

Molecular Engineering of Supported Metal Oxide Catalysts: Oxidation Reactions over Supported Vanadia Catalysts*

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1 Introduction

Supported metal oxide catalysts consist of an active metal oxide component (e.g., oxides of V, Mo, Cr, W, Re, etc.) deposited on the surface of an oxide support (e.g., Al_2O_3 , SiO_2 , TiO_2 , etc.). In certain instances, the supported metal oxide catalysts are also combined with noble metals in order to enhance the catalytic properties of the noble metal component (e.g., $\text{Pt/CeO}_2/\text{Al}_2\text{O}_3$ and $\text{Pt/SnO}_2/\text{Al}_2\text{O}_3$). Such catalysts are extensively employed in the chemical, petroleum and pollution control industries.¹⁻⁴ The industrial development of supported metal oxide catalysts over the past five decades is listed chronologically in Table 1. The $\text{V}_2\text{O}_5\text{-K}_2\text{S}_2\text{O}_7/\text{SiO}_2$ catalyst employed for sulfuric acid manufacture since ~1918, via the oxidation of SO_2 to SO_3 , is intentionally not listed in Table 1 because, unlike the other supported metal oxide catalysts, the active vanadia component is present as a molten salt under reaction conditions (supported liquid phase catalyst). The initial industrial applications of supported metal oxide catalysts were limited to hydrocarbon dehydrogenation/hydrogenation and olefin polymerization/metathesis reactions. In more recent years, the number of applications of supported metal oxide catalysts for oxidation reactions has grown significantly due to their excellent oxidation characteristics in the manufacture of certain chemical intermediates and pollution control strategies. Among the supported metal oxide catalysts employed for oxidation reactions, supported vanadia catalysts have emerged as the most versatile oxidation catalysts.⁵ For example, supported vanadia catalysts are industrially used to oxidize *o*-xylene to phthalic anhydride ($\text{V}_2\text{O}_5/\text{TiO}_2$),^{6,7} ammoxidation of alkyl aromatics to aromatic nitriles ($\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and $\text{V}_2\text{O}_5/\text{TiO}_2$)⁷ and the selective catalytic reduction (SCR) of NO_x emissions with NH_3 to N_2 ($\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ and $\text{V}_2\text{O}_5/\text{MoO}_3/\text{TiO}_2$)⁸. In conventional SCR applications, the oxidation of the SO_2 in the flue gas to SO_3 is minimized because of the potential formation of deleterious ammonium sulfates, but in the DESONOX process the oxidation of SO_2 to SO_3 is desired for the simultaneous manufacture of sulfuric acid ($\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$)⁹. In addition to the current commercial applications,

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supported vanadia catalysts are also capable of performing many other oxidation reactions: oxidation of methane to formaldehyde (V_2O_5/SiO_2),¹⁰ oxidation of ethane to ethylene (V_2O_5/SiO_2),¹¹ oxidation of propane to propylene (V_2O_5/Nb_2O_5),¹²⁻¹⁴ oxidation of butane to butenes,^{15,16} oxidation of butane to maleic anhydride ($V_2O_5/P_2O_5/TiO_2$, $V_2O_5/P_2O_5/Al_2O_3$, and $V_2O_5/P_2O_5/SiO_2$)¹⁷⁻²⁰ and pentane oxidation to maleic anhydride and phthalic anhydride.²¹

The present chapter will primarily focus on oxidation reactions over supported vanadia catalysts because of the widespread applications of these interesting catalytic materials.^{5,6,22-24} Although this article is limited to well-defined supported vanadia catalysts, the supported vanadia catalysts are model catalyst systems that are also representative of other supported metal oxide catalysts employed in oxidation reactions (e.g., Mo, Cr, Re, etc.).^{25,26} The key chemical probe reaction to be employed in this chapter will be methanol oxidation to formaldehyde, but other oxidation reactions will also be discussed (methane oxidation to formaldehyde, propane oxidation to propylene, butane oxidation to maleic anhydride, CO oxidation to CO_2 , SO_2 oxidation to SO_3 and the selective catalytic reduction of NO_x with NH_3 to N_2 and H_2O). This chapter will combine the molecular structural and reactivity information of well-defined supported vanadia catalysts in order to develop the molecular structure-reactivity relationships for these oxidation catalysts. The molecular structure-reactivity relationships represent the molecular ingredients required for the molecular engineering of supported metal oxide catalysts.

Table 1 Industrial Development of Supported Metal Oxide Catalysis

1940's -	CrO_3/Al_2O_3	n-butane dehydrogenation to butene
1950's -	CrO_3/SiO_2	ethylene polymerization
1960's -	MO_3/Al_2O_3	hydrodesulfurization (HDS) of Crude Oil
-	WO_3/Al_2O_3	hydrodesulfurization (HDS) of Crude Oil
-	MoO_3/Al_2O_3	higher n-alkane dehydrogenation
-	V_2O_5/TiO_2	oxidation of o-xylene to phthalic anhydride
1970's -	TiO_2/SiO_2	epoxidation of propylene by hydrogen peroxide
-	Re_2O_7/Al_2O_3	olefin metathesis
-	$V_2O_5/WO_3/TiO_2$	selective catalytic reduction (SCR) of NO_x emissions
-	$Pt/Pd/Rh/CeO_2/Al_2O_3$	automotive pollution control
1980's -	$Pt/SnO_2/Al_2O_3$	gasoline reforming
-	V_2O_5/TiO_2	ammoxidation of alkyl aromatics
-	$Fe_2O_3/CrO_3/Al_2O_3$	oxidation of H_2S to elemental sulfur (Super Claus)
1990's -	$CuO/CrO_3/Al_2O_3$	oxidation of VOCs to Cl-VOCs
-	V_2O_5/TiO_2	oxidation of Dioxin and PCB emissions
-	$V_2O_5/MoO_3/TiO_2$	selective catalytic reduction (SCR) of NO_x emissions
-	Fe_2O_3/SiO_2	oxidation of H_2S to elemental sulfur (Super Claus)
-	NiO/ZrO_2	N_2O decomposition to N_2 and O_2
-	SO_4/ZrO_2	sollic acid catalyst
-	WO_3/ZrO_2	sollic acid catalyst

2 Molecular Characterization

The catalysis science of supported metal oxide catalysts, especially supported vanadia catalysts, has lagged behind their industrial development.^{25,26} In the 1970s, two models were proposed for the active metal oxide component: a three-dimensional microcrystalline phase (e.g., small metal oxide crystallites) or a two-dimensional surface metal oxide overlayer (e.g., surface metal oxide monolayer). In the 1980s, many studies demonstrated that the active metal oxide components were primarily present as two-dimensional surface metal oxide overlayers, below monolayer coverage, and that the surface metal oxide overlayers control the catalytic properties of supported metal oxide catalysts. The synergistic interaction between the surface vanadia overlayer and the underlying oxide support prompted Gellings to state “. . . that neither the problem of the structure of supported vanadium oxide nor that of the special role of TiO₂ as a support have definitely been solved. Further work on these and related topics is certainly necessary.”²² In more recent years, many fundamental studies have focused on the molecular structural determination of the surface vanadia phase and to a lesser extent the molecular structure-reactivity relationships of supported vanadia catalysts.²⁷⁻³⁰

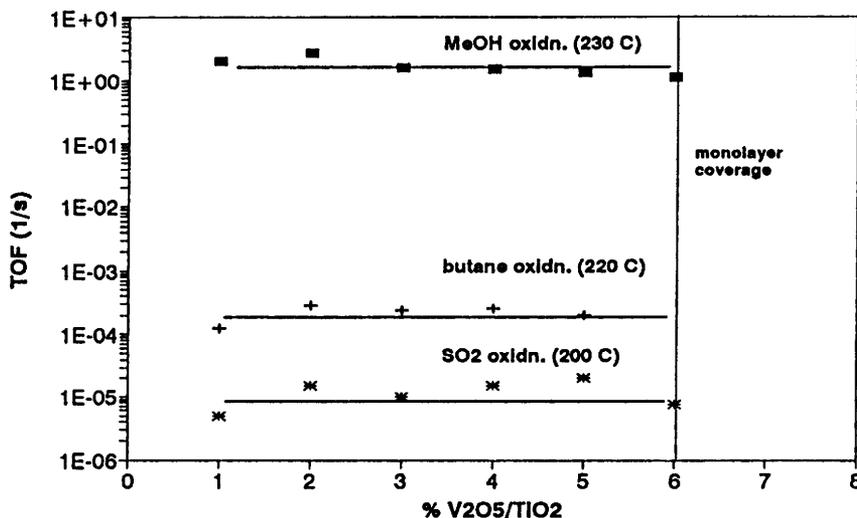
The molecular structures of the active surface vanadia species have been elucidated with the use of multiple molecular spectroscopies: X-ray absorption spectroscopy (XANES/EXAFS),³¹ solid state nuclear magnetic resonance (NMR),^{32,33} Raman,^{26,33-37} IR^{26,37} and oxygen-18 exchange experiments.^{30,37} These combined characterization studies revealed that, at elevated temperatures and under oxidizing conditions or dehydrated conditions at room temperature, the surface vanadia species was present as both isolated and polymerized VO₄ units containing one terminal V=O bond and three bridging V-O-M bonds (where M=V or the support cations). For silica-supported vanadia catalysts, however, only isolated surface VO₄ units were present because of the inability to achieve high surface vanadia coverages on this somewhat unreactive surface.³³ Thus, the active surface vanadia species in supported metal oxide catalysts possess terminal V=O, bridging V-O-V and bridging V-O-Support bonds.

3 Which Metal Oxide Bonds Are Critical for Oxidation Reactions: V=O, V-O-V or V-O-Support?

3.1 Bridging V-O-V Bonds. – Several recent *in situ* Raman studies have demonstrated that the ratio of bridging V-O-V bonds to terminal V=O bonds increases with surface vanadia coverage on oxide supports, with the exception of V₂O₅/SiO₂ which only possesses isolated surface vanadia species and no bridging V-O-V bonds.³³⁻³⁶ Consequently, the role of bridging V-O-V bonds in oxidation reactions can be chemically probed by examining the reaction turnover frequency, TOF - number of molecules reacted per surface vanadia site per second, as a function of surface vanadia coverage. The numbers of surface vanadia sites were determined from the amount of vanadia present in the catalysts since

Raman spectroscopy demonstrated 100% dispersion of the supported vanadia phase. The number of molecules reacted was determined by the conversion of the reactants, under differential reaction conditions and the absence of heat and mass transfer limitations, in fixed-bed reactor studies. The TOFs for several oxidation reactions over V_2O_5/TiO_2 catalysts, monolayer coverage for this TiO_2 support (Degussa P-25, $\sim 55 \text{ m}^2/\text{g}$) corresponds to $\sim 6\%$ V_2O_5/TiO_2 , are presented in Figure 1.

OXIDATION REACTIONS DO NOT DEPEND ON V-O-V CONCENTRATIONS



- Only ONE surface vanadia site required for above oxidation reactions

Figure 1 Oxidation reactions do not depend on V-O-V concentrations.

The TOFs for methanol oxidation to formaldehyde (95-99% selectivity), butane oxidation to maleic anhydride and CO/CO_2 (30% maleic anhydride selectivity) and SO_2 oxidation to SO_3 are independent of surface vanadia coverage. This observation suggests that these oxidation reactions do not depend on the surface concentration of bridging V-O-V bonds since the reaction TOFs do not correlate with the surface density of bridging V-O-V bonds. Furthermore, the constant TOFs with surface vanadia coverage suggest that only one surface vanadia site is required for the activation of these molecules during the oxidation reactions.

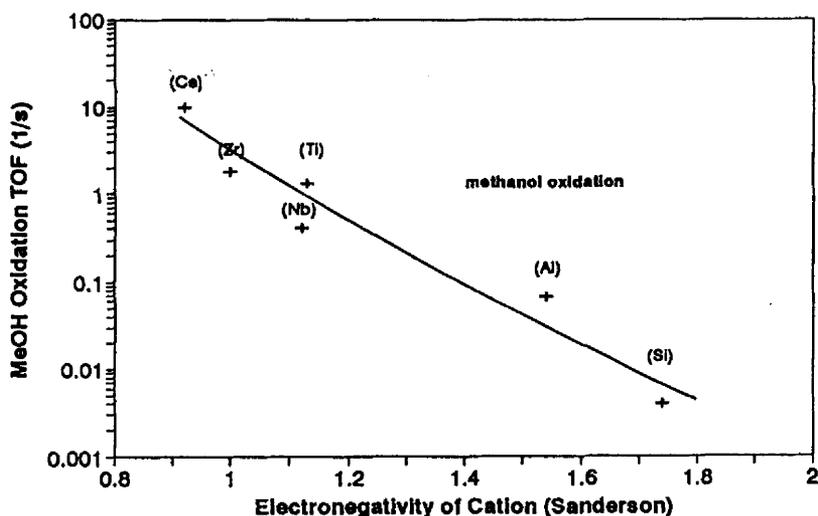
3.2 Terminal V=O Bonds. – The terminal V=O bonds can also be directly monitored with *in situ* Raman spectroscopy during the oxidation reactions, and

the vibrational frequency of the terminal V=O bond is directly related to its bond strength (stronger or shorter bonds vibrate at high cm^{-1} and weaker or longer bonds vibrate at lower cm^{-1}). *In situ* Raman measurements during butane oxidation over several vanadia supported catalysts ($\text{V}_2\text{O}_5/\text{TiO}_2$, $\text{V}_2\text{O}_5/\text{ZrO}_2$ and $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$) revealed essentially the same terminal V=O bond strength for all the catalysts, 1025–1028 cm^{-1} , but the butane oxidation TOFs varied by more than an order of magnitude.²⁰ Consequently, the butane oxidation TOFs do not correlate with the characteristics of the terminal V=O bond, which suggests that this bond is not critical to this oxidation reaction. A similar lack of correlation between the terminal V=O bond characteristics and the methanol oxidation TOFs was also previously found for $\text{V}_2\text{O}_5/\text{TiO}_2$, $\text{V}_2\text{O}_5/\text{ZrO}_2$, $\text{V}_2\text{O}_5/\text{Nb}_2\text{O}_5$, $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and $\text{V}_2\text{O}_5/\text{SiO}_2$ catalysts.²⁹ Additional support for this conclusion comes from oxygen-18 labeled experiments of the terminal V=O bond.³⁸ In these experiments, the oxygen-18 label was introduced into the surface vanadia species prior to initiation of the butane oxidation reaction with oxygen-16. The exchange rate of the oxygen-18 labeled terminal V=O bond was monitored with *in situ* Raman spectroscopy during butane oxidation. The experiment demonstrated that the terminal V=¹⁸O bond was very stable and that ~30 minutes was required to completely exchange the oxygen-18 with oxygen-16 in the terminal V=O bond. This corresponds to an oxygen exchange rate that is approximately 20 times longer than the characteristic reaction time. Thus, the *in situ* Raman spectroscopy experiments during oxidation reactions over supported vanadia catalysts suggest that the terminal V=O bond is not critical to oxidation reactions.

3.3 Bridging V-O-Support Bonds. – Unlike the terminal V=O bonds and the bridging V-O-V bonds, the bridging V-O-Support bond can not be directly monitored with Raman spectroscopy because it is not Raman active due to its slightly ionic character.²⁶ IR spectroscopy, unfortunately, also cannot detect this band because of strong IR absorption by the oxide supports in the region of interest (~600–700 cm^{-1})²⁶. The characteristics of the bridging V-O-Support bond, however, can be altered by varying the specific oxide support or the oxide support ligand (e.g., oxides of Ce, Zr, Ti, Nb, Al and Si). The methanol oxidation TOFs over a series of supported vanadia catalysts is shown in Figure 2.

The methanol oxidation TOFs vary by approximately four orders of magnitude with the specific oxide support ($\text{CeO}_2 > \text{ZrO}_2 \sim \text{TiO}_2 > \text{Nb}_2\text{O}_5 > \text{Al}_2\text{O}_3 > \text{SiO}_2$)²⁹. This strong influence of the oxide support suggests that the bridging V-O-Support bond controls the specific catalytic activity or TOF. In Figure 2, the methanol oxidation TOFs are correlated with the Sanderson electronegativities of the oxide support cations. This correlation suggests that a higher electron density of the bridging oxygen in the V-O-Support bond, corresponding to lower electronegativity of the oxide support cation, enhances the methanol oxidation TOF. It is necessary to examine the mechanism and kinetics of methanol oxidation in order to fully understand the influence of the oxide support ligands upon the reaction TOFs.

THE BRIDGING V-O-SUPPORT BOND CONTROLS THE SPECIFIC CATALYTIC ACTIVITY (TOF)



- electron density of bridging oxygen (V-O-Support) increases with decreasing electronegativity of support cation

Figure 2 The bridging V-O-Support bond controls the specific catalytic activity.

4 Methanol Oxidation Reaction Kinetics and Influence of the Oxide Support

The mechanism and kinetics of methanol oxidation over oxide supports have been extensively examined in recent years.^{39,40} It has been shown that methanol reversibly interacts with oxide supports by forming a surface methoxy species, CH_3O , and a surface hydroxyl group, OH , and that the rate determining step is breaking of a methyl C-H bond to form formaldehyde. Thus, the kinetics of methanol oxidation can be represented by an equilibrated adsorption step, where K is the equilibrium adsorption constant, and a rate determining reaction step, where k is the Arrhenius rate constant. This results in the following kinetic expression in the presence of excess oxygen and low concentrations of methanol, where $[\text{CH}_3\text{OH}]$ represents the partial pressure of methanol:

$$r = K k [\text{CH}_3\text{OH}] \quad (1)$$

$$K = A_1 \exp(-H/RT) \quad (2)$$

$$k = A_2 \exp(-E/RT) \quad (3)$$

where A_1 and A_2 are pre-exponential factors, and E and H are the reaction activation energy and the methanol heat of adsorption (an exothermic value),

respectively. When the inhibition of water is also considered in the kinetic expression for an oxidized surface,³⁹ the equilibrium adsorption constant becomes a function of both the adsorption of methanol and the adsorption of water:

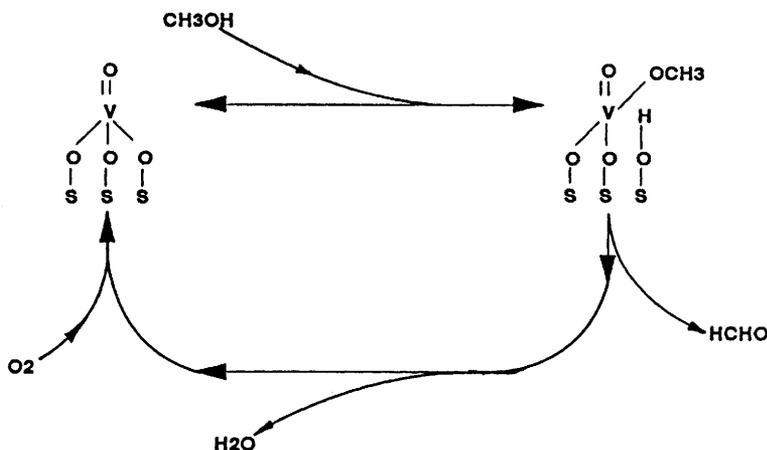
$$K = K_{\text{methanol}} / (K_{\text{water}})^{1/2} \quad (4)$$

and the reaction rate is modified by $1/[\text{H}_2\text{O}]^{1/2}$. The above kinetic rate expression, equation (1), suggests that the variations in the TOF of the different supported vanadia catalysts may be due to either changes in (1) the surface reaction rate constant, k , (2) the equilibrium adsorption constant, K , or (3) simultaneous changes in both the values of K and k .

In order to discriminate between these different possibilities, methanol oxidation temperature programmed reaction spectroscopy (TPRS) studies were undertaken over the series of supported vanadia catalysts since such experiments directly measure the fundamental surface reaction rates.⁴¹ The TPRS experiments were conducted by adsorbing methanol on the supported vanadia catalysts at 100 °C, corresponding to monolayer coverage, and then increasing the sample temperature to monitor the decomposition of the surface methoxy species to formaldehyde via a mass spectrometer. The methanol oxidation TPRS experiments revealed that the rate constants, k , for the decomposition of the surface methoxy intermediate to formaldehyde were identical, decomposition temperature of ~210 °C, over the series of supported vanadia catalysts (with the exception of the $\text{V}_2\text{O}_5/\text{SiO}_2$ system to be discussed below). This suggests that the difference in the methanol oxidation TOFs among the supported vanadia catalysts is primarily related to the difference in the equilibrium adsorption constant, K .

Combination of this new insight about the role of the equilibrium adsorption constant with the electronegativity trend of the specific oxide support ligand, see Figure 2, suggests the methanol oxidation catalytic cycle shown in Figure 3: The adsorption of methanol occurs at the bridging V-O-S bond by protonation of the bridging oxygen and formation of a V-OCH₃ intermediate. The efficiency of this dissociative adsorption step, reflected in the magnitude of the equilibrium adsorption constant, is dependent on the stability of the bridging V-O-S bond. A higher electron density on the bridging oxygen, corresponding to a lower electronegativity of the oxide support ligand, results in a more basic bridging oxygen that enhances the adsorption of the mildly acidic methanol molecule. Conversely, a lower electron density on the bridging oxygen, corresponding to a higher electronegativity of the oxide support ligand, results in a less basic bridging oxygen that depresses the adsorption of the mildly acidic methanol molecule. Thus, the different TOFs for methanol oxidation over the series of supported vanadia catalysts should be related to the concentration of surface methoxy species during methanol oxidation. Preliminary *in situ* IR experiments were undertaken during methanol oxidation to directly measure the concentration of surface methoxy species on the supported vanadia catalysts, and the initial results appear to be consistent with this hypothesis.⁴² The decomposition of the surface methoxy intermediate to formaldehyde probably only occurs on the surface vanadia site since the same surface reaction rate constant, k , is reflected in the

METHANOL OXIDATION CATALYTIC CYCLE



- **Transient Temperature Programmed Reaction Studies Reveal that C-H Bond Breaking of CH₃O_{ads} Is Rate Determining Step**

Figure 3 Methanol oxidation catalytic cycle.

TPRS experiments for this reaction step. The two hydrogens released in the methanol adsorption and the surface methoxy decomposition steps are eventually converted to water. Spectroscopic details about the formation of water are presently not available, but the formation of water most likely proceeds via the condensation of two surface hydroxyl groups. The reduced surface vanadia site is readily reoxidized back to vanadium (+5) by gas phase oxygen as shown by *in situ* Raman measurements.⁴²

The V₂O₅/SiO₂ system, however, did not follow the above trend. The surface methoxy intermediate was significantly more stable on this catalyst, decomposition temperature of ~300 °C compared to ~210 °C for the other supported vanadia catalysts. This suggests that the surface reaction rate constant, *k*, for surface methoxy decomposition to formaldehyde is significantly lower for the silica supported vanadia catalyst compared to the other supported vanadia catalysts. Consequently, the low TOF for methanol oxidation over the silica supported vanadia catalyst is due to both a lower equilibrium adsorption constant, due to the high electronegativity of the silica ligand, and a lower surface reaction constant, *k*.

The apparent activation energies for methanol oxidation over the series of support vanadia catalysts is a composite of the activation energy and the heats of adsorption:

$$E_{\text{app}} = E + H_{\text{methanol}} - 1/2 H_{\text{water}} \quad (5)$$

Fundamental TPRS studies have shown that the activation energy for breaking the C-H bond of methoxy is approximately ~ 23 kcal/mol.³⁹ The similar apparent activation energies for methanol oxidation over all the supported vanadia catalysts,²⁹ 19-23 kcal/mol, suggests that the apparent heats of adsorption,

$$H_{\text{app}} = H_{\text{methanol}} - 1/2 H_{\text{water}} \quad (6)$$

on the supported vanadia catalysts are not large and do not significantly vary among the catalysts (minor differences may be lost in the experimental error). This suggests that the lower Arrhenius rate constant for methanol oxidation over silica supported vanadia catalysts is primarily due to a lower pre-exponential factor (an entropic effect). Weber recently proposed a model that predicted that differences in methanol oxidation TOFs among supported vanadia catalysts should be related to differences in an entropy effect in the Arrhenius constant, and the current findings between V_2O_5/SiO_2 and the other supported vanadia catalysts are consistent with this model.⁴³ However, this model does not account for the different methanol oxidation TOFs among the other supported vanadia catalysts because these differences are related to the equilibrium adsorption constant. Stiegman recently proposed that the energy level of the bridging V-O-Support bond should determine the reactivity of this bond, reflected in the Arrhenius rate constant, during methanol oxidation and the current findings between V_2O_5/SiO_2 and the other supported vanadia catalysts are also consistent with this model.⁴⁴ However, it appears that the differences in reactivity of the bridging V-O-S bond are mostly related to the adsorption step, K , rather than the Arrhenius rate constant, k , for the decomposition of surface methoxy to form formaldehyde. Thus, theoretical models of oxidation reactions should not only consider the surface reaction rate constants, k , but also the equilibrium adsorption constants, K , which may also significantly contribute to the overall specific reaction rates or TOF.

5 Influence of the Oxide Support upon Different Oxidation Reactions

The above studies with methanol oxidation over the different supported vanadia catalysts demonstrated the dramatic effect of the specific oxide support on the reaction TOF, approximately four orders of magnitude for methanol oxidation. Several other oxidation reactions over the same series of supported vanadia catalysts were also investigated to determine if the effect of the oxide support is a general phenomenon, and the results are listed in Table 2.

For all the oxidation reactions listed in Table 2, it was found that the specific oxide support had a significant effect on the oxidation reaction TOF. The methanol oxidation TOF was the most sensitive to the oxide support ($\sim 10^4$ factor), followed by butane oxidation^{20,38} and selective catalytic reduction of NO by NH_3 ⁴⁵ ($\sim 10^2$ factor), and oxidation of CO ⁴⁶ and SO_2 ⁴⁷ (~ 10 factor) were the least sensitive. The differences in order of magnitude of the support effect on the

Table 2 Support Effect is a General phenomenon for Oxidation Reactions

Oxidation reaction	Support effect on TOF (for vanadia catalysts)
CH ₃ OH \longrightarrow H ₂ CO+H ₂ O	$\sim 10^4$
CH ₃ CH ₂ CH ₂ CH ₃ \longrightarrow maleic anhydride +H ₂ O	$\sim 10^2$
NO+NH ₃ \longrightarrow N ₂ +H ₂ O	$\sim 10^2$
CO \longrightarrow CO ₂	~ 10
SO ₂ \longrightarrow SO ₃	~ 10

• In general: CeO₂ > ZrO₂ \sim TiO₂ > Nb₂O₅ > Al₂O₃ > SiO₂

different reactions most likely reflect different reaction requirements of the various reactants. More detailed kinetic and mechanistic studies of these oxidation reactions, similar to the methanol oxidation studies reported above, are required to fully understand how the oxide support ligand affects these reactions. Furthermore, in general, the relative trend in TOF followed the pattern CeO₂ > ZrO₂ \sim TiO₂ > Nb₂O₅ > Al₂O₃ > SiO₂ for these oxidation reactions. Thus, it appears that the bridging V-O-Support bond plays a critical role in all of these oxidation reactions and is a general phenomenon in oxidation reactions.

6 Number of Surface Sites Required for Oxidation Reactions

Information about the number of surface sites required for an oxidation reaction, or activation of the reactant molecule, can 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 the surface vanadia coverage (surface density of sites) and reactions requiring multiple surface sites will exhibit a TOF that increases with the surface vanadia coverage (surface density of sites). From such an analysis, the number of surface vanadia sites required for various oxidation reactions is presented in Table 3.

Table 3 Number of Surface Sites required for Various Oxidation Reactions

Oxidation reactions	No. of required surface sites
CH ₃ OH \longrightarrow H ₂ CO+H ₂ O	1
CH ₃ CH ₂ CH ₃ \longrightarrow CH ₃ CHCH ₂ +H ₂ O	1
CH ₃ CH ₂ CH ₂ CH ₃ \longrightarrow maleic anhydride +H ₂ O	1-2*
NO+NH ₃ \longrightarrow N ₂ +H ₂ O	1-2*
CH ₄ \longrightarrow H ₂ CO+H ₂ O	1
CO \longrightarrow CO ₂	1
SO ₂ \longrightarrow SO ₃	1

* Reactions more efficient over two adjacent sites

The oxidation of methanol to formaldehyde,²⁹ propane to propylene,⁴⁸ methane to formaldehyde,⁴⁹ CO to CO₂⁴⁶ and SO₂ to SO₃⁴⁷ require only one surface vanadia site. In the case of methanol oxidation, where the molecular mechanism is known, IR studies have confirmed that the surface methoxy intermediate is coordinated to only one surface vanadia species.⁴⁰ Such detailed molecular information is currently not available about the other oxidation reactions over the supported vanadia catalysts. The selective oxidation of butane to maleic anhydride^{20,38} and the bimolecular NO/NH₃ reaction³⁰ exhibit a significant increase of the TOF with surface coverage and suggests that multiple sites, most probably two sites, are required for these oxidation reactions (see additional discussion below in Section 7). Although the oxidation of butane to maleic anhydride and the selective catalytic reduction of NO with NH₃ are more efficient over several adjacent vanadia sites, these reactions have also been shown to occur over isolated vanadia sites present at low surface vanadia coverages and on the silica support (see Section 2 above).^{20,30,38} Consequently, all oxidation reactions can proceed over isolated surface vanadia sites, but oxidation reactions involving multisteps and bimolecular reactions proceed more efficiently over several adjacent surface vanadia sites.

7 Influence of Surface Metal Oxide Additives upon Oxidation Reactions

7.1 Promoters. – Many supported vanadia catalysts also possess secondary metal oxides additives that act as promoters (enhance the reaction rate or improve product selectivity). Some of the typical additives that are found in supported metal oxide catalysts are oxides of W, Nb, Si, P, etc. These secondary metal oxide additives are generally not redox sites and usually possess Lewis and Bronsted acidity.⁵⁰ Similar to the surface vanadia species, these promoters preferentially anchor to the oxide substrate, below monolayer coverage, to form two-dimensional surface metal oxide species. This is schematically shown in Figure 4.

Such secondary surface metal oxide additives, in general, only indirectly interact with the surface vanadia species via lateral interactions⁵⁰ or possibly even electronic effects through semiconducting oxide supports.⁵¹ The lateral interactions may also slightly affect the ratio of polymerized to isolated surface vanadia species due to surface crowding by the secondary metal oxide additives.⁵⁰ The influence of the secondary metal oxide additives upon an oxidation reaction depends on the specific requirements of the reactions. For oxidation reactions requiring one surface vanadia site, such as the oxidation of methanol to formaldehyde, such secondary metal oxide additives have only a minor effect since they are generally not redox sites and the oxidation reaction only proceeds on the surface vanadia sites.⁵⁰ The acidic character of the secondary metal oxide additives, however, can sometimes lead to byproducts since the acid sites can catalyse the formation of dimethyl ether from methanol. For oxidation reactions most efficiently proceeding over adjacent surface redox-surface acid dual sites, such as the oxidation of butane to maleic anhydride^{38,52}

HOW DO PROMOTERS FUNCTION ?

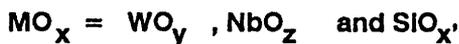
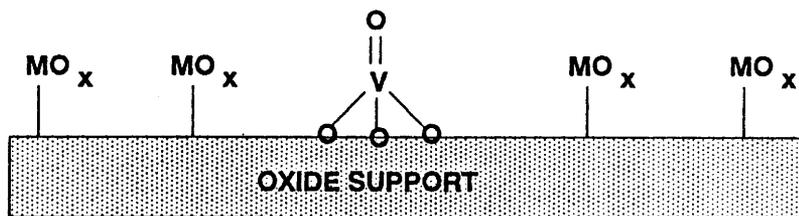


Figure 4 *How do promoters function?*

and the selective catalytic reduction of NO with NH₃,^{30,53} significant enhancement in reaction rate and product selectivity by the presence of these acidic secondary metal oxide additives is observed. Thus, redox reactions requiring one surface vanadia site are generally not promoted by such secondary metal oxide additives, but redox-acid dual site reactions are generally promoted by such secondary metal oxide additives.

7.2 Poisons. – Unlike secondary surface metal oxide additives that indirectly interact with the surface vanadia sites via lateral interactions, poisons are surface metal oxide additives that directly interact with the surface vanadia sites and decrease the TOF. For example, the addition of surface potassium oxide to supported vanadia catalysts results in both a structural change and a reactivity change of the surface metal oxide species.⁵⁰ This interaction, at submonolayer coverages, reflects the attractive interaction between these two surface metal oxide species. The presence of the surface potassium oxide poison alters the V-O bond lengths and the ratio of polymeric and isolated surface vanadia species (favoring isolated surface vanadia species). The interaction of the surface potassium oxide poison with the surface vanadia species is schematically shown in Figure 5.

These structural changes are accompanied by significant reactivity modifications of the surface vanadia species. The addition of the surface potassium oxide species decreases the reducibility of the surface vanadia species in temperature programmed reduction (TPR) studies and the TOF for methanol oxidation.^{23,50} The most likely reason for this behavior is that the surface potassium oxide species is intimately coordinated to the bridging V-O-Support bond and retards its participation in these redox processes. Thus, all oxidation reactions, involving one surface vanadia site as well as dual surface vanadia-acidic sites, will be retarded by the surface potassium oxide additive. The basic properties of the surface potassium oxide additive may also affect the product selectivity by

HOW DO POISONS FUNCTION ?

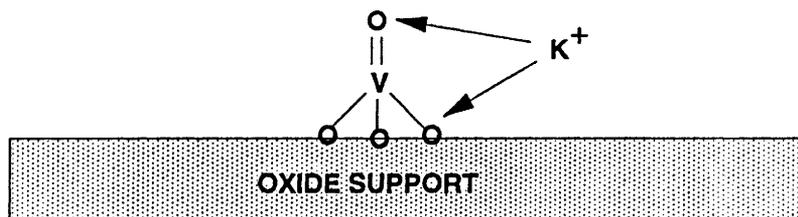


Figure 5 How do poisons function?

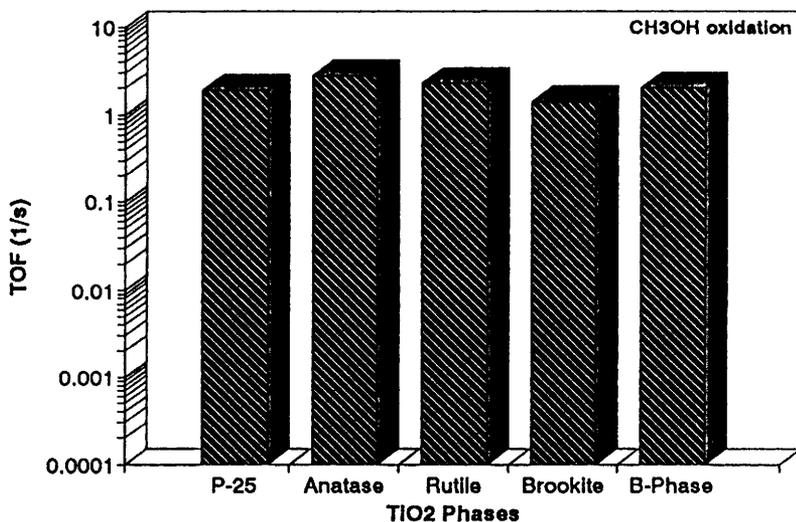
neutralizing surface Lewis and Bronsted sites. This may be a desirable feature for redox reactions where the acidic sites lead to unwanted byproducts (e.g., conversion of CH_3OH to CH_3OCH_3). Thus, the addition of basic poisons to supported vanadia catalysts retards the TOF for all oxidation reactions, but may enhance the product selectivity by neutralizing surface acid sites that may be responsible for side reactions.

8 Influence of the Specific Oxide Support Phase

The influence of the specific oxide support phase upon the structure and reactivity of the surface vanadia species was also recently investigated.⁵⁴ A series of titania-supported vanadia catalysts were synthesized over a series of TiO_2 supports possessing different phases (anatase, rutile, brookite and B). Raman and solid state vanadium-51 characterization studies revealed that the same surface vanadia species were present in all the different $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts⁵⁴. The reactivity of the surface vanadia species on the different oxide supports was probed by methanol oxidation and the TOFs are shown in Figure 6 (all the catalysts contained 1% V_2O_5)

Essentially the same methanol oxidation TOFs were obtained on the different oxide supports. The Degussa P-25 titania support (90% anatase; 10% rutile) was also examined, as shown in Figure 6, because it possesses very low levels of surface impurities and represents a good reference sample. The invariance of the methanol oxidation TOF with the specific phase of the titania support reveals that the oxidation reaction is controlled by a local phenomenon, the bridging V-O-Support bond, rather than long range effects, the structure of the TiO_2 support. Thus, the phase of the oxide support does not appear to influence the molecular structure or reactivity of the surface vanadia species.

SUPPORT PHASE DOES NOT AFFECT OXIDATION REACTIONS



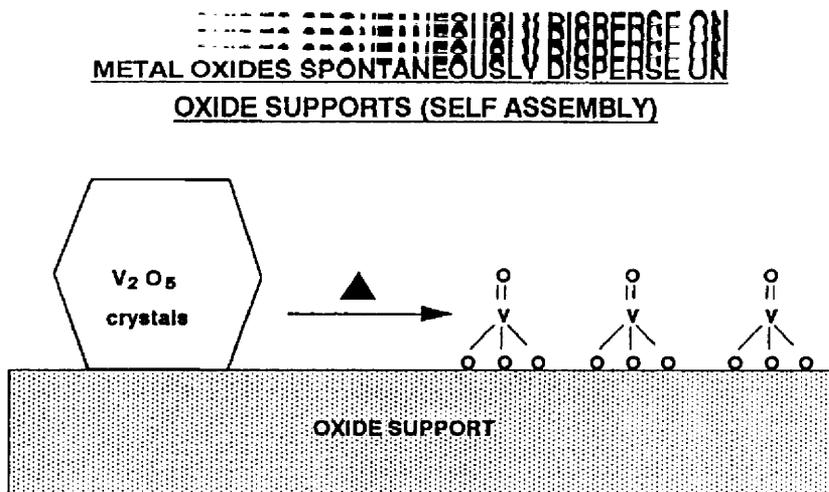
- oxidation reaction controlled by stability of bridging V-O-Ti bond (a local phenomenon !)

Figure 6 Support phase does not affect oxidation reactions.

9 Influence of Preparation Method

The influence of different preparation methods upon the structure and reactivity of supported vanadia catalysts has recently been investigated by several laboratories.⁵⁵⁻⁵⁸ These studies concluded that the same surface vanadia species forms on a specific oxide support independent of the preparation method, even when starting with V₂O₅ crystals. The reason for this phenomenon is that vanadium oxide spontaneously disperses on oxide supports to form surface vanadia species, which is schematically depicted in Figure 7.

This spontaneous dispersion, or self-assembly, of vanadium oxide on oxide supports is driven by the minimization of the surface free energy of the system: the surface free energy of V₂O₅ is significantly less than the surface free energy of most typical oxide supports (e.g., Al₂O₃, TiO₂, ZrO₂, etc.).⁵⁸ Furthermore, the surface vanadia species are able to readily rearrange and surface diffuse at typical catalytic reaction temperatures because of the low melting point (695 °C) and, consequently, Tamman temperature (370 °C) of V₂O₅. Thus, the preparation method cannot influence the final state of equilibrated supported vanadia catalysts.



- **spontaneous dispersion thermodynamically driven to minimize surface free energy of system**
- **preparation methods can NOT influence thermodynamic equilibrium (final state)**

Figure 7 Metal oxides spontaneously disperse on oxide supports (self assembly).

10 Conclusions

The above molecular structural and reactivity studies provide the foundation for the molecular ingredients required to molecularly engineer supported vanadia catalysts for oxidation reactions. The number of active surface sites is determined by the surface vanadia coverage in the two-dimensional vanadia overlayer (a catalyst synthesis parameter). The specific activity of the active surface sites is controlled by the specific oxide support ligand (a catalyst synthesis parameter), but is not influenced by the specific phase of the oxide support. The specific activity of the active surface sites is not a function of surface vanadia coverage for oxidation reactions efficiently proceeding over isolated surface vanadia sites (oxidation of methanol to formaldehyde, methane to formaldehyde, propane to propylene, CO to CO₂, SO₂ to SO₃, etc.), but the specific activity is a strong function of surface vanadia coverage for oxidation reactions that proceed more efficiently over several adjacent surface vanadia sites (selective oxidation of butane to maleic anhydride, selective catalytic reduction of NO_x with NH₃ to N₂ and H₂O, etc.). The specific activity of the active surface sites can be further enhanced by the introduction of acidic secondary surface metal oxide additives (a catalyst synthesis parameter), but only for oxidation reactions that proceed more efficiently over several adjacent surface vanadia sites. The specific preparation

method does not influence the nature of the active surface sites since the same surface vanadia sites are formed in equilibrated catalysts from all the different catalyst preparations. Thus, the critical molecular engineering or catalyst synthesis parameters that control the overall activity of supported vanadia catalysts during oxidation reactions are (1) the specific oxide support material (in general, $\text{CeO}_2 > \text{ZrO}_2 \sim \text{TiO}_2 > \text{Nb}_2\text{O}_5 > \text{Al}_2\text{O}_3 > \text{SiO}_2$), (2) the surface area of the oxide support (more of the two-dimensional vanadia overlayer can be accommodated with higher surface area supports, but the thermal stability of such supported vanadia catalysts decreases with increasing surface area), (3) the vanadia content of the final catalyst (monolayer surface coverage corresponds to ~ 1 wt.% V_2O_5 per $10 \text{ m}^2/\text{g}$ of support), (4) the introduction of secondary acidic surface metal oxide additives (e.g., W, Nb, P, etc.), but only for oxidation reactions that proceed more efficiently over several adjacent sites. These molecular engineering principles have also been successfully extended to the synthesis of multilayered supported vanadia catalysts (e.g., a surface vanadia overlayer on a two-dimensional surface titania phase coordinated to a silica support⁵⁹) as well as to other supported metal oxide oxidation catalysts (e.g., Mo^{60} , $\text{Cr}^{61,62}$ and Re^{63}).

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