

CHAPTER III

THEORY

Supported vanadium oxides have been reported to be selective catalysts in a number of catalytic reactions, *i.e.* the oxidation of methanol, methane and olefins, the oxidation and ammoxidation of aromatic hydrocarbons and the selective catalytic reduction of NO_x . Recently, they have been shown to be selective catalysts in the ODH reactions [Chaar *et al.* (1988), Sam *et al.* (1990), Gao *et al.* (1995) and Busca (1996)]. The advantages of supported metal oxides include higher mechanical strength, better thermal stability and larger surface area. However, the catalytic behavior of supported vanadium oxide is modified by the nature of the metal oxide support and the vanadium loading [Blasco (1997)].

3.1 Stability of the surface vanadia monolayer

The surface vanadia monolayer is stable on many typical oxide supports (Al_2O_3 , TiO_2 , ZrO_2 , Nb_2O_5 and CeO_2). The surface vanadia overlayer is also stable and not converted to crystalline V_2O_5 particles during oxidation reactions. The surface vanadia monolayer can be converted to crystalline V_2O_5 or vanadia species dissolved in the oxide support only after high temperature treatments that cause the collapse of the oxide support surface area, which reduces the number of available adsorption sites for the surface vanadia species [Wachs *et al.* (1997)]. In the case of $\text{V}_2\text{O}_5/\text{TiO}_2$ (anatase) catalysts, high temperature treatments also transform the TiO_2 (anatase) phase to the TiO_2 (rutile) phase that can accommodate dissolved V^{4+} species in the rutile lattice [Bond (1991)]. The stability of the surface vanadia monolayer is reflected in the long life of such industrial oxidation catalysts [Wachs *et al.* (1997)].

3.2 Molecular structures of surface vanadia species

On TiO_2 (anatase) support, different $[\text{VO}]_x$ species on the surface of the TiO_2 are detected. They include: isolated monomers VO_x , polymeric $[\text{VO}_x]_n$ species and V_2O_5 in amorphous or crystalline form. At very low vanadia loading, only monomeric isolated forms have been observed. With increase in loading their amount increases and a new type of vanadyls is formed. The appearance of polymeric forms has been observed. Their amount and the size (number of vanadium atoms in species) increase with the loading. At loading exceeding 1 monolayer amorphous and crystalline V_2O_5 are also observed [Machej *et al.* (1991)]. Figure 3.1 shows the different $[\text{VO}_x]_n$ species on the surface of the TiO_2 (anatase) supported.

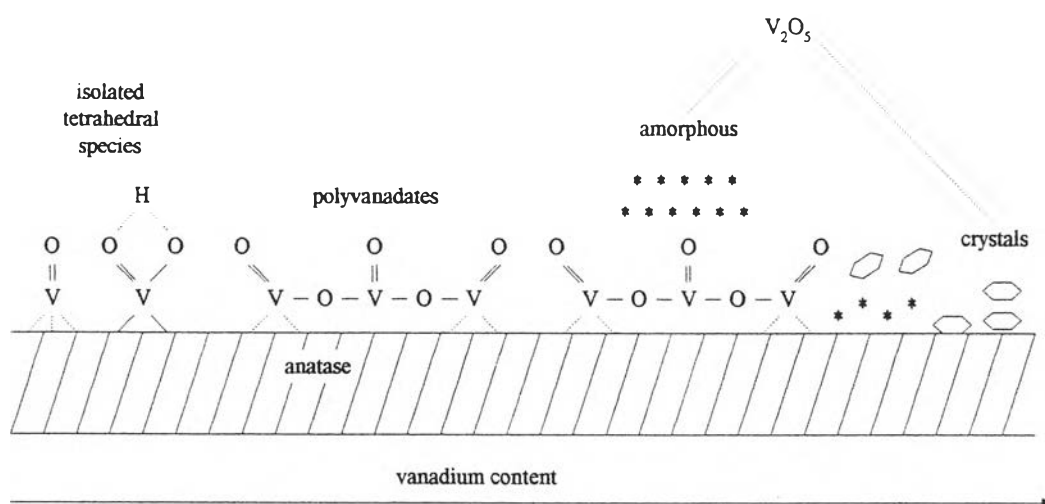


Figure 3.1 Different $[\text{VO}_x]_n$ species on TiO_2 anatase support.

The molecular structures of the surface vanadia species have been extensively investigated in the past few years. It has been revealed that the surface structures and oxidation states of the surface vanadia species are dynamic and are strongly dependent on the environment (oxidizing and reducing gases and temperature). Thus the experimental results under well-defined environments will be focused.

3.2.1 Dehydrated conditions

Dehydrated conditions are created by heating the supported vanadia catalysts to elevated temperature, 300-700°C, in a flowing oxygen-containing stream that does not contain any reducing gases. Such a treatment desorbs adsorbed moisture from the catalyst surface and maintains the surface vanadia species in the V^{5+} oxidation state.

- $V_2O_5/(Al_2O_3, TiO_2, ZrO_2, Nb_2O_5 \text{ and } CeO_2)$

The dehydrated surface vanadia species on these oxide supports are primarily present as isolated and polymerized VO_4 units. The molecular structures of these surface vanadia species are tentatively thought to consist of a terminal $V=O$ bond and three bridging V-O-support and two bridging V-O-V bonds for the polymerized species. There may also be a minor amount of surface VO_6 units (octahedral coordination) present at monolayer [Went and Oyama (1990) in Wachs *et al.* (1997)].

- V_2O_5/MgO

Unlike the above supported vanadia catalysts, the magnesium oxide supported vanadia catalysts cannot form a complete close packed surface vanadia monolayer because of the acid-base reaction between acidic vanadia and basic magnesia. The strong interaction between vanadia and magnesia results in the formation of a mixed metal oxide compound rather than a stable surface vanadia overlayer on the magnesia support [Deo (1992) in Wachs *et al.* (1997) and Okuhara (1993)]. Depending on the composition of the mixture, various magnesium vanadate can be formed. The phase diagram of this system indicates that magnesium orthovanadate ($Mg_3(VO_4)_2$), magnesium pyrovanadate ($Mg_2V_2O_7$) and magnesium metavanadate (MgV_2O_6) are stable compounds. The structure of $Mg_3(VO_4)_2$ is characterized by chain of edge-sharing MgO_6 units linked together by isolated VO_4 tetrahedra. $Mg_2V_2O_7$ is made up of corner-sharing VO_4 tetrahedra that form V_2O_7 units and MgV_2O_6 is made up of metavanadate chains of edge-sharing VO_5 units [Kung and Kung (1997)]. The

vanadia coordination in bulk V-Mg-O mixed metal oxide catalysts consists of VO_4 , VO_5 and VO_6 units. Thus, the magnesia supported vanadia catalyst system possesses both surface and bulk vanadia species.

3.2.2 Hydrocarbon oxidation reaction environments

The influence of hydrocarbon oxidation reaction environments upon the oxidation states of the surface vanadia species in supported vanadia catalysts has been examined for several reactions with in situ Raman spectroscopy. During typical methane oxidation conditions, the surface vanadium oxide species is mostly present in the V^{5+} oxidation state and possesses the same structure reported above for dehydrated conditions. Even exposing the supported vanadia catalysts to a reducing methane stream in the absence of oxygen only slightly reduces the surface vanadia species for $\text{V}_2\text{O}_5/\text{TiO}_2$ and $\text{V}_2\text{O}_5/\text{CeO}_2$, but no measurable reduction was detected for the surface vanadia species in the case of silica during methane oxidation reflects the weak reducing power of methane compared to other hydrocarbon (see below). During butane oxidation to maleic anhydride and CO_x , the concentration of V^{5+} surface vanadia species was partly decreased by the reaction environment, ~10-35% decrease in the Raman signal, for all supported vanadia catalysts with the exception of $\text{V}_2\text{O}_5/\text{SiO}_2$ [Wachs *et al.*(1996a)]. In the presence of a reducing butane stream in the absence of oxygen, the surface vanadia species on alumina was completely reduced reflecting the greater reducing power of butane compared to methane. The relative extent of reduction of the V^{5+} surface vanadia species, at high surface coverage, during butane oxidation follows the pattern: $\text{TiO}_2 > \text{CeO}_2 > \text{ZrO}_2 > \text{Al}_2\text{O}_3 > \text{SiO}_2$. The surface vanadia species are more extensively reduced during butene oxidation than butane oxidation since even the surface vanadia species on silica was reduced during butene oxidation [Wachs *et al.*(1996b)]. Thus, the in situ Raman studies provide new insights into the behavior of surface vanadia species during hydrocarbon oxidation reaction: (1) the dehydrated V^{5+} surface vanadia species appears to be the predominant surface vanadia species, (2) the extent of reduction of

the surface vanadia species depends on the reducing power of the hydrocarbon (butene>butane>methane) and (3) the specific oxide support.

3.3 Surface reducibility and properties of catalyst oxygen

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.* (1994), Guerrero-Ruiz *et al.* (1992), Owen *et al.* (1992), 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 propene selectivity [Corma *et al.* (1993a), Sam *et al.* (1990)]. The basic catalyst surface has also been claimed [Bhattacharyya *et al.* (1992), Corma *et al.* (1993b), 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 propene 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 propene [Chaar *et al.* (1987), Guerrero-Ruiz *et al.* (1992), Kung *et al.* (1992), Nguyen *et al.* (1991) and Sam *et al.* (1990)].

On the other hand, the reduction of the V₂O₅/TiO₂(anatase) catalysts has been studied by TPR [Bond and Tahir (1991)] technique, using mainly hydrogen or CO as a reducing agent and in the conditions in which titania is not reduced. The reduction of the V₂O₅/TiO₂ system has also been observed in the presence of ammonia. All the authors agree that the vanadia phase is more easily reduced at low loading of the deposited phase than at the supra-monolayer content of vanadia, the order of reducibility being

monolayer > amorphous > crystalline vanadia

Bell *et al.* (1992) reported that both monomeric vanadyls and polymerized vanadates are shown to be present at the monolayer range of loading, the same stoichiometry of reduction (with hydrogen as a reducing agent) has been observed. The authors claim moreover that the terminal V=O groups in the both species are removed preferentially to the bridging oxygen atoms of the polymeric species.

3.4 Influence of metal oxide additives

3.4.1 Noninteracting additives

Noninteracting additives are defined as surface metal oxides that preferentially coordinate with the oxide support rather than the surface vanadia species under dehydrated conditions. Typical noninteracting additives are surface oxides of W, Nb, S, Si, Mo, Ni, Co and Fe. Consequently, the noninteracting additives can only indirectly affect the molecular structure of the surface vanadia species via lateral interactions. Such lateral interactions have been found to influence the ratio of polymerized to isolated surface vanadia species in supported metal oxide catalysts: Fe > Ni ~ Co > S > Mo ~ W > Nb > Si.

3.4.2 Interacting additives

Interacting additives are defined as surface metal oxide that preferentially coordinate with the surface vanadia species rather than the oxide support under dehydrated conditions. Typical interacting additives are P and alkali/alkali earth oxides (K, Na, Ca, etc.) that tend to form complex with the acidic surface vanadia species [Ramis *et al.* (1993)]. The basic alkali/alkali earth additives do not change the trigonal-pyramidal coordination of the dehydrated surface vanadia species, but do affect the V-O bond lengths by significantly increasing the terminal V=O bond length and, consequently, decreasing the bridging V-O bond lengths [Ramis *et al.* (1993)].

Thus, the basic surface additives do not form three-dimensional mixed vanadate compounds, but just alter the V-O bond lengths of the surface vanadia species. However, the interaction between P and the surface vanadia species can result in the formation of crystalline VOPO₄ phase, at the expense of the surface vanadia phase, after calcination due to the strong interaction between these two oxides. The formation of crystalline VOPO₄ can only be avoided if the surface phosphorous oxide species is first anchored to the oxide support surface before the introduction of the vanadia precursor.

Thus, interacting additives can both modify the local structure of the surface vanadia species, affecting the V-O bond lengths, as well as form crystalline mixed metal oxide phases because of their chemical affinity for vanadia.

3.5 Mechanism of action of V₂O₅/TiO₂ catalyst in oxidation of hydrocarbons

It has been generally accepted that selective oxidation of hydrocarbons requires the presence of three essential types of centers on a catalyst surface: (a) the sites for activation of the C-H bond in a hydrocarbon molecule which is a rate determining step in most oxidation processes, (b) the sites for insertion of oxygen into an organic molecule species adsorbed on the surface after step (a), (c) centers for reoxidation (or adsorption of molecular oxygen). Most of experimental works as well as quantum chemical calculations indicate that it is an oxygen atom (most probably O²⁻ ion on the catalyst surface) which is an active center for a rupture of a C-H bond. The ability of an oxygen atom (ion) to abstract a hydrogen atom from a C-H bond can be related to its nucleophilicity (basicity). The activity of the oxidation reaction would then increase with the increase in the oxygen basicity. The rate of the insertion of oxygen (step (b)) would depend in the first place on a Metal-O bond energy, and in the second place on a number of oxygen atoms in the vicinity of an organic adsorbed species.

It is obvious that more oxygen atoms are required for oxidation reactions in which organic anhydrides are formed than for the formation of aldehydes or for the ODH reactions. For the ODH reactions oxygen atoms are only necessary to form water from the abstracted hydrogen, though evidently the formation of water also occurs in the reactions which form the oxygenated products. Undesirable total combustion would require a high number of oxygen atoms and low Metal-O bond energy. Both the oxygen nucleophilicity and the Metal-O bond energy depend on: (1) the nature and oxidation state of a cation constituting an oxide lattice (primary parameters) and (2) environment of an active center, which decide the coordination of an active oxygen site, and the Metal-O bond order (secondary parameters). The secondary parameters can be manifested in the dependence of the catalytic performance on morphology of an oxide grain (for bulk oxides) and on the structure of dispersed active species (for supported oxides). For reoxidation of a catalyst which involves chemisorption of an oxygen molecule followed by the reaction: $O_2 + e \rightarrow O_2^- + e \rightarrow 2O^- + 2e \rightarrow 2O^{2-}$, the presence of reduced cations (V^{4+} , V^{3+}) and the easy electronic transfer from a catalyst to an adsorbed O_2 molecule is required. Finally other factors for an oxide catalyst to be selective include the easy desorption of the formed products, which depends on the acid-base properties of a catalyst, these being interrelated with the valence state of the cation. The desorption of acidic product such as phthalic anhydride or maleic anhydride would require rather high acidity (high acid strength) of the catalyst, whereas for the desorption of an olefin *e.g.* in an ODH reaction, low acidity and rather higher basicity would be the conditions for a selective catalyst [Grzybowska-Swierkosz (1997)].