Structure and reactivity of surface vanadium oxide species on oxide supports

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Abstract

Supported vanadium oxide catalysts, containing surface vanadia species on oxide supports, are extensively employed as catalysts for many hydrocarbon oxidation reactions. This paper discusses the current fundamental information available about the structure and reactivity of surface vanadia species on oxide supports: monolayer surface coverage, stability of the surface vanadia monolayer, oxidation state of the surface vanadia species, molecular structures of the surface vanadia species (as a function of environment and catalyst composition), acidity of the surface vanadia species and reactivity of the surface vanadia species. Comparison of the molecular structure and reactivity information provides new fundamental insights into the catalytic properties of surface vanadia species during hydrocarbon oxidation reactions: (1) the role of terminal V=O, bridging V–O–V and bridging V–O-support bonds, (2) the number of surface vanadia sites required, (3) the influence of metal oxide additives, (4) the influence of surface acidic and basic sites, (5) the influence of preparation methods and (6) the influence of the specific oxide support phase. The unique physical and chemical characteristics of supported vanadia catalysts, compared to other supported metal oxide catalysts, for hydrocarbon oxidation reactions are also discussed.

Keywords: Supported vanadia catalysts; Surface vanadia species; Structure; Reactivity; Hydrocarbon oxidation

1. Introduction

Supported vanadium oxide catalysts contain a vanadia phase deposited on the surface of an oxide support (e.g., Al_2O_3, TiO_2, SiO_2, etc.). Characterization studies have revealed that the deposited vanadia phase consists of a two-dimensional surface vanadia overlayer as well as V_2O_5 crystallites above monolayer coverage

[1–5]. In recent years, such supported vanadia catalysts have found wide commercial application as oxidation catalysts: selective oxidation of o-xylene to phthalic anhydride [6,7], ammoxidation of alkyl aromatics [8,9], selective catalytic reduction of NO_x with NH_3 [10] and controlling the oxidation of SO_2 to SO_3 during SCR [10–12]. In addition to these oxidation reactions, supported vanadia catalysts have also been investigated for the oxidative dehydrogenation of alkanes to olefins [13], oxidation of butane to maleic anhydride [14–17], pentane oxidation to maleic anhydride [18] and the selective oxidation of methanol to formaldehyde [19] or methyl formate [20].

In spite of the importance of supported vanadia catalysts, many significant fundamental questions still remain unanswered about these oxidation catalysts (see extensive European catalysis community study appearing in a recent issue of Catalysis Today [2]): (1) monolayer coverage of the surface vanadia species, (2) stability of the surface vanadia monolayer, (3) oxidation state of the surface vanadia species after calcination, (4) the molecular structures of the surface vanadia species, (5) influence of different environments upon the molecular structures and oxidation state, (6) acidity of the surface vanadia species and (7) influence of the oxide support and metal oxide additives on the molecular structures and reactivity. Progress in the fundamental understanding of supported vanadia catalysts has primarily been hampered by (1) the use of oxide supports in many studies that contain significant amounts of impurities (e.g., P, K, etc.), (2) comparison of characterization studies of supported vanadia catalysts that have been performed under different conditions (e.g., ambient vs. in situ), and (3) the use of characterization techniques which are not always appropriate or optimum for the desired information. In order to minimize these potential complications, the present paper will primarily focus on well-defined model supported vanadium oxide catalysts that are free of impurities and where such additives, promoters and poisons, are only introduced into the catalysts in a controlled manner. The objective of this paper is to address the above fundamental issues about supported vanadia catalysts rather than to be a comprehensive literature review (see references [1–8] for more extensive literature reviews of supported vanadia catalysts).

2. Monolayer surface coverage

Monolayer surface coverage is defined as the maximum amount of amorphous or two-dimensional vanadia in contact with the oxide support. Monolayer surface coverage of the surface vanadia overlayer on oxide supports has been estimated from structural calculations [2,4] and experimental determinations [3,5]. From the V–O bond lengths of crystalline V_2O_5, monolayer surface coverage is estimated at 10 VO_x per nm^2 for a bidimensional polyvanadate layer and at 2.5 VO_x per nm^2 for isolated monomeric vanadia units [2,4]. These calculations, however, assume that the molecular structure of the surface vanadia overlayer are similar to that present

in crystalline V_2O_5. As will be shown below, the surface vanadia overlayer on oxide supports does not possess the structure of crystalline V_2O_5 and, consequently, monolayer surface coverage determinations based on such structural calculations represent only a rough approximation. Monolayer surface coverage of the surface vanadia overlayer can be experimentally determined with several different characterization techniques that both physically (Raman, IR, XPS, solid state [51]V NMR and UV–VIS DRS) and chemically (TPR, chemisorption and oxidation reactions) discriminate between the surface vanadia overlayer and the crystalline V_2O_5 phases [3]. The determination of monolayer surface coverage is significantly facilitated by the experimental observation that the completion of the monolayer precedes the formation of crystalline V_2O_5 [3]. Among these characterization methods, Raman spectroscopy has been found to be exceptionally sensitive to both the presence of the surface vanadia overlayer and the crystalline V_2O_5 phases. Monolayer surface coverage of the vanadia overlayer on different oxide supports was recently determined from Raman spectroscopy measurements and found to be approximately 7–8 VO_x per nm^2 [5,19]. The same monolayer surface VO_x coverage was found for different oxide supports (Al_2O_3, TiO_2, ZrO_2, Nb_2O_5 and CeO_2) with the exception of silica supported vanadia, which exhibited a maximum surface coverage of only 0.7 VO_x per nm^2. The much lower monolayer surface coverage on silica is due to the somewhat lower density and reactivity of the silica surface hydroxyls since the surface vanadia species titrate the oxide support hydroxyls upon anchoring to the support [5]. Certain preparation methods, however, can enhance the surface coverage of the surface vanadia species on silica [5]. These preparation methods involve the use of silica supports that possess a high surface concentration of hydroxyls [21], nonaqueous preparations involving reactive organometallic precursors [22,23] and electrochemical deposition of oxides in reduced oxidation states [24]. These preparation methods increase the surface vanadia coverage on silica to approximately 2–3 VO_x per nm^2 [21,25], which happens to correspond to the calculated surface density of isolated vanadate species. Furthermore, the monolayer surface coverage of the supported vanadia catalysts, $\sim$7–8 VO_x per nm^2, is approximately twice as that found for other supported metal oxide catalysts (oxides of Mo, Cr, Nb, W and Re), and suggests the presence of a closed packed monolayer for the surface vanadia species [5].

The above experimental determinations of monolayer surface vanadia coverage were experimentally determined for well-defined model supported vanadia catalysts that did not possess surface impurities. However, many commercial oxide supports, especially pigment grade titania, possess significant amounts of surface impurities (typically monolayer quantities). These surface impurities (e.g., P, K, Ca, Na, etc.) have a high affinity for vanadia and tend to readily complex with vanadia to form an amorphous phase [26]. In such impurity containing systems, the formation of crystalline V_2O_5 particles is delayed until the vanadia overlayer titrates the oxide support surface as well as the surface impurities. Consequently, it appears that the formation of several vanadia monolayers are required before the

formation of crystalline V_2O_5 as was demonstrated by HR-TEM studies for pigment grade titania supported vanadia catalysts [27]. Thus, the apparent monolayer surface vanadia coverage on impurity containing oxide supports can be about 2–4 times greater than that found for the well-defined model supported vanadia catalysts.

3. Stability of the surface vanadia monolayer

The surface vanadia monolayer is stable after its initial formation on many typical oxide supports (Al_2O_3, TiO_2, ZrO_2, Nb_2O_5 and CeO_2). The driving force for the stability of the surface vanadia monolayer is the lower free energy of this structural arrangement than the exposed high surface area oxide supports [28]. This driving force is so strong that the surface vanadia monolayer is spontaneously formed from thermal treatments of physical mixtures of the oxide support and crystalline V_2O_5 [28–30]. In the case of silica, the surface vanadia species will migrate to other oxide supports due to a repulsion between silica and vanadia and the strong driving force to form a stable monolayer on other oxide supports [31]. This repulsion between the surface vanadia species and silica is also responsible for the transformation of surface vanadia species on silica to large crystalline V_2O_5 particles when small V_2O_5 crystallites are present [32]. The surface vanadia monolayer on oxide supports is also stable under reducing and reaction environments. XPS measurements possess the same surface V/support cation ratio for both oxidized and hydrogen reduced catalysts reflecting no change in the dispersion of the surface vanadia overlayer upon reduction [33]. In situ Raman studies reveal that the surface vanadia monolayer is also stable and not converted to crystalline V_2O_5 particles during oxidation reactions: methanol [34], methane [35], butane [36], butene [36] and SCR of NO_x with NH_3 [37,38]. 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 [39]. In the case of V_2O_5/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 [1,2,6,7]. The stability of the surface vanadia monolayers is reflected in the long life of such industrial oxidation catalysts [6–12].

4. Oxidation state of calcined surface vanadia monolayer

There has been some discussion over the years about the oxidation state of the surface vanadia species in calcined supported vanadia catalysts [4]. Only V(5+) is observed in calcined supported vanadia catalysts by XPS, when the sample is not

artificially reduced by the measuring conditions, and only traces of V(4+) are detected in EPR and UV–VIS DRS measurements. Furthermore, calcined supported vanadia catalysts give rise to solid state ^{51}V NMR signals which cannot be obtained for V(4+) species, and the presence of V(4+) species would also broaden the ^{51}V NMR signal of the V(5+) species [21]. However, chemical titration of extracted vanadia by H_2SO_4 has suggested that the surface vanadia species in the monolayer are present as V(4+) [41]. Recent characterization of a standard supported vanadia catalyst, EUROCAT OXIDE vanadia–titania catalyst, has demonstrated that this chemical titration method may actually result in the reduction of the V(5+) species by sulfuric acid and that extreme care must be taken when employing this method since it may not lead to reproducible results [4]. Thus, calcined supported vanadia catalysts possess V(5+) species with only trace amounts of V(4+) species.

5. Molecular structures of surface vanadia species

The molecular structures of the surface vanadia species have been extensively investigated in the past few years with many different spectroscopies [3]: Raman [5,42], IR [5,43], XANES/EXAFS [44], solid state ^{51}V NMR [21,45,46], UV–VIS DRS [47,48], chemiluminescence [49,50] and EPR [51]. These studies have 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, moisture and temperature). Unfortunately, the dynamic nature of the surface vanadia species has resulted in some confusion in the published literature since many studies have compared measurements taken under different experimental conditions (in many cases even in the same study). In order to minimize such problems, the present paper will only focus on experimental results under well-defined environments.

5.1. 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 [5].

5.1.1. V_2O_5/SiO_2

The dehydrated silica supported vanadia catalyst system has been characterized by all the molecular spectroscopies already mentioned above [3,5,42–51], with the exception of IR spectroscopy because of the overlap of the silica support IR absorption bands with the vibrations of the surface vanadia species [3]. There is

unanimous agreement among all researchers that the surface vanadia species on silica consists of isolated VO_x units containing one terminal V=O bond and three bridging V–O–Si bonds (trigonal pyramidal coordination). It is interesting that the maximum surface vanadia coverage achieved to date on silica, 2–3 VO_x per nm^2, corresponds to that expected for isolated surface VO_x units [2,4,21,25]. Future studies will determine if this is just coincidental or the maximum surface coverage for isolated surface VO_4 units in a monolayer.

5.1.2. $V_2O_5/(Al_2O_3, TiO_2, ZrO_2, Nb_2O_5$ and $CeO_2)$

The dehydrated surface vanadia species on other oxide supports all essentially possess identical molecular structures as probed by Raman [3,42,43], IR [3,43], and solid state ^{51}V NMR [45,52]. These molecular structural studies suggest that the dehydrated surface vanadia species on these oxide supports are primarily present as isolated and polymerized VO_4 units. The relative concentrations of isolated and polymerized surface vanadia species have not been quantified by the above Raman studies. Oxygen-18 isotopic labeling experiments demonstrated that these surface vanadia species only possess one terminal V=O bond [37,53]. 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 bonds for the isolated species, and a terminal V=O bond with one 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 mono-layer coverages, but additional studies are required to establish this possibility [42,47].

5.1.3. V_2O_5/MgO

Unlike the above supported vanadia catalysts, the magnesia supported vanadia catalyst system cannot form a complete close packed surface vanadia monolayer because of the acid–base reaction between acidic vanadia and basic magnesia [40]. 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 [40,52]. 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.

5.2. Oxygen/steam environments

Moisture is usually present in many oxidation reactions as a component in the feed as well as a product of the reaction. The influence of oxygen/steam environments at elevated temperatures, 120–500°C, upon the dehydrated surface vanadia species was recently investigated with in situ Raman spectroscopy [54]. For the silica supported vanadia catalysts, moisture had no effect on the Raman spectrum reflecting the hydrophobic nature of the dehydroxylated silica surface.

For the other supported vanadia catalysts (V_2O_5 on Al_2O_3, TiO_2, Nb_2O_5 and CeO_2), the presence of flowing oxygen/steam had an effect on the surface vanadia species. Above 300°C, the surface vanadia species retained their molecular structures and the Raman band of the terminal V=O bond only shifted downward by several cm^{-1}. The slight shift is due to hydrogen bonding of small amounts of moisture present on the surface at these elevated temperatures. Isotopic oxygen exchange experiments revealed that the reversibly adsorbed moisture is also able to rapidly undergo oxygen exchange with the terminal V=O bond at these high temperatures. At approximately 200°C and below, the Raman band of the terminal V=O bond significantly shifted downward due to monolayer quantities of adsorbed moisture. Thus, at these lower temperatures the surface vanadia species present in these supported vanadia catalysts become extensively solvated in the presence of moisture.

5.3. Ambient conditions

Ambient conditions corresponds to room temperature and ambient air. The ambient air contains moisture which readily adsorbs on the surface of the supported vanadia catalysts at room temperatures [3,5]. The amount of adsorbed moisture from ambient conditions corresponds to many monolayers-equivalent of water. Under these conditions the bridging V–O-support bonds are hydrolyzed by the moisture and the solvated surface vanadia species dissolve in the thin aqueous layer. These molecular structural transformations are readily monitored by Raman [5], solid state [51]V NMR [21,45], XANES/EXAFS [44] and UV–VIS DRS [47]. The molecular structures of the solvated surface vanadia species are determined by the net pH of the aqueous thin film, which depends on the surface point of zero charge of the oxide support and the amount of the surface vanadia species. The molecular structures present under ambient conditions correspond to the typical vanadium oxide structures found in aqueous solution: orthovanadate (VO_4), pyrovanadate (V_2O_7), metavanadate ($VO_3)_n$ and decavanadate ($V_{10}O_{28}^{6-}$). The hydration–dehydration processes of the supported vanadia catalysts are completely reversible.

5.4. Reducing environments

Exposure of the surface vanadia (5+) species to reducing H_2 and CO environments results in the formation of surface vanadia (4+) and vanadia (3+) species [55–57]. The oxide supports (Al_2O_3, TiO_2, ZrO_2 and SiO_2) are not reduced during the reduction of the surface vanadia species with the exception of CeO_2, which exhibits the presence of minor amounts of reduced Ce(3+) [33]. The average oxidation states of the reduced surface vanadia species have been determined by temperature programmed reduction (TPR) and gravimetric measurements (primarily for alumina and silica catalysts) [55]. More specific information about the

distribution of oxidation states has been obtained with XPS and UV–VIS DRS studies [33,56]. However, there currently appears to be a lack of consensus among these publications as to the distribution of the V(4+) and V(3+) species. It is clear that a systematic series of studies are needed to quantify the influence of various parameters (reducing environment, surface vanadia coverage, specific oxide support, etc.) upon the distribution of the reduced surface vanadia (4+) and (3+) species in supported vanadia catalysts.

Direct information about the molecular structures of the reduced surface vanadia species can be obtained from in situ EPR for isolated V(4+) [2,47,57], and UV–VIS DRS measurements for V(4+,3+) [47,56,57] and XANES/EXAFS for V(4+,3+) (no known studies at this point). The published EPR studies have detected V(4+) species in supported vanadia catalysts, but there does not appear to be any consensus about the structural assignments: distorted VO$_6$, square-pyramidal VO$_5$ or trigonal-pyramidal VO$_4$ V(4+) species [57]. For the vanadia–titania system, Paganini et al. recently summarized the current status of the EPR literature: "A scrutiny of the EPR literature in the field indicates however that the values reported for the spectral parameters ... of V(IV) on TiO$_2$ are rather spread. This is certainly due to the complexity of the system (heterogeneity of the surface with simultaneous presence of several species) but also to a certain approximation used sometimes to derive the parameters from the experimental spectra. The EPR spectra of V(IV) in fact are complicated by the high number of hyperfine levels ... and by the second order effects that tend to produce an asymmetric hyperfine structure with unequal separation of the various lines. In this situation the use of a computer simulation to correctly derive the parameters from the experimental spectra is needed but has been seldom used ...". Thus, more detailed EPR studies with well-defined model supported vanadia catalysts are required to reliably extract the fundamental coordination information about the reduced surface V(4+) species. The published UV–VIS DRS studies only report oxidation states and do not discuss the coordination of the reduced surface vanadia species [56,57]. Thus, dependable studies addressing the molecular structures of the reduced surface vanadia species are rare at present and a more systematic series of experiments are required to determine the influence of various variables (specific oxide support, specific reducing gas, steam, temperature, etc.).

5.5. 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 [35]. Even exposing the supported vanadia catalysts to a reducing methane stream in the absence of oxygen only slightly

reduces the surface vanadia species for V_2O_5/TiO_2 and V_2O_5/CeO_2, but no measurable reduction was detected for the surface vanadia species in the case of silica supported vanadia catalysts. The stability of the V(5+) surface vanadia species during methane oxidation reflects the weak reducing power of methane compared to other hydrocarbons (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, $\sim$10–35% decrease in the Raman signal, for all supported vanadia catalysts with the exception of V_2O_5/SiO_2 [36]. 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 coverages, during butane oxidation follows the pattern: $TiO_2 > CeO_2 > ZrO_2 > Al_2O_3 > SiO_2$. However, the surface vanadia coverage was also found to be a critical variable since the polymerized surface vanadia species, which are more concentrated at higher surface concentrations, are more easily reduced than the isolated surface vanadia species. 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 [36]. During methanol oxidation to formaldehyde, the reduction of the V(5+) surface vanadia species was more extensive, 30–60% decrease in the Raman signal, for all the supported vanadia catalysts with the exception of V_2O_5/SiO_2 [58]. In the case of silica supported vanadia, the surface vanadia species remained in the V(5+) oxidation state and formed stable vanadyl methoxy species [34]. The surface vanadia species could be completely reduced in a methanol stream in the absence of oxygen. Thus, the in situ Raman studies provide new insights into the behavior of surface vanadia species during hydrocarbon oxidation reactions: (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 (methanol > butene > butane > methane), (3) the specific oxide support and (4) the ratio of polymerized to isolated surface vanadia species (polymerized > isolated). The greater stability of the V(5+) silica supported vanadia species may be directly related to the fact that only isolated surface vanadia species are present in this catalyst.

The in situ Raman studies, however, did not provide any molecular structural information about the reduced surface V(4+) or V(3+) species formed during the hydrocarbon oxidation reactions since no new Raman bands were observed [35,36,58]. It appears that the reduced V(4+) or V(3+) surface vanadia species in the supported vanadia catalysts do not give rise to strong and detectable Raman signals. Molecular structural information about the reduced surface vanadia species present under reaction conditions can be obtained from in situ UV–VIS DRS and EXAFS/XANES experiments, but such studies are currently not available in the literature. Thus, our fundamental knowledge of supported vanadia

catalysts will be further advanced once information becomes available about the molecular structures of the in situ reduced surface vanadia species during hydrocarbon oxidation reactions.

5.6. Influence of metal oxide additives

5.6.1. 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 [59–62]. 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. In the case of silica supported vanadia catalysts, the addition of surface molybdena species did not alter the surface vanadia structure since only isolated surface vanadia species were present with and without the additive [35].

5.6.2. Interacting additives

Interacting additives are defined as surface metal oxides that preferentially coordinate with the surface vanadia species rather than the oxide support under dehydrated conditions. Typical interacting additives are P and alkali/alkaline earth oxides (K, Na, Ca, etc.) that tend to complex with the acidic surface vanadia species [59,62]. The basic alkali/alkaline 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 [52,59,62]. 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 $VOPO_4$ phases, at the expense of the surface vanadia phase, after calcination due to the strong interaction between these two oxides [14,59]. The formation of crystalline $VOPO_4$ 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 [59]. In the case of silica supported vanadia catalysts, the weak interaction between silica and the surface metal oxides and the significant mobility of the surface metal oxide species results in the formation of crystalline vanadate compounds for P as well as the alkali/alkaline earth additives independent of the order of introduction of the additives [14]. 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.

5.6.3. Pigment grade oxide supports

Pigment grade oxide supports, especially titania, contain monolayer quantities of surface impurities. For example, in the V_2O_5/TiO_2 EUROCAT OXIDE catalyst study the presence of significant amounts of surface P, K, Nb, Si, Ca, Na, Fe and Cr were found in the catalysts [4]. These impurities typically arise from either the manufacturing processes employed to produce pigment grade titania or are added to passivate the surface photocatalytic activity of these materials [63]. Anatase pigments are generally precipitated from a sulfuric acid solution at relatively mild temperatures and surface additives such as P, K, Nb, Si, Ca and Na are added to suppress their surface photocatalytic activity. Rutile pigments are formed at very high temperatures from oxidation of $TiCl_3$ in the presence of small amounts of $AlCl_3$ and, consequently, their surfaces are usually covered by a significant amount of alumina as well as other impurities (Cl and Si). The presence of significant amounts of multiple surface impurities on such pigment grade titanias and the interactions among these impurities may create multiple surface vanadia species, which greatly complicates the molecular structural analysis. The V_2O_5/TiO_2 EUROCAT OXIDE catalyst studies employed pigment grade TiO_2 (anatase) and were primarily characterized under ambient conditions where the samples are hydrated. The solid state ^{51}V NMR measurements revealed that the hydrated surface vanadia species in the V_2O_5/TiO_2 EUROCAT OXIDE catalysts were primarily present in an octahedral coordination as would be expected for a hydrated oxide surface possessing a net surface pH at point of zero charge of less than ~6 [3]. The coordination of the dehydrated surface vanadia species in the V_2O_5/TiO_2 EUROCAT OXIDE catalysts was not determined with ^{51}V NMR and in situ FT-Raman measurements revealed the presence of a terminal V=O bond, which may represent only a fraction of the total surface vanadia species present. Thus, the molecular structures of surface vanadia species in pigment grade TiO_2, especially anatase, are still not well understood.

5.7. Influence of preparation methods

The influence of preparation methods upon the molecular structure of the hydrated and dehydrated surface vanadia species has also been examined [3,5,28,64,65]. Many different synthesis methods have been used in the preparation of supported vanadia catalysts: vapor phase grafting with $VOCl_3$ [55,66], nonaqueous impregnation with vanadium alkoxides [19,59] and vanadium acetate [67], aqueous impregnation of vanadium oxalate [68], as well as dry impregnation with crystalline V_2O_5 [28,65,69]. Commercial preparations usually employ aqueous impregnation with vanadium oxalate because of its high solubility in water and the absence of undesirable volatile organic solvents. However, some researchers have claimed that certain preparations may result in superior catalytic properties [66]. A series of titania supported vanadia catalysts were synthesized by the various preparation methods mentioned above and molecularly characterized with

Raman spectroscopy and solid state [51]V NMR, both under ambient and dehydrated conditions [64]. All the catalysts were found to contain the same surface vanadia species independent of the initial synthesis method after equilibration of the catalysts after prolonged calcination. The absence of a "preparation memory effect" is due to the high mobility of V_2O_5 (Tamman temperature of 370°C) and the strong driving force of the mixed oxide system to lower its surface free energy by forming a monolayer of surface vanadia species, which possesses a low surface free energy, on the high surface free energy oxide support [28,65]. The formation of the monolayer is even observed during hydrocarbon oxidation reactions over physical mixtures of V_2O_5 and TiO_2 [30]. Thus, the same thermodynamically stable surface metal oxide species are formed independent of the specific synthesis method. In the case of silica supported vanadia catalysts, where different preparation methods can affect the surface coverage of the surface vanadia species, the same isolated surface vanadia species results from all the different syntheses [21,25,42,44,48].

5.8. Influence of the specific structure of the oxide support

The influence of the specific structure or modification of the oxide support upon the molecular structure of the dehydrated surface vanadia species on well-defined TiO_2 supports (anatase, rutile, brookite and B) was investigated with solid state [51]V NMR and Raman spectroscopy [70]. The same dehydrated surface vanadia species, already discussed above in Section 5.1.2, were found to be present on all the different TiO_2 modifications suggesting that there is no effect of long range order of the oxide substrate upon the local structure of the surface vanadia species. It may also be possible that the different oxide support surfaces restructure to the same equilibrated structure due to the strong interaction with the surface vanadia overlayer, but no fundamental information is currently available about the surface structures of typical oxide supports. However, many publications usually assume that the surface structures of oxides are just simple extensions of the bulk oxide structures without any direct knowledge. Fundamental surface science studies employing single crystal oxide supports should be able to provide some insight into this issue [71].

For pigment grade titania, it has been proposed in the literature that the surface vanadia phase possesses a different structure on TiO_2 (anatase) and TiO_2 (rutile) [72]: an epitaxial V_2O_5 layer forms on anatase because of the crystallographic match of these two oxides, but not on rutile because of the absence of a crystallographic fit. However, this early model neglected two critical issues (1) the oxide supports are in direct contact with an amorphous surface vanadia phase rather than crystalline V_2O_5 and (2) the pigment grade TiO_2 anatase and rutile supports employed in the study were contaminated with monolayer levels of different surface impurities, which prevented direct contact between the oxide supports and the crystalline V_2O_5 particles. This study demonstrates why

special care must be exercised when investigating pigment grade oxide support materials.

5.9. Dissolved vanadia species

In addition to the surface vanadia species discussed above, some studies have proposed that dissolved vanadia species may also coexist in the titania support when a surface vanadia monolayer is formed [73,74]. Electrical conductivity measurements have shown a significant increase in the electrical conductivity of TiO_2 upon the addition of a surface vanadia monolayer [4,73]. The increase in electrical conductivity has been proposed to originate from the incorporation of isolated V(5+) species into the top layer of the titania support because a free electron is necessary to compensate for the V(5+) in the Ti(4+) matrix. However, no direct spectroscopic identification or molecular structural determination of such incorporated V(5+) species are available at present. Electrochemical reduction of aqueous vanadia in the presence of a single crystal of TiO_2 (rutile) has shown the incorporation of several equivalent monolayers of V(4+) into the TiO_2 (rutile) matrix before the formation of a V(5+) monolayer [74]. This situation does not appear to occur to a great extent with TiO_2 (rutile) powders employing conventional catalyst synthesis methods since a monolayer of surface vanadia V(5+) is readily formed upon calcination [70]. Centi et al. report that minor amounts of dissolved V(4+) species are present in V_2O_5/TiO_2 (rutile) catalysts, but not in V_2O_5/TiO_2 (anatase) catalysts after *o*-xylene oxidation [74]. Several studies have also demonstrated that interstitial V(5+) species are present in V_2O_5/TiO_2 (anatase) catalysts that are synthesized via coprecipitation of vanadia and titania salts [74]. However, conventional catalyst synthesis methods employ deposition of vanadia on a preformed titania support rather than coprecipitation and, consequently, should not contain dissolved V(5+) species. Additional direct spectroscopic information is needed about the quantity and structure of dissolved vanadia species in titania supports to fully understand these complex oxide systems.

6. Acidity of surface vanadia species

The oxide supports only possess surface Lewis acid sites and the relative strength of these sites is $Al_2O_3 > Nb_2O_5 > TiO_2 > ZrO_2$, and no surface Lewis acid sites are detected for SiO_2 [75]. In contrast to the oxide supports, unsupported V_2O_5 crystalline powders possess both surface Brønsted and surface Lewis acid sites [76]. The formation of the surface vanadia species on the oxide supports is accompanied by a decrease in the number of surface Lewis acid sites and an increase in the number of surface Brønsted acid sites [75,77]. Only a very small fraction of the surface vanadia species are also surface Brønsted acid sites since the

concentration of surface Brønsted acid sites, measured by pyridine adsorption, corresponds to only 5–10% of the surface vanadia species at monolayer coverage. The exact location of the surface Brønsted acid sites is not clear at present since solid state ^{1}H NMR studies cannot clearly discriminate between different locations due to similar NMR peak positions [78]. Several in situ IR studies have assigned an OH vibration for dehydrated titania supported vanadia catalysts to Brønsted V–OH sites [79,80]. However, for well-defined model supported vanadia catalysts, without surface impurities, no OH vibrations are observed at monolayer coverage due to titration of the support surface hydroxyls by the surface vanadia overlayer [75,81]. The acidic characteristics of the surface vanadia overlayer are influenced by the specific oxide support ligand, but the molecular structural characterization studies above (see Section 3) reveal that the same dehydrated surface vanadia species are present on all the oxide supports (with the exception of silica). This suggests that the surface Brønsted hydroxyls may be located as bridging V–OH-support sites, but no direct spectroscopic evidence is currently available to support any assignment for the location of the surface Brønsted acid site. Reduction of the surface vanadia species removes the surface Brønsted acid sites which are only present for the oxidized V(5+) surface vanadia species [82]. Thus, probing surface acidity with reducing probe molecules will alter the surface Brønsted acidity properties of the supported vanadia catalysts [4]. In contrast to the above supported vanadia catalysts, neither surface Brønsted or surface Lewis acid sites are detected for surface vanadia species on SiO_2 [37]. The absence of surface Brønsted acid sites for surface vanadia species on silica is in agreement with the acidic properties of other well-dispersed oxides on silica [75], and suggests that the presence of surface Brønsted acid sites occasionally reported for silica supported vanadia catalysts must be attributed to the presence of crystalline V_2O_5 particles or surface impurities. In summary, both the surface vanadia species and the crystalline V_2O_5 particles possess surface Brønsted acid sites, but surface vanadia species on SiO_2 do not possess surface Brønsted acid sites.

7. Reactivity of surface vanadia species

The in situ characterization studies (Section 5.5) revealed that dehydrated surface vanadia species are present during hydrocarbon oxidation reactions and, consequently, the reactivity properties need to be related to the dehydrated surface vanadia species. According to the Mars–Van Krevelen redox mechanism, the oxidation of hydrocarbons proceeds by two steps: (1) the reactant hydrocarbon molecule initially reduces an oxidized surface site and (2) the reduced surface site is subsequently reoxidized with gas phase molecular oxygen [83]. Thus, the reactivity properties of the supported vanadia catalysts will be compared with the structural properties of the dehydrated surface V(5+) species rather than the dehydrated, reduced surface vanadia V(4+) and V(3+) species.

7.1. Reduction studies

The reduction characteristics of supported vanadia catalysts have been investigated with different probe molecules: hydrogen, butane, and ammonia. Among these reduction studies, reduction with hydrogen is most common. Hydrogen temperature programmed reduction (TPR) studies of supported vanadia catalysts have been reported from several different laboratories with very similar trends for the ease of reduction [2,19,84–86]: $CeO_2 > ZrO_2 > TiO_2 > Al_2O_3 > SiO_2$. These results suggest that the reduction of the surface vanadia species is strongly influenced by the specific oxide support since the same dehydrated surface vanadia species are present on all the supports with the exception of silica. The hydrogen TPR studies could generally not discriminate between the reduction characteristics of isolated and polymerized surface vanadia species because only one hydrogen TPR peak was observed in these studies. A recent high resolution TPR study did reveal the presence of two reduction peaks for the surface vanadia species which may reflect the coexistence of isolated and polymerized surface vanadia species [55]. In situ Raman studies during the reduction of V_2O_5/TiO_2 catalysts revealed that both the isolated and polymerized surface vanadia species were about equally reduced by hydrogen [87]. In contrast, reduction with ammonia [88] or butane [89] exhibited preferential reduction of the polymerized surface vanadia species over the isolated surface vanadia species. The differences between hydrogen and ammonia or butane may be related to the stronger reducing properties of hydrogen which may not be very discriminating among the different surface vanadia sites.

The influence of surface metal oxide additives, support phase and preparation methods upon the reduction of supported vanadia catalysts has also received some attention. The addition of noninteracting additives to supported vanadia catalysts (e.g., WO_3 to V_2O_5/TiO_2) slightly enhanced the reduction of the surface vanadia species [90]. The same effect is also observed when the surface metal oxide coverage is increased due to lateral interactions in the monolayer and the reduced number of surface hydroxyl groups [91]. The introduction of interacting surface additives such as K significantly retard the reduction of the surface vanadia species, but the introduction of surface P had only a slight effect on the reduction of the surface vanadia species [92]. Unfortunately, no characterization studies were performed on the P doped vanadia–titania catalyst to determine if this additive was interacting with the surface vanadia species. The reduction characteristics of the titania supported surface vanadia phase only varied slightly with the support type (TiO_2(P-25), TiO_2 (Eurotitania) and TiO_2 (anatase, washed)) [93]. The slight variations in the reduction properties of the surface vanadia species were most probably associated with residual surface impurities present in the anatase and Eurotitania supports. Different precursors, $VOCl_3$ and $VO(O^iBu)_3$, were used to graft vanadia to titania supports, but the specific preparation method had essentially no effect on the reduction characteristics of the surface vanadia species [93].

Thus, the reduction characteristics of the surface vanadia species are not sensitive to the specific preparation methods or the specific structure of the oxide support, but are very sensitive to the presence of surface metal oxide additives (especially interacting basic surface oxides).

7.2. Hydrocarbon oxidation reactions

The catalytic properties of well-defined model supported vanadia catalysts have recently been investigated for several different hydrocarbon oxidation reactions: methanol oxidation to formaldehyde, methane oxidation to formaldehyde, propane oxidative dehydrogenation to propene, butane oxidative dehydrogenation to butene and butane partial oxidation to maleic anhydride. The reactivity properties of these catalysts will be compared with the corresponding structural information presented above (see Section 5) in order to develop molecular structure-reactivity/selectivity relationships for supported vanadia catalysts during hydrocarbon oxidation reactions.

7.2.1. Role of terminal V=O bonds

The terminal V=O bonds have been proposed by many investigators to contain the critical oxygen involved in hydrocarbon oxidation reactions over supported vanadia catalysts [4]. However, the combination of in situ Raman and hydrocarbon oxidation reactivity studies have recently suggested that the reaction properties are not related to the characteristics of the terminal V=O bonds in supported vanadia catalysts. Butane oxidation over a series of supported vanadia catalysts was found to vary by over an order of magnitude in TOF, but identical V=O Raman features were observed for these catalysts [36]. A similar lack of correlation between the terminal V=O bond Raman characteristics and methanol oxidation TOF was also found for supported vanadia catalysts [19]. Furthermore, oxygen-18 labeling of the terminal V=O bond during butane oxidation revealed that this bond is very stable and has an exchange time that is approximately 20 times longer than the characteristic reaction time [36]. Consequently, the available data suggests that the terminal V=O bonds do not contain the critical oxygen that affects the reactivity of supported vanadia catalysts during hydrocarbon oxidation reactions.

7.2.2. Role of bridging V–O–V bonds

The surface concentration of bridging V–O–V bonds increases with surface vanadia coverage due to the increase in the ratio of polymerized to isolated surface vanadia species with the exception of V_2O_5/SiO_2 (see Section 5.1 above). The TOF for the oxidation of methanol to formaldehyde over V_2O_5/TiO_2, as well as other supported vanadia catalysts, is independent of the surface vanadia coverage indicating that the oxygen associated with the bridging functionality does not

critically affect this reaction [9]. Similarly, the TOF for the oxidative dehydrogenation of propane to propylene over V_2O_5/Nb_2O_5 was not dependent on the concentration of the bridging V–O–V bonds [94]. For hydrocarbon oxidation reactions where the TOF increases with surface vanadia coverage it is not clear if this trend is due to an increase in the surface concentration of bridging V–O–V bonds or other factors (e.g., surface acidity, lateral interactions, number of active sites, etc.). The TOFs for the oxidative dehydrogenation of propane to propylene and butane to butene over V_2O_5/Al_2O_3 were found to increase with surface vanadia coverage, by as much as an order of magnitude, suggesting that other factors may also play a role for alumina supported vanadia catalysts [13,95,96]. The TOF for the oxidation of butane to maleic anhydride over V_2O_5/TiO_2 was also found to slightly increase, by a factor of 2–3, with surface vanadia coverage because of the requirement of several surface vanadia sites for this hydrocarbon oxidation reaction (see discussion below) [36]. Although the bridging V–O–V bonds do not appear to significantly influence many of the oxidation reactions, more systematic studies with well-defined model supported vanadia catalysts are required to fully understand the role of bridging V–O–V bonds in hydrocarbon oxidation reactions.

7.2.3. Role of bridging V–O-support bonds

The characteristics of the bridging V–O-support bond can be altered by varying the specific oxide support or oxide support ligands without changing the structure of the surface vanadia species (with the exception of silica). The bridging V–O-support bond appears to be associated with the critical oxygen required for hydrocarbon oxidation reactions since changing the specific oxide support dramatically affects the TOF: approximately four orders of magnitude for methanol oxidation to formaldehyde [19] and two-orders of magnitude for butane oxidation to maleic anhydride [36]. The general trend appears to be $CeO_2>ZrO_2\sim TiO_2>Nb_2O_5>Al_2O_5>SiO_2$, which inversely correlates with the Sanderson electronegativity of the oxide support cations [97]. This suggests that bridging oxygens in V–O-support bonds that are more electronegative or basic, corresponding to oxide support cations with a lower electronegativity, are associated with the critical oxygen required for hydrocarbon oxidation reactions over supported vanadia catalysts.

7.2.4. Number of surface vanadia sites

Information about the number of critical surface vanadia sites required in hydrocarbon oxidation reactions can also be obtained by examination of the variation of the TOF with surface vanadia coverage. In general, reactions requiring only one surface site will exhibit a TOF that is independent of surface vanadia coverage. The invariance of the TOF for methanol oxidation to formaldehyde with surface vanadia coverage over supported vanadia catalysts suggests that only one surface vanadia site is required for this reaction. This observation is consistent with

IR studies that have shown that surface methoxy is coordinated to only a single surface vanadia site [98]. The oxidation of methane to formaldehyde over V_2O_5/SiO_2 catalysts also exhibits a constant TOF with surface vanadia coverage suggesting that only one surface vanadia site is involved with this reaction, and is consistent with the isolated nature of the surface vanadia species on silica [35]. The invariance of the TOF for the oxidative dehydrogenation of propane to propylene over V_2O_5/TiO_2 as a function of surface vanadia coverage also suggests that only one surface vanadia site is required for this reaction [94]. An increase in the TOF with the surface vanadia coverage may reflect the requirement of multiple surface vanadia sites or the influence of other factors (e.g., surface acidity, influence of bridging V–O–V bonds, structural changes, etc.). Some of these other factors can be discriminated with the addition of metal oxide additives to the supported vanadia catalysts as discussed below.

7.2.5. Influence of metal oxide additives

Information about the number of surface sites required for hydrocarbon oxidation reactions can also be probed by the addition of noninteracting surface metal oxide additives. The addition of surface niobia is especially informative since it has a minimal effect on the surface vanadia structure, see Section 5.6 above, and its presence primarily increases the number of adjacent surface metal oxide sites for the surface vanadia species. The introduction of surface niobia species to V_2O_5/TiO_2 catalysts does not affect the TOF for methanol oxidation and is consistent with the above conclusion that only one surface vanadia site is required for this reaction [59]. In contrast, the addition of the surface niobia species to V_2O_5/TiO_2 catalysts increases the TOF for the oxidation of butane to maleic anhydride [36]. This increase in TOF reflects the requirement of multiple surface metal oxide sites for this hydrocarbon oxidation reaction. In contrast to noninteracting additives that mainly affect oxidation reactions requiring multiple surface sites, interacting additives affect all hydrocarbon oxidation reactions since they directly alter the structure and reactivity of the surface vanadia sites. As mentioned above (see Section 7.1), interacting additives and especially interacting basic surface oxides retard the reduction of surface vanadia species. Consequently, the TOFs for all hydrocarbon oxidation reactions are decreased when basic additives are introduced. The negative effect of the basic additives on the TOFs for methanol oxidation and propane oxidation over V_2O_5/TiO_2 catalysts have been reported in the literature [59,99]. In the case of V_2O_5/SiO_2, the situation is even more drastic since the basic metal oxide additives also convert the two-dimensional surface vanadia species to three-dimensional crystalline mixed metal oxide phases [100]. Interacting acidic additives such as P may have a different effect on various oxidation reactions. For methanol oxidation to formaldehyde, the presence of surface phosphate species slightly decreases the TOF [59]. However, for butane oxidation to maleic anhydride the presence of surface phosphate species increases the TOF [36].

7.2.6. Influence of surface acid and basic sites

The surface vanadia species possesses both Lewis and Brønsted acid properties and the ratio of Brønsted acidity to Lewis acidity increases with surface vanadia coverage (see discussion above in Section 6). However, neither of these characteristics appear to influence the oxidation of methanol to formaldehyde [19] and the oxidative dehydrogenation of propane to propylene [94] over V_2O_5/TiO_2 since these oxidation reactions exhibit the same behavior at all surface vanadia coverages. The oxidation of butane to maleic anhydride does show a slight enhancement in activity and selectivity with surface vanadia coverage, but this is mostly due to the requirement of multiple surface vanadia sites for this reaction rather than surface acidity properties [36]. The acidity and basicity of the noninteracting and interacting additives also affect the activity and selectivity properties of the surface vanadia species on titania during hydrocarbon oxidation reactions (see Section 7.2.5 above for their influence on activity). The surface niobia species, a noninteracting additive possessing Lewis acidity [75], has no effect on the selectivity of formaldehyde during methanol oxidation [59], but does have a positive effect on the maleic anhydride selectivity during butane oxidation [36]. The formaldehyde selectivity during methanol oxidation is slightly enhanced by the presence of basic interacting additives and decreased by the presence of acidic interacting additives [59]. The propylene selectivity during propane oxidative dehydrogenation is enhanced by the presence of basic interacting additives [99]. In contrast, the maleic anhydride selectivity during butane oxidation is enhanced by the presence of acidic interacting additives [36]. It is tempting to conclude from this limited data that the selectivity of oxidative dehydrogenation reactions, oxidation of methanol to formaldehyde and propane to propylene, is enhanced by basic additives and that the selectivity of hydrogen abstraction-oxygen insertion reactions, butane oxidation to maleic anhydride, is enhanced by acidic additives. However, many more hydrocarbon oxidation reactions need to be examined before these observations can be generalized.

7.2.7. Influence of the specific structure of the oxide support

Methanol oxidation over a series of V_2O_5/TiO_2 catalysts possessing different titania structures (anatase, rutile, brookite and B) was recently investigated. The characterization studies, reported above in Section 5.8, demonstrated that the same surface vanadia species are present on the different titania support modifications. The reactivity of these supported vanadia catalysts was probed by methanol oxidation [70]. The methanol oxidation to formaldehyde studies revealed that essentially the same TOF was obtained for all the different V_2O_5/TiO_2 catalysts. A similar conclusion was reached for o-xylene oxidation over V_2O_5/TiO_2 catalysts containing anatase and rutile titania [101]. Thus, the specific structure of the oxide support does not appear to affect the reactivity of the surface vanadia species.

7.2.8. Dissolved vanadia species

An increase in electrical conductivity of TiO_2 is observed upon the addition of a surface vanadia monolayer to titania, see Section 5.9 above. This increase in electrical conductivity is attributed to the incorporation of isolated V(5+) species into the top layer of the titania support [73]. It has been hypothesized that this increase in electrical conductivity of vanadia–titania catalysts may influence their catalytic properties [4]. Comparison of the electrical conductivity properties and the corresponding methanol oxidation TOFs for a series of V_2O_5/TiO_2 catalysts demonstrated that there is no relation between these two parameters [102]. The presence of significant amounts, monolayer quantities, of dissolved V(4+) species in V_2O_5/TiO_2 (rutile) catalysts has also recently been proposed by Haber [73]. However, the methanol oxidation catalytic data exhibited similar TOFs for V_2O_5/TiO_2 (rutile) and the other titania modifications, see Section 7.2.7 above, which suggests that only a trace amount of dissolved V(4+) species may be present in such a catalyst during hydrocarbon oxidation reactions.

8. Conclusions

Supported vanadia catalysts possess unique properties among supported metal oxide catalysts. The surface density of the surface vanadia monolayer is typically about twice that of other supported metal oxide catalysts (e.g., oxides of Mo, Cr, Re, etc.) [103]. The higher surface density of surface vanadia species increases the number of catalytic active sites and minimizes unwanted side reactions from exposed oxide support sites [104]. The weak acidic character of bulk vanadia relative to other transition metal oxides (e.g., oxides of Mo, Cr, Re, etc.) may also minimize unwanted side reactions [76,105]. Furthermore, the reactivity per site, the TOF, for the surface vanadia species in oxidation reactions is generally significantly greater than the corresponding TOF over supported molybdena and chromia catalysts [103,104]. As a result of these physical and chemical characteristics, supported vanadia catalysts tend to be among the most active and selective supported metal oxide catalysts for hydrocarbon oxidation reactions.

There has been significant progress in recent years in the determination of the molecular structures of the surface vanadia species present in supported metal oxide catalysts. Much has been learned about the structures of the surface V(5+) species. In contrast, there is still little known about the molecular structures of the reduced surface V(4+) and V(3+) species because these structures are more difficult to characterize. It is anticipated that much progress will also be seen in the near future in the determination of the molecular structures of the reduced surface vanadia species. More detailed molecular structural information is also anticipated from model single crystal studies employing surface science characterization techniques.

Comparison of the surface vanadia molecular structural information with the corresponding reactivity/selectivity information has provided some insights into the reactivity properties of the surface vanadia species. The terminal V=O bond does not appear to critically influence the reactivity properties of the surface vanadia species during hydrocarbon oxidation reactions. The bridging V–O–V bond also does not affect many oxidation reactions, but for those reactions that may be influenced by this bridging bond the TOF may only increase by as much as an order of magnitude. The bridging V–O-support bond, however, appears to be the most critical bond since its properties can change the TOF for hydrocarbon oxidation reactions by as much as four orders of magnitude. The specific phase of the oxide support as well as the specific preparation method do not appear to influence the molecular structure or reactivity of the surface vanadia species. The number of surface vanadia sites required for a hydrocarbon oxidation reaction is dependent on the specific reactant molecule. Oxidation reactions requiring only one surface vanadia sites are generally not sensitive to the surface vanadia coverage and the presence of noninteracting metal oxide additives. Oxidation reactions requiring multiple surface vanadia sites are very sensitive to surface vanadia coverage and the presence of noninteracting metal oxide additives. However, interacting additives influence all hydrocarbon oxidation reactions since they modify the surface vanadia sites. Acidic and basic additives also influence the selectivity of hydrocarbon oxidation reactions, but the effect appears to be reaction specific and cannot be generalized with the limited data currently available. Thus, the new fundamental insights into the structure and reactivity of surface vanadia species on oxide supports is establishing a foundation for the molecular engineering of such catalysts for hydrocarbon oxidation reactions. These insights will also assist the development of a solid theoretical foundation for the area of hydrocarbon oxidation reactions.

Pigment grade titanias possess monolayer quantities of impurities/metal oxide additives that greatly complicate the study of such oxide surfaces for supported vanadia catalysts [4]. Much more careful work is required to better understand the molecular structure-reactivity/selectivity properties of such industrially important hydrocarbon oxidation catalysts. It is especially important to distinguish between the findings of such complicated pigment grade supported vanadia catalysts and well-defined model supported vanadia catalysts in order to minimize the confusion in the literature.

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