) towards the catalyst. With oxygen presence in the feed gas, both conversion and selectivity were found to increase slightly as external current increased, indicating the effect of electrical current could be exhibited by an oxide catalyst. However, in the absence of oxygen in the feed gas, EOP could lead to an even higher selectivity : 84 and 86.9% respectively for a 24 V-Mg-O and a 24 V-Mg-O (Ag) catalyst. In the case of 24 V-Mg-O (Ag) catalyst, the role of Ag was found to be “non-chemical”; it simply increased the three-phase (gas/catalyst/Ag electrode) interfacial area. They noted that for both the catalytic and the electrocatalytic process, a surface oxygen ion (or vacancy) was suggested to be involved whereas the rate determining step involved heterolytic splitting of the C<sub>3</sub>H<sub>8</sub> molecule leading to the formation of a surface bonded C<sub>3</sub>H<sub>7</sub> ion and a surface hydroxyl ion. The higher selectivity to C<sub>3</sub>H<sub>6</sub> in the case of EOP was attributed to the relatively weaker surface bond between C<sub>3</sub>H<sub>7</sub> and the vanadium ion and thereby less vulnerable towards deep oxidation.

Yoon et al. (1994) found that cobalt molybdates showed high catalytic activities for the oxidative dehydrogenation of propane to propylene. Composition of the catalyst strongly affects surface acidic properties, resulting in a drastic activity change. Co<sub>0.95</sub>MoO<sub>4</sub> calcined at 550 °C showed the highest catalytic performance, giving 60 % selectivity to propylene at 19 % conversion of propane.

Zhang et al. (1994) investigated the catalysts based on rare earth complexes such as CeO<sub>2</sub>/2 CeF<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>/4 CeF<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>/4 CeF<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>/4 CeF<sub>3</sub> in the oxidative dehydrogenation of propane. These catalysts were active for the oxidative dehydrogenation of propane with very high selectivity to propane. At 500 °C and 6000 h<sup>-1</sup>, using CeO<sub>2</sub>/2 CeF<sub>3</sub> as the catalyst, the conversion of propane was 41.3%, selectivity to propane reached 81.1%, propene yield was 33.5%. XRD results indicated that F<sup>-</sup> and O<sup>-</sup> were exchanged in the lattices. Raman spectra showed that the O<sub>2</sub><sup>-</sup> might be the active oxygen species in propane oxidative dehydrogenation

In 1995, the catalytic oxidative dehydrogenation of propane and work function measurements in similar conditions have been investigated on  $V_2O_5/TiO_2$  catalyst by Boisdron et al. A good correlation obtained between the work function results and the catalytic tests, showed that the reactivity of propene was much higher than that of propane and explaining the yield limitation often observed in propane oxidation in agreement with a consecutive reaction mechanism



The value of  $K$  ( $K=k_1/k_2$ ), which depends on the type of catalyst was used to evaluate the selectivity to propane and for classification of oxidative dehydrogenation catalysts. They noted that the rate-determining step of propane oxidative dehydrogenation as well as of propene oxidation could be attributed to the attack of the oxidized site by the hydrocarbon. In addition, the work function measurements have shown that propane reacts with the  $O^{2-}$  species of the solid and that propene reacted with the  $O^-$  species; however, one could not eliminate the possibility that under catalytic conditions propene can also react with  $O^{2-}$  species.

Caldararu et al. (1995) obtained information on the peculiarities of propene interaction with the surface of polycrystalline tin dioxide by observing changes in electrical conductance. They had observed that the values of conductances increased after contact with propene, and related this phenomenon to the presence of some adsorbed species, which could be removed only on heating in air flow ; static annealing in air did not restore the initial surface conductivity. They suggested that the strong adsorption of propene was facilitated by the low mobility of the bulk lattice oxygen of tin oxide which in turn determined the surface proton mobility coupled with the ability of this material to catalyzed dehydrogenation reaction.

Abello et al. (1996) have studied the oxidative dehydrogenation of propane to propene over molybdenum supported on  $MgO-\gamma-Al_2O_3$ . They observed that the oxidation of propene to carbonoxides reduced the dehydrogenation selectivity. The

characterization results indicated the incorporation of Mo over the magnesia-alumina support led to the formation of large and very stable  $\text{MgMoO}_4$  particles. Furthermore, the composite support was not fully covered for a molybdate layer and there was a small amount of  $\text{MoO}_3$  on the  $\text{MgMoO}_4$  particles. They proposed that  $\text{Mo}^{5+}$  ions were the active sites for the oxidative dehydrogenation of propane. This reduced active form was present on the surface as a small fraction of the total  $\text{Mo}^{6+}$ , and it is generated by propane reduction of the surface.

Au et al. (1996) have presented the preparation and characterization of rare earth orthovanadates for propane oxidative dehydrogenation. High purity rare earth orthovanadates,  $\text{YVO}_4$ ,  $\text{LaVO}_4$ ,  $\text{CeVO}_4$ ,  $\text{NdVO}_4$ ,  $\text{SmVO}_4$  and  $\text{EuVO}_4$ , were prepared by the citrate method and characterized by XRD, FT-IR, LRS and TPR techniques. The selectivity of propene over  $\text{EuVO}_4$ ,  $\text{SmVO}_4$ ,  $\text{YVO}_4$  and  $\text{LaVO}_4$  was higher than that over  $\text{NdVO}_4$  and  $\text{CeVO}_4$ , indicating that the easier the orthovanadates could be reduced, the lower the selectivity. The correlation between the reducibility and the selectivity of the catalysts implied that the  $\text{V}^{4+}/\text{V}^{3+}$  couple might involve in the dehydrogenation process.

Cadus et al. (1996) studied the oxidative dehydrogenation of propane to propene over Mg-Mo-O catalysts. They proposed that the active site would be a coordinately unsaturated form of  $\text{Mo}^{5+}$  which generated on the surface by propane reduction. Besides, the slight excess of  $\text{MoO}_3$  which was necessary for the catalyst to become an active one for the oxidative dehydrogenation of propane probably contributed to the formation of  $\text{Mo}^{5+}$ .

Carrazan et al. (1996) have investigated the catalytic synergy in the oxidative dehydrogenation of propane over V-Mg-O catalysts. They observed synergetic effects in magnesium orthovanadate and magnesium pyrovanadate when  $\alpha\text{-Sb}_2\text{O}_4$  presented in the system. The principal effect was an increase in the selectivity with a decrease in propane conversion. In magnesium pyrovanadate with  $\alpha\text{-Sb}_2\text{O}_4$  system, propane conversion increased strongly with a moderate increase in propene yield. They noted that no formation of a new phase or contamination in the presence of  $\alpha\text{-Sb}_2\text{O}_4$  took



place when magnesium orthovanadate was used. This result was contrast to magnesium pyrovanadate with  $\alpha$ - $\text{Sb}_2\text{O}_4$  system. There was a new phase,  $\text{MgSb}_2\text{O}_6$ , formed during the catalytic test. It seemed that  $\text{MgSb}_2\text{O}_6$  was responsible for the high increase in propane conversion, that increase corresponded mainly to complete oxidation. Furthermore, they explained synergetic effects by using remote control mechanism. In catalysts containing magnesium orthovanadate with  $\alpha$ - $\text{Sb}_2\text{O}_4$  system, the rate of spill-over oxygen produced by  $\alpha$ - $\text{Sb}_2\text{O}_4$  (donor) would be that of inhibiting the nonselective sites. The same mechanism explained the synergetic effects found in the mixtures of magnesium orthovanadate and magnesium pyrovanadate. Both phases probably had a dual role, donor and acceptor.

Finocchio et al. (1996a) studied the interaction of n-butane, 1-butene, 1,3-butadiene and of  $\text{C}_4$  oxygenates on the surface of oxidized magnesium chromite and magnesium vanadate catalysts by FTIR. They found that the interaction of magnesium vanadates with butane did not give detectable adsorbed species. Because above 350 °C, the resulting partially oxidized surface species desorbed or further transformed very fast whereas the interaction of 1-butane and of butadiene over this surface was extremely weak. Thus, it did not give rise to any detectable reaction. They noted that the polar molecules like alcohol reacted with the surface of magnesium vanadates, giving rise to dissociate adsorption. The behavior observed upon 2-butanol adsorption suggested that the main way of its transformation was its dehydration to n-butene. The key step determining selectivity was suggested to be the evolution of the alkoxides that over the vanadates could in part decompose to the olefin.

Ji et al. (1996) have investigated the oxidative dehydrogenation of ethane over alkali-doped La/CaO catalysts at temperatures of 550 - 650°C. The addition of alkali metals (Li, Na, and K) to La/CaO increases the ethylene selectivity. For Li- and Na-doped La/CaO catalysts the ethane conversion remained almost unaltered. The increase of ethylene selectivity over the two catalysts was believed to be mainly produced by coordinate action of lithium and lanthanum or sodium and lanthanum. However, the Li- doped La/CaO catalyst exhibited stronger coordinate action than the

Na-doped La/CaO catalyst. Catalyst characterization revealed that the strong coordinate action of components in Li/La/CaO was probably related to the chemical and crystal structure of the catalyst which was favorable for the oxidative dehydrogenation of ethane. Their results also showed that addition of potassium, being a poor dopant, to La/CaO resulted in a sharp decrease in catalytic activity.

Korili et al. (1996) studied the oxidative dehydrogenation of n-pentane on two pure magnesium vanadate phases,  $Mg_2V_2O_7$  and  $Mg_3V_2O_8$ , prepared by the citrate method. When compared under the same reaction conditions, both phases exhibited similar overall pentane conversions, but the selectivity to dehydrogenation products was much better in the case of the orthovanadate phase,  $Mg_3V_2O_8$ . Furthermore, addition of  $Sb_2O_4$  could improve the selectivity to dehydrogenation products only in the case of the orthovanadate phase. Conversion per unit mass of the active phase was slightly improved by the presence of antimony oxide in all cases.

Oganowski et al. (1996) found that the activity of the V-Mg-O oxide system in the oxidative dehydrogenation of ethylbenzene to styrene can be promoted by Cr, Co and Mo doping. They noted that chromium or cobalt doping increased the activity of the V-Mg-O catalyst and molybdenum doping greatly increased the catalytic selectivity. They explained the activity increase as a result of the formation of additional active centers on the interphase boundaries. The selectivity increased with the increase in the number of oxygen atoms directly engaged in the conversion of ethylbenzene to styrene. The quaternary oxide system V-Cr-Co-Mg-O appeared to be the best catalyst.

Pantazidis et al. (1996a) have investigated the role of acid-base, redox and structural properties of V-Mg-O catalysts in the oxidative dehydrogenation of propane. They used electrical conductivity measurements, microcalorimetry, TPO and DRIFT spectroscopy to study over V-Mg-O catalysts in a wide range of V contents (5 - 45 wt.%). They noted that the most active and selective catalysts combined both a strong Lewis acidity and a mild basicity. The actual Lewis centers were related to anionic vacancies being electron acceptors, while the required surface basicity would

support the activation steps such as H abstractions and also propene desorption. In addition, they summarized that the highest propene yields were observed for V-Mg-O catalysts with low-to-medium V contents (around 14 wt.%). This composition would ensure the fast redox turn-over involved in the propane-to-propene process.

In 1996, Parmaliana et al. investigated the oxidative dehydrogenation of propane to propylene on commercial base  $\text{SiO}_2$  and medium loaded  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$  catalysts at 450 - 525 °C. They noted that the addition of  $\text{MoO}_3$  and  $\text{V}_2\text{O}_5$  to the  $\text{SiO}_2$  supports implied a higher selectivity to propylene and correspondingly a lower production of  $\text{CO}_x$ , a slight cracking activity and a significant decrease in the amount of oxygenates. Besides, the direct relationship between the density of reduced sites, evaluated in steady-state conditions by  $\text{O}_2$  chemisorption, and the reaction rate proved the occurrence of a "concerted reaction" mechanism involving the activation of gas-phase  $\text{O}_2$  on the reduced sites of the catalyst surface.

The influence of  $\text{V}_2\text{O}_5$  loading on the catalytic behavior of  $\text{V}_2\text{O}_5/\text{SiO}_2$  catalysts in the oxidative dehydrogenation of propane to propylene has been investigated by Puglisi et al. (1996). They found that the increase in the  $\text{V}_2\text{O}_5$  loading implied a lowering in the selectivity to propylene along with a corresponding increase in  $\text{CO}_x$  selectivity. On low loaded  $\text{V}_2\text{O}_5/\text{SiO}_2$  catalysts, the reaction effectively proceed with the participation of activated oxygen species (surface mechanism), while on highly loaded systems the reaction mainly occurred via the less effective redox mechanism involving a direct participation of lattice oxygen ions.

In situ electrical characterization of three magnesium vanadate reference phase ( $\text{MgV}_2\text{O}_6$ ,  $\text{Mg}_2\text{V}_2\text{O}_7$ ,  $\text{Mg}_3\text{V}_2\text{O}_8$ ) used in oxidative dehydrogenation of propane to propene has been examined by Soenen et al. (1996). From intrinsic semiconductors in oxygen at reaction temperature 520°C, these solids became n-type semiconductors under propane at the same temperature. This clearly demonstrated that the active oxygen species were surface lattice anions whose departure from the surface (when oxygenates were evolved) created anionic vacancies subsequently filled by gaseous oxygen.

The comparison of the electrical behavior of the three V-Mg-O phases indicated that  $\text{Mg}_2\text{V}_2\text{O}_7$  was the most reactive phase in in situ conditions with the most numerous labile surface anions. In addition, they also found that the higher value of the oxidation rate of this solid as compared with its reduction rate showed a surface state close to oxygen stoichiometry and allowed prediction of a zero kinetic order which has already confirmed. No ionosorbed oxygen species such as  $\text{O}_2^-$ ,  $\text{O}^-$ , or  $\text{O}^{2-}$  could be detected.

Watling et al. (1996) have tested the oxidative dehydrogenation of propane over a series of catalysts, which included  $\text{Nb}_2\text{O}_5$  supported monolayer  $\text{V}_2\text{O}_5$  catalysts, bulk vanadia-niobia with different vanadium oxide loadings and prepared by four different methods,  $\text{V}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$ . The preparation method influenced drastically the surface concentration of vanadia. The intrinsic activity (TOF) of the samples studied indicated that vanadium containing active sites were indispensable for catalytic oxidative dehydrogenation of propane. Variations in the chemical environment of the vanadium ion did not cause significant changes in activity per site and, hence, all samples showed similar TOF when the rates were normalized to the concentration of V on the surface. Selectivity to propene on the other hand strongly depended on the nature of the catalyst because readsorption and interaction of propene with the acid sites led to total oxidation.

Yokoyama (1996) studied the addition of various metals to Pt-coated ceramic foam monoliths for the autothermal oxidative dehydrogenation of ethane to ethylene at  $900^\circ\text{C}$  at contact time of 5 ms. The addition of several other methods to Pt-monoliths increased both  $\text{C}_2\text{H}_6$  conversion and  $\text{C}_2\text{H}_4$  selectivity in the order;  $\text{Sn} > \text{Cu} > \text{Pt alone} > \text{Ag} > \text{Mg} > \text{Ce} > \text{Ni} > \text{La} > \text{Co}$ . No deactivation or volatilization of the catalysts was observed. For Pt-Sn, an increase in the Sn/Pt ratio from 1/1 to 7/1 increased both the conversion and the selectivity. Moreover, Pt existed in the forms of only and  $\text{Pt}_3\text{Sn}$  alloys for Pt-Sn catalysts and the  $\text{PtSn}/\text{Pt}_3\text{Sn}$  ratio increased with the increase in Sn addition.

Zhaorigetu et al. (1996) studied the effect of the presence of  $\text{CO}_2$  in feed for oxidative dehydrogenation of propane on rare earth vanadates. The catalysts used for this reaction were  $\text{LaVO}_4$ ,  $\text{CeVO}_4$ ,  $\text{PrVO}_4$ ,  $\text{SmVO}_4$  and  $\text{CrVO}_4$ . In the case of the presence of  $\text{CO}_2$  in feed, they found that the total oxidation of propane decreased with increasing  $\text{C}_3\text{H}_6$  selectivity and yield. The depressing of the  $\text{CO}$  and  $\text{CO}_2$  formation seemed to result from the blocking of the total oxidation sites of the catalyst by reversible chemisorption of  $\text{CO}_2$ . The effect of  $\text{CO}_2$  addition was thus of less importance at high conversion since enough  $\text{CO}_2$  was formed in the reaction to block the basic oxidizing sites of the catalyst.

Guerrero-Ruiz et al. (1997) have studied surface and lattice oxygen atoms over vanadium pentoxide, magnesium oxide and magnesium vanadate phases ( $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$ ,  $\text{Mg}_3\text{V}_2\text{O}_8$  and  $\beta\text{-MgV}_2\text{O}_6$ ) by isotopic exchange with  $\text{C}^{18}\text{O}_2$ . They found that on  $\text{MgO}$  an important surface exchange process occurred with  $\text{C}^{18}\text{O}_2$  of the gas phase, while this exchange was very low on  $\text{V}_2\text{O}_5$  and pure  $\text{V-Mg-O}$  phases. A comparison of the different magnesium vanadate phases in the same experimental conditions indicated that the  $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$  phase (which exhibited the highest selectivity for oxidative dehydrogenation of propane to propene) showed the lowest lattice oxygen exchange with  $\text{C}^{18}\text{O}_2$  of the gas phase.

Tellez et al. (1997) have presented the oxidative dehydrogenation of butane using a conventional fixed-bed reactor and inert membrane catalytic reactors with different feed arrangements. This reaction was studied at temperatures between 450 and 550°C. They concluded that the oxygen distribution arrangement had a direct effect on the average state of oxidation of the catalyst in the reactor, and also in the variation of the degree of reduction along the bed. In the fixed-bed reactor, the degree of reduction was low near the reactor entrance and high in the rest of the bed. This would give a decrease in selectivity in the entrance region due to the formation of coke. In the inert membrane reactor with permeation of  $\text{He}+\text{O}_2$ , a high degree of reduction and a high butane concentration would be present near the bed entrance, thus increased the rate of coking in this region, which would lower the selectivity, as

coke burning took place with part of the available oxygen. The advantages of this reactor are the oxygen distribution and the low residence time. Thus, it keeps coke formation to a minimum near the reactor entrance. In addition, the use of the membrane also helped keep reactor operation stable and safe. The membrane reactor had relatively small temperature variations under conditions in which the fixed bed reactor would give intense hot spots or even run away.

## 2.2 Comment on previous works

From the above reviewed literature, several oxide systems have been investigated in the oxidative dehydrogenation such as  $\text{ZnFe}_2\text{O}_4$  [Qiu et al (1989) and Armendariz (1992)], Mo-V-Nb oxide [Burch and Swarnakar (1991)],  $\alpha$ - and  $\beta$ - $\text{NiMoO}_4$  [Mazzocchia (1991)], Bi-V-O [Cherrak(1992)], rare earth vanadate [Castiglioni(1993) and Au et al. (1996)], vanadium aluminophosphate [Concepcion (1993)], cobalt molybdate [Yoon et al. (1994)],  $\text{V}_2\text{O}_5/\text{TiO}_2$  [Boisdron et al. (1995)],  $\text{MgMoO}$  [Cadus et al. (1996)], alkali-doping La/CaO [Ji et al. (1996)], vanadium magnesium oxide [Char et al. (1987,1988), Sam (1990) and Carrazon (1996)],  $\text{SbO}_2$  loading on vanadium magnesium oxide [Korili et al. (1996)]. Among of these catalysts, vanadium supported on magnesium oxide (V-Mg-O) is the catalyst which many research groups have paid more attention than any compounds, due to the catalytic properties of the V-Mg-O catalyst e.g. the activity and the propene selectivity are better than the others. Additionally, the absence of oxygenate product is observed, which can eliminate separation step. To investigate the catalyst structure, many researchers believe that the complex phases of V-Mg-O catalyst which related in the oxidative dehydrogenation are  $\text{Mg}_3\text{V}_2\text{O}_8$ ,  $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$  and  $\text{MgV}_2\text{O}_6$  phase [28,56]. The catalytic properties of the V-Mg-O depends on the ability of the catalyst to supply its lattice oxygen ions to the adsorbed hydrocarbon, which is called the reducibility of catalyst. In V-Mg-O catalyst, 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, which led to dominant propene selectivity [29,88]. Thus, the reducibility of catalyst relates to the structure of the surface lattice oxygen

ion. The important structures of V-Mg-O are V-O-V and V=O . To develop the structure of V-Mg-O catalysts, alkali doping is an interesting technique which can promote or inhibit the performance of V-Mg-O catalyst.

In this research, therefore, the effect of alkali metals on a V-Mg-O catalyst is investigated in the oxidative dehydrogenation of propane to propene included the structure of catalyst, the propane selectivity and the relationship between the basicity on the catalyst surface and the efficiency of the oxidative dehydrogenation.



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