CHAPTER II

LITERATURE REVIEW

During last decades a great deal of research interest has been focused on supported vanadia systems since their widespread use as heterogeneous catalysts in a great variety of selective oxidation reactions. It has been known that V_2O_5 is rather less active and selective catalyst for several hydrocarbon oxidation reactions. However, spreading vanadium oxide onto metal oxide supports can improve the catalytic performance of these catalysts. Supported vanadia can exhibit interesting catalytic properties depending on the composition of the catalysts and on the nature of the support. V_2O_5 supported on TiO_2 is one of the most important catalytic system that has received much attention and finds applications especially for oxidation reactions. The beneficial influence of the support, TiO_2, appears to be connected to its chemical and structural properties suitable for producing a high dispersion of the supported phase. In addition, basic oxide, MgO has been reported to show strong interaction to vanadium oxide. This V-Mg-O catalyst is a suitable catalyst in oxidative dehydrogenation of alkane in which high selectivity of alkene is obtained. For this reason, several researchers attempted to study the structure and nature of these catalysts for improving catalytic performance of them.

2.1 Reviewed literature

Chaar *et al.* (1987) reported 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 oxygenated 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 surface. 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) studied the oxidative dehydrogenation of propane to propene. They reported that vanadium-magnesium oxide catalysts were active and selective for this reaction. A selectivity of up to 65% was obtained at 10% conversion, but decreased with increasing conversion. The major products were propene, CO and CO_2. No oxygenates were formed. The reaction rate was 0.6 ± 0.15 order in propane and zeroth order in oxygen. For comparison, the rate for butane oxidative dehydrogenation was 0.85 ± 0.15 in butane and zeroth order in oxygen. Both reactions probably proceeded by first breaking a methylene C-H bond to form an adsorbed alkyl radical species.

Nieto *et al.* (1990) investigated the selective oxidation of propene with oxygen in the presence of steam on Al_2O_3-, SiO_2- and TiO_2 (anatase)-supported vanadium oxide. They found that V_2O_5/TiO_2 preparations were more highly active catalysts than the V_2O_5/Al_2O_3 of V_2O_5/SiO_2 preparations. While the V_2O_5/TiO_2 catalysts were highly active and selective toward acetic acid, the V_2O_5/Al_2O_3 and V_2O_5/SiO_2 catalysts were much less active and were selective toward acetone. They indicated that the structure of surface vanadia defined by the active phase-support interaction played an important role in the selective oxidation reaction.

Bhattacharyya *et al.* (1992) have investigated the effects of different promoters (Cr_2O_3, MoO_3 and 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: 24V-Mg-O+Cr_2O_3 > 24V-Mg-O+MoO_3 > 24V-Mg-O > 24V-Mg-O+TiO_2 and the order of

selectivity was 24V-Mg-O+TiO$_2$ > 24V-Mg-O+Cr$_2$O$_3$ > 24V-Mg-O > 24V-Mg-O+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 24V-Mg-O incorporating both Cr$_2$O$_3$ and 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 V^{4+} ↔ V^{3+} redox cycle for this oxidation reaction.

Kung *et al.* (1992) studied the effect of potassium in the preparation of magnesium orthovanadate and pyrovanadate on the oxidative dehydrogenation of propane and butane. The mixed oxides prepared by two different methods, with or without the use of potassium, were compared. Mg orthovanadate, when free of potassium, is a selective oxidative dehydrogenation catalyst for propane and butane. The presence of residence potassium in the oxide lowered the selectivity, especially in the butane reaction. In contrast, Mg pyrovanadate is quite selective for propane dehydrogenation but not for butane dehydrogenation. Moreover, they found that the presence of potassium increased thermal stability of Mg pyrovanadate against reaction with magnesium to form Mg orthovanadate.

Owen *et al.* (1992) reported their study on the effect of oxide structure and cation reduction potential of vanadates on the selective oxidation 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 (Mg$_3$(VO$_4$)$_2$) was a rather selective catalyst for butane oxidation than magnesium pyrovanadate (Mg$_2$V$_2$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 VO$_4$ units resulted in a condition that the adsorbed molecule could only interact with on VO$_4$ unit. In

magnesium pyrovanadate, on the other hand, the V_2O_7 units, which consisted of two corner-shared VO_4 units, provided that the size of the molecular was sufficiently large to do so. Propane interacted with only one 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 VO_4 units in the V_2O_7 group. Thus, in the case of magnesium pyrovanadate, this interaction led to combustion of the molecule.

In 1993, the structures of vanadium oxide overlayers on supports (MgO, Al_2O_3 and SiO_2) were studied by Okuhara *et al.* (1993). They revealed that the structure of V_2O_5 was very sensitive to the supports and the preparation method. The Al_2O_3 surface stabilized the V_2O_5 overlayers as thin films, independent of the preparation method. V_2O_5/SiO_2 ($V_2O_5 > 5$ wt%) prepared by the impregnation method consisted of small crystallites. On the other hand, on MgO, the vanadium was not in the form of V_2O_5. They reported that vanadium reacted readily with the surface of MgO to form new phases such as $Mg_3V_2O_8$ and $Mg_2V_2O_7$.

Ramis and Busca (1993) have investigated the effect of dopants and additive on the state of surface vanadyl centers of vanadia-titania catalysts. They observed that the V=O stretching frequency and its first overtone on vanadia-titania-based catalysts were sensitive to the presence of dopants and additives. Alkali and alkali earth metal cations decreased strongly the V=O stretching frequency. Doping of TiO_2 and of vanadia-titania with alkali cations caused the formation of new stronger basic sites. Vanadyl cations, that are Lewis acidic, probably were attracted by these new stronger basic sites and O=V-O-Ti bridges were substituted by O=V-O-M bridges (M = alkali or alkali earth cation). As a result of the increased basicity of ligands, coordinatively unsaturated vanadyl centers have their Lewis acidity weakened.

Gao *et al.* (1994) prepared and characterized three pure magnesium vanadate phases of MgV_2O_6, $\alpha-Mg_2V_2O_7$ and $Mg_3V_2O_8$ for selective oxidation of propane to propene. These three phases were prepared by 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_2O_6 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: α-$Mg_2V_2O_7$ > $Mg_3V_2O_8$ > MgV_2O_6 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.

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

Galli and López Nieto (1995) reported the catalytic properties of undoped and K-doped Al_2O_3 supported vanadia catalysts for the oxidation of ethane and n-butane. They observed that isolated tetrahedral V^{5+} species were mainly in both undoped and K-doped samples. Thus it could be proposed that the presence of potassium did not change the nature of vanadium species. However, the incorporation of potassium decreased both the reducibility of surface vanadium species and the number of surface acid sites. They found that the presence of potassium on the vanadium catalysts strongly influenced their catalytic properties, increasing the selectivity of C_4-olefins from n-butane and decreasing the selectivity to ethene form ethane. They suggested that the selectivity to oxydehydrogenated products depended on both the acid-base character of catalysts and the length of the fed alkane. Catalysts with acid character favored the selective oxidative dehydrogenation of ethane while catalysts with basic character favored the oxydehydrogenation of n-butane.

The influence of potassium addition to the TiO_2 support on the structure of V_2O_5/TiO_2 and its catalytic properties in the oxidative dehydrogenation of propane has been investigated by Courcot et al. (1996). They found that the presence of potassium on the TiO_2 surface modified the physicochemical properties of V_2O_5/TiO_2 catalyst, leading to: (a) a decrease in the reducibility of the vanadia phase at low vanadium concentration; (b) a decrease in the surface potential (electronic work function); (c) a decrease in acidity for ODH of propane. Furthermore, the pattern of the activity and selectivity changed with the total V content depended on the pattern amount of potassium on the support surface: with K < 1ML (ML = monolayer) , the maximum activity and selectivity was observed at a vanadium content corresponding to ca.40% of a V_2O_5 ML. At higher K content, higher amounts of vanadium (> 1 ML) were required to obtain the same catalytic performance. Finally, they reported that polymeric (VO_x) species seemed to be more active and selective in the ODH of propane than monomeric species or bulk V_2O_5.

Zazhigalov et al. (1996) studied the changes in the properties of two V-P-O compositions with P/V ratio equals 1.09 and 1.20 caused by introduction of alkali and alkali earth (Li, Na, K, Cs, Be, Mg, Ca and Ba) at different concentration on oxidation of n-butane to maleic anhydride. They reported that the incorporation of these elements which can easily donate electrons to the structure of vanadyl phosphate leaded to an increases of the effective negative charge on oxygen atom (increase of basic properties) and of the rate of butane oxidation. Moreover, they found that the presence of additives caused an increase of the surface P/V ratio and corresponding changes of acidic properties of the catalysts. The highest increase of the rate of butane oxidation was achieved by introduction of Na, K and Cs. The rate of hydrocarbon transformation rose with the increase of the concentration of additives. An increase of maleic anhydride selectivity was observed after introduction of Mg, Ba and Ca and the best results were obtained at their low concentration (Metal/V = 0.02). They concluded that the preparation of a catalyst characterized by high activity in butane oxidation and high selectivity to maleic anhydride required a fine tuning of the basicity of surface oxygen atoms to accelerate the activation of butane and of the

acidity of the surface to secure the appropriate residence time of the reaction intermediates.

Courcot (1997) reported the effect of sequence of potassium introduction to V_2O_5/TiO_2 catalysts on the physicochemical properties and catalytic performance in oxidative dehydrogenation of propane. Two series of K-promoted V_2O_5/TiO_2 catalysts were prepared by: (a) deposition of vanadia on K-doped TiO_2 support (TiKV preparation) and (b) deposition of K on vanadia-titania catalysts (TiVK preparation). They indicated the higher amounts of surface K on the TiVK catalysts than on the TiKV ones. The vanadium species on TiKV samples include V_2O_5 and polymeric $[VO_x]_n$ species. The TiVK sequence led to the formation of potassium vanadates (KV_3O_8 and possibly KVO_3) and the decrease in the amount of V_2O_5. The TiVK catalysts were more active and selective in the ODH of propane and more basic than the TiKV samples. They also suggested that the type of vanadium containing species is not the single decisive factor to account for the modification of the catalytic performance of V_2O_5/TiO_2 catalysts in the presence of potassium. The modification of acid-base properties (decrease in the acidity and increase in the basicity for K-doped samples) can also be important.

Guerrero-Ruiz et al. (1997) have investigated surface and lattice oxygen atoms over vanadium pentoxide, magnesium oxide and magnesium vanadate phases (α-$Mg_2V_2O_7$, $Mg_3V_2O_8$ and β-MgV_2O_6 by isotopic exchange with $C^{18}O_2$. They found that on MgO an important surface exchange process occurred with $C^{18}O_2$ of the gas phase, while this exchange was very low on V_2O_5 and pure V-Mg-O phases. A comparison of the different magnesium vanadate phases in the same experimental conditions indicated that the α-$Mg_2V_2O_7$ phase (which exhibited the highest selectivity for oxidative dehydrogenation of propane to propene) showed the lowest lattice oxygen exchange with $C^{18}O_2$ of the gas phase.

The effects of support (Al_2O_3, SiO_2, TiO_2 and ZrO_2) on the structure and catalytic behavior of supported vanadia in the oxidative dehydrogenation of propane

examined over a wide range of vanadium surface densities were investigated by Khodakov *et al.* (1999). They found that the structure and dispersion of VO_x species depended on their surface density and on their interaction with a given support. Supports surfaces predominantly covered with polyvanadate structures of small V_2O_5 clusters containing V-O-V or V=O linkages leaded to high oxidative dehydrogenation rates and selectivities. The composition of the support influences the VO_x species into monovanadates, polyvanadates and V_2O_5 clusters and thus the catalytic behavior of supported vanadia in oxidative dehydrogenation reactions. The concentration of polyvanadate structures increases with increasing VO_x surface density. Raman and UV-visible spectra showed an excellent correlation between oxidative dehydrogenation rates and the density of polyvanadate species on all support surfaces. Furthermore, they suggested that sites required for the oxidative dehydrogenation also catalyzed the undesired combustion of propene.

2.2 Comment on previous works

From the above reviewed literature, it can be seen that vanadium oxide shows the strong interaction with supports. On TiO_2 the high dispersion of vanadium oxide species is observed. In contrast, acidic vanadium oxide reacts with basic MgO to form a new compound, V-Mg-O in which the magnesia phase plays the role of basic centers during the ODH of propane. Moreover, several studies are carried out to investigate the influence of basic metal such as alkali or alkali earth on the catalytic performance of supported vanadia catalysts. Their interaction can both improve or inhibit the performance of the catalysts.

Although the vanadia-titania and V-Mg-O systems have been received much attention, there are no information about the combination of these two systems. In this research, therefore, the system consists of oxides of vanadium, titanium and magnesium is investigated to study the catalytic property in the oxidation reactions.