

## CHAPTER II

### LITERATURE REVIEW

Total oxidation or combustion is the strongest oxidation. It is used to oxidise hydrocarbon to water and CO<sub>2</sub>. A large body of patent literature is concerned with the development of catalysis for this reaction. They can exhibit interesting catalytic properties depending on composition of V-Mg-O/TiO<sub>2</sub> catalysts, nature of supports and methods of preparation.

#### 2.1 Reviewed literature

Charr *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<sub>3</sub> (VO<sub>4</sub>)<sub>2</sub>. 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<sub>2</sub>O<sub>5</sub> 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.

Bhattacharyya *et al.* (1992) investigate the effects of different promoters (Cr<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub> and TiO<sub>2</sub>) 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 variable: the reaction temperature, contact time and n-butane feed concentration indicated the order of activity as follow: 24V-Mg-O + Cr<sub>2</sub>O<sub>3</sub> > 24V-Mg-O + MoO<sub>3</sub> > 24V-Mg-O > 24V-Mg-O + TiO<sub>2</sub> and the order of selectivity was 24V-Mg-O + TiO<sub>2</sub> > 24V-Mg-O + Cr<sub>2</sub>O<sub>3</sub> > 24V-Mg-O > 24V-Mg-O + MoO<sub>3</sub>. 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  $\text{Cr}_2\text{O}_3$  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.

Corma *et al.* (1993) studied a series of V-Mg-O catalysts using MgO or magnesium oxalate and aqueous solutions of vanadyl-oxalate or ammonium metavanadate as vanadium sources. Large differences in the V/Mg surface atomic ratios were observed on the different catalysts after calcination, indicating differences in the V-Mg interaction, which are related to the catalysts preparation procedure. These differences could be explained by the chemical modifications that occur in the vanadium or magnesium starting materials during the impregnation step. In addition, a new preparation procedure of V-Mg-O catalysts which allows a homogeneous dispersion of vanadium along the catalyst was presented. By X-ray diffraction, IR, UV-VIS and X-ray photoelectron spectroscopic characterization of the 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, are observed. After the calcination step, the formation of magnesium vanadates depended only on the vanadium content of the catalysts.  $\text{Mg}_3\text{V}_2\text{O}_8$  was 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. However, the crystallinity of the magnesium vanadate phases, as well as the distribution of vanadium along the support strongly depended on the preparation procedure.

Ramis and Busca (1993) 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  $\text{TiO}_2$  and of vanadia-titania with alkali cations caused the formation of new stronger basic sites. Vanadyl cations, that were 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  $\text{MgV}_2\text{O}_6$ ,  $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$  and  $\text{Mg}_3\text{V}_2\text{O}_8$ . 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  $\text{MgV}_2\text{O}_6$  phase, which was a function of calcination temperature, appeared to have a strong effect on the infrared spectra.

Pantazidis *et al.* (1996) investigated the acid strength of the VMgO samples by ammonia adsorption in a wide range of vanadium contents (5-45 wt%). For higher loading, the strong acidity decreased while weaker acid sites developed above 25 wt% V. This maximum in strong acidity was observed for the 14V/VMgO sample. In contrast, the total intrinsic acidity measured by irreversible ammonia adsorption increased regularly over the range of vanadium addition. Additionally, the basicity of the VMgO samples measured by sulphur dioxide adsorption remained unchanged for loading up to 25 wt% V. At higher loading, the basicity decreased to vanish on the 45V/VMgO sample. The intrinsic basicity measured by the amount of irreversibly adsorbed  $\text{SO}_2$  per surface unit was found to markedly decrease from unpromoted to promoted magnesia, then to be stable up to 25 wt% V addition, then to decrease again and to vanish at very high V contents. Surface basicity was also investigated by carbon dioxide adsorption followed by in situ DRIFT spectroscopy. Pure MgO and low V content samples showed a strongly carbonated surface with the presence of unidentate, bidentate and free carbonated. As vanadium content increased, the amount of unidentate species markedly decreased. Only bidentate carbonates were observed at 14 wt% V, while no  $\text{CO}_2$  adsorption was observed on the 25V/VMgO and 45V/VMgO samples.

Burrows *et al.* (1999) interpreted a change in the oxidation state of the vanadium from  $V^{5+}$  to  $V^{3+}$  in the EXAFS spectrum under typical reaction conditions in the XRD profile as a phase transformation of magnesium orthovanadate to a cubic spinel structure,  $MgV_2O_4$  (with a lattice parameter of 8.42 Å). Furthermore, this transformation has been found to be reversible on re-exposure to air at typical reaction temperatures, although the XRD pattern demonstrated that the crystallinity of the orthovanadate was of poorer quality compared to the unused material. In particular, HREM revealed the presence of a disordered V-containing layer on the MgO which undergoes partial ordering under typical reaction conditions. It would appear these conditions were not severe enough to effect a complete  $Mg_3V_2O_8$  to  $MgV_2O_4$  transformation which correlated well with the partial ordering of the overlayer and partially transformed bulk V-Mg-O particles. Hence, the XRD pattern did not revert to that of the "as-prepared" material when the catalyst was exposed to air at 500°C. It was apparent that under mildly reducing atmospheres the conversion of bulk magnesium orthovanadate to a cubic spinel structure was confined to the first few atomic layers with the interior of these particles in a disordered state. Only when the reaction atmosphere had been changed to pure propane did the complete conversion to a stable bulk spinel phase occur. It was interesting to note that, after subsequent exposure to air at 500°C for 5 h, the bulk spinel particles remained unchanged, although it was conceivable that a few surface layers had back transformed to the orthovanadate

Chaiyasit (2000) studied the acid/base properties of  $TiO_2$ . The basic support, promotes dehydrogenation reaction of 1-propanol and 2-propanol to form propionaldehyde. At the initial reaction temperature (200-300°C) the main product is propionaldehyde and there are some formation of acetaldehyde, propylene,  $CO_2$  and with trace amount of formaldehyde and ethylene. When increasing reaction temperature (350-500°C), the main product are propionaldehyde, propylene and  $CO_2$  and with trace of formaldehyde, acetaldehyde, methane, and ethylene. It is found that 1-propanal and 2-propanal conversion using Co-Mg-O/ $TiO_2$  catalyst can not produce carboxylic acid.

Valenzuela and Corberan (2000) studied the performance of V-Ca-O catalysts for the oxidative dehydrogenation of propane, being compared with that of similar V-Mg-O catalysts, and their differences interpreted in terms of their physico-chemical properties. The V-Ca-O catalyst showed the same initial selectivity to propene as the most selective V-Mg-O composition, but it decreased faster with increasing propane conversion. Vanadium species present in the catalyst surface were different for the two supports: isolated  $V^{5+}$  tetrahedra on CaO and magnesium orthovanadate and pyrovanadate on MgO. The intrinsic activity of isolated vanadium centres in the surface of the V-Ca-O catalyst was more than one order of magnitude higher than that of dimeric or polymeric tetrahedral species in the magnesium-containing catalysts.

Chao and Ruckenstein (2002) studied the mesostructured V-Mg-O at room temperature using vanadium acetylacetonate and magnesium chloride as source materials. The effect of a number of factors, such as the nature of surfactant, pH and vanadium/magnesium molar ratio in the formation of mesoporous V-Mg-O phase were investigated for a fixed molar concentration of surfactant. The synthesized samples were examined by X-ray diffraction, Brunauer-Emmett-Teller analysis, transmission electron microscopy, and energy dispersive spectroscopy. It was found that the ordered arrangement (crystallinity) of the pores was strongly dependent on the vanadium/magnesium molar ratios in the initial batches; too large or too small ratios were unfavorable to the crystallinity and generated distorted hexagonal (wormlike) mesostructures. The optimum vanadium/magnesium molar ratio regarding the crystallinity was found to be in the range 1:1 to 1:1.5, and the mesoporous phase had a lamellar structure.

## 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  $\text{TiO}_2$ , the high dispersion of vanadium oxide species is observed. However, acidic vanadium oxide reacts with basic  $\text{MgO}$  to form a new compound. Moreover, preparation and V/Mg ratio have effect on the catalytic property [Corma *et al* (1993), Pentazidis *et al* (1996), Chao and Ruckenstein (2002)].

Furthermore, there are no information about the combustion anhydride in the reaction over supported vanadium oxide catalyst. In this research, the system consists of oxides of vanadium, titanium and magnesium to study the catalytic property in the combustion anhydride. VMgOTi catalysts have basic property that should be oxidized with carboxylic acid and anhydride.