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Understanding the effect of modifying elements in supported vanadia bilayered catalysts for methanol oxidation to formaldehyde

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Understanding the effect of modifying elements in supported vanadia bilayered catalysts for methanol oxidation to formaldehyde

by

William Collins Vining

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemical Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Alexis T. Bell, Chair Professor Roya Maboudian Professor T. Don Tilley

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Abstract

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Doctor of Philosophy in Chemical Engineering

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Professor Alexis T. Bell, Chair

The field of heterogeneous catalysis has long been interested in understanding the role of site structure on reactivity and selectivity for the rational design of catalysts. Vanadia is of particular interest because of its potential to be highly active and selective for a variety of reactions, such as oxidative dehydrogenation of alkanes to alkenes, or the oxidation of n-butane to maleic anhydride.

When supported, vanadia can exist in several environments depending on its At the lowest loadings, below 2 V/nm^2 , the vanadium exists surface coverage. predominantly in well dispersed, tetrahedral structures with 3 V-O-support bonds and 1 V=O bond. At higher loadings, above 2 V/nm^2 , V-O-V bonds form on the surface, and at loadings above 7 V/nm², the vanadia begins to form 3 dimensional domains of V_2O_5 . Methanol oxidation rates over catalysts with varying vanadia loadings have shown no significant effect of the V surface density on the formaldehyde formation rate. However, significant differences in the formaldehyde production rates are observed for different supports. Changing the support from silica to titania or zirconia, will result in increases in the production of formaldehyde from methanol by over an order of magnitude for similar vanadia surface coverages. These differences in rate are observed even though the reaction mechanism is believed to be the same regardless of the support. The mechanism is thought to proceed as follows. First methanol dissociatively adsorbs across a V-Osupport bond, producing V-OCH₃ and M-OH (M = Si, Ti, Zr, Ce) in a quasi-equilibrated step. Next a surface oxygen abstracts hydrogen from the methoxy group in the rate determining step, and formaldehyde desorbs. The final steps are fast and involve the production of H₂O from neighboring hydroxyls and the reoxidation of the catalyst by gasphase oxygen.

When vanadia is supported on bulk TiO_2 , ZrO_2 , or CeO_2 , the support surface area is relatively small (~200 m²/g at its highest), and the bulk support causes side reactions which make it difficult to understand the role of the vanadia. Furthermore, by using a bulk support, only the vanadia surface coverage can be varied, such that the effect of different V structures can be elucidated, but not that of V-O-M bonds. Therefore, high surface area silica with a variable coverage of two-dimensional TiO_2 , ZrO_2 , and CeO_2 layers are used to support isolated vanadate structures to vary the quantity of vanadia bound to the modifying layer. These bilayered catalysts can be used to determine the effect of the V-O-support bonds on the formaldehyde production rate.

Three mesoporous silica supports, MCM-48 (1550 m²/g), MCM-41 (1353 m²/g), and SBA-15 (700 m²/g) were used as the high surface area silica. Ti was grafted to the MCM-48 surface using Ti(OⁱPr)₄ and a maximum surface coverage of 2.8 Ti/nm² was obtained after 3 graftings. The grafting of zirconium was performed using Zr-2-methyl-2-butoxide on MCM-41, and a maximum loading of 2.1 Zr/nm² was achieved after 3 graftings. The final modifying element, cerium, was grafted onto SBA-15 using Ce(O^tBu)₄ for a maximum surface coverage of 0.9 Ce nm⁻². After treating the MO_x/SiO₂ (M = Ti, Zr, Ce) support to achieve the desired V surface coverage of approx. 0.7 V/nm².

The resulting catalysts contain amorphous two-dimensional layers of TiO₂, ZrO₂, or CeO₂ with V existing in a pseudo-tetrahedral structure on the surface. As the surface density of the modifying element layer increases, the quantity of vanadia bound to TiO₂, ZrO₂, or CeO₂ increases. For the VO_x/ZrO₂/SiO₂ catalysts, the fraction of vanadia bound to the zirconia layer was able to be quantified and determined to be 35% of all V for a Zr surface density of 2.8 Zr nm⁻².

Even for small quantities of modifying elements (0.2 M nm⁻²), the apparent rate constant for formaldehyde production on VO_x/MO₂/SiO₂ (M = Ti, Zr, Ce) is an order of magnitude higher than for VO_x/SiO₂ catalysts at the same V surface density. Regardless of the modifying element used, the increase in apparent rate constant is comparable for all catalysts. As the modifying element surface density is increased, the apparent rate constant also increases, which is a result of an increasing fraction of V bound to the MO_x layer. Each of these bilayered catalysts can be described using a two-site model of VO_x/SiO₂ and VO_x/MO₂ (M = Ti, Zr, Ce) with the latter being responsible for the increased apparent rate constant.

This higher activity for the VO_x/MO_2 site is due to a lower apparent activation energy. For VO_x/SiO_2 , the apparent activation energy is 23 kcal mol⁻¹, but is approximately 17 kcal mol⁻¹ for VO_x/MO_2 sites. The apparent activation energy can be expressed as the sum of the heat of methanol adsorption and the activation energy for Habstraction. My results indicate that the lower apparent activation energy observed for the bilayered catalysts is a result of a decrease in the activation energy for H-abstraction. This lower energy pathway occurs because the MO_x layer can abstract H from surface methoxy groups. For VO_x/SiO_2 , however, the vanadyl oxygen abstracts H in a higher energy step. To my family

and friends

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List of Abbreviations and Symbols

ΔE_{ads}	Methanol adsorption energy
$\Delta E^{\ddagger}_{app}$	Apparent activation energy for methanol oxidation to formaldehyde
$\Delta E_{rls}^{\ddagger}$	Activation energy of rate limiting step in methanol oxidation
ΔG°	Standard state of Gibbs energy
ΔH_1	Heat of methanol adsorption
BET	Brunauer Emmett Teller theory of adsorption of gas molecules on a solid
рш	Sufface Parrott Joynar Halanda thaary
DJII CoAcM	Caria derived from Ca(acac), grafted on MCM 41
CeAcS	Ceria derived from Ce(acac) ₃ grafted on SBA ₋₁₅
CeiPM	Ceria derived from $Ce(\Omega^{i}Pr)_{i}$ grafted on MCM-41
CetBM	Ceria derived from $Ce(O^{T}Ru)_{\ell}$ grafted on MCM-41
CetBS	Ceria derived from $Ce(O^{T}Bu)_{4}$ grafted on SBA-15
[0]	Number of oxygen vancancies
DFT	Density Functional Theory
DME	Di methyl ether
DPPH	2.2-diphenyl-1-picrylhydrazyl
E_2	Apparent activation energy for rate determining step
E_{SiO_2}	Apparent activation energy for vanadia bound to silica
E_{ZrO_2}	Apparent activation energy for vanadia bound to zirconia
EF	Eigenvector following
EPR	Electron Paramagnetic Resonance
EXAFS	Extended x-ray absorption fine spectra
$F(\mathbf{R}_{\infty})$	Kubelka-Munk Function
GSM	Growing string method
h	Planck's constant
I _{i,j}	Mass spectrometer ionization signal for component j at mass i .
ICP	Inductively-coupled plasma
K ₁	Equilibrium constant for methanol adsorption
K_1	Pre-exponential factor for methanol adsorption
k ₂	Rate constant for rate limiting step in methanol oxidation
k_2	Pre-exponential factor for rate determining step
k_{app}	Apparent rate constant for methanol oxidation to formaldehyde
k_{app}°	Pre-exponential factor for methanol oxidation to formaldehyde
$k_{app,x,D}$	Apparent rate constant for active site with oxygen vacancy
$k_{app,x,O}$	Apparent rate constant for active site without oxygen vacancy
K _{ads}	Equilibrium constant for methanol adsorption
k_B	Boltzmann's constant
K _{def,x,Si}	Equilibrium constant for O-vacancy exchange in Ti-Si bond
$K_{def,x,Ti}$	Equilibrium constant for O-vacancy exchange in Ti-Ti bond
K _{eq}	Equilibrium constant for methanol adsorption
k _{rls}	Rate constant for rate limiting step in methanol oxidation

$k^{\circ}_{SiO_2}$	Apparent pre-exponential factor for vanadia bound to silica
k_{zro_2}	Apparent pre-exponential factor for vanadia bound to zirconia
$\kappa(A)$	Condition number of matrix A
$\kappa(T)$	Transmission coefficient for tunneling
MCM-41	Mesoporous silica with two-dimensional channels
MCM-48	Mesoporous silica with three-dimensional channels
[MeOH]	Gas-phase concentration of methanol
MEOH	Methanol
MF	Methyl formate
NMR	Nuclear Magnetic Resonance
[0]	Number of sites without an oxygen vacancy
O.D.	Outer diameter
Р	Pressure
P(xTi V)	Fraction of V sites that contain x Ti support bonds
$q^{\ddagger}_{CH_2O\bullet S}$	Partition function for transition state leading to the formation of
	formaldehyde
q _{MeOH}	Partition function for methanol
q _{MeOH•S}	Partition function for active site with adsorbed methanol
q_S	Partition function for active site
R	Ideal gas constant
RF _{i,j}	Response factor for component <i>j</i> on mass <i>i</i>
r _{app}	Apparent rate of formaldehyde production
σ_{ads}	Symmetry factor for methanol adsorption
σ_{rls}	Symmetry factor for rate limiting step
SBA-15	Mesoporous silica with two-dimensional channels
STM	Scanning Tunneling Microscopy
$\theta_{x,D}$	Surface density of active sites with an oxygen vacancy
$\theta_{x,O}$	Surface density of active sites without an oxygen vacancy
[Ti]	Number of titanium atoms
Т	Temperature
TEM	Transmission electron microscopy
TOF	Turn-over frequency
TPR	Temperature Programmed Reduction
TPR _x	Temperature Programmed Reaction
TPD	Temperature Programmed Desorption
UHP	Ultra-high purity
V	Volume
[V]	Number of vanadium atoms
$[V-D]_x$	Number of active sites next to an oxygen vacancy
$[V-O]_x$	Number of active sites without an oxygen vacancy
VCetBS	Vanadia and ceria derived from Ce(O'Bu) ₄ grafted on SBA-15
υ	Frequency of electromagnetic wave
x_j	Mass fraction of component <i>j</i>
XANES	x-Ray absorption near edge spectra
XRD	x-Ray diffraction

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Chapter 1

Introduction

Environmental concerns along with the dwindling supply of petrochemical reserves have led to the search for new, more efficient chemical processes, which utilize environmentally friendly, renewable feedstocks [1]. Catalysts play a key role in these processes by better utilizing reactants, improving yields of desired products, and reducing energy costs. Heterogeneous catalysts are of interest because of higher product selectivities, greater reactant efficiencies, and reduced separation costs. Therefore, developing improved heterogeneous catalysts for current and future applications is of significant importance.

Several catalyst properties can play a significant role in the activity and selectivity of a given reaction, such as the structure and oxidation state of the active site, and the types of elements present. In order to rationally design catalysts for new applications, the structures, oxidation states, and mechanisms for current catalysts must be elucidated such that more general structure-reactivity relationships may be developed. The development of these relationships will enable the creation of new processes and the improvement of existing ones. Some of the benefits include higher selectivity toward desired products or more efficient utilization of reactants.

Because of the complexity of most industrial catalysts, model catalysts are often used to develop these structure-activity relationships. Examples of previously studied model catalysts include single metal-oxo groups grafted on the support [2,3], and isolated metal atoms incorporated into the support surface [4]. The use of these model catalysts allows for the characterization of known, uniform structures from which structureactivity relationships may be derived.

In particular, vanadium is an element of interest because of its potential to efficiently convert many reactants to desired products, such as methanol oxidation to formaldehyde, sulfur dioxide to sulfur trioxide for the production of sulfuric acid production using V_2O_5 , and the oxidative dehydrogenation of alkanes to alkenes [5 and references therein]. Extensive work has been performed on supported vanadium oxide model catalysts. Previous work has determined that for surface densities less than 2 V nm^{-2} , vanadium exists on the surface in pseudo-tetrahedral O=V(-OM)₃ (M = support oxide metal cation, e.g., Si, Ti, Zr) species. For higher surface densities, polyvanadates form on the surface, up to a coverage of 7 V nm⁻², upon which crystalline V_2O_5 begins to form [6]. Methanol oxidation rates have been shown to be invariant with increasing vanadia surface density below a monolayer [7], yet when different metal oxides are used as supports, the formaldehyde production rate increases by several orders of magnitude. For example, at low surface densities of vanadia on the catalyst surface, the apparent rate constant for methanol oxidation increased from 1.3×10^{-2} (atm•s)⁻¹ for VO_x/SiO₂ to 1.9 $(atm \cdot s)^{-1}$ for VO_x/TiO₂, an increase of two orders of magnitude [5,8]. Similar observations have been made for methanol oxidation when higher surface coverages of vanadia on different metal oxide supports are used. The previous results show the formaldehyde production rate varies according to the general trend: VO_x/SiO₂ << $VO_x/TiO_2 \sim VO_x/ZrO_2 < VO_x/CeO_2$ [9].

The mechanism for isolated vanadate species supported on silica has been suggested to proceed as shown in Figure 1.1 [5,10]. Initially, methanol dissociatively adsorbs across a V-O-Si bond producing V-OCH₃ and Si-OH in a quasi-equilibrated step. Next, a proton is abstracted to the vanadyl oxygen in the rate-determining step and formaldehyde and water desorb. Finally, gas-phase oxygen fully re-oxidizes the reduced catalyst. For low gas-phase concentrations of water, the reaction mechanism can be written as

$$r_{app} = K_{eq} k_{rls} [MeOH] \tag{1.1}$$

where r_{app} is the apparent rate, K_{eq} is the equilibrium constant for methanol adsorption, k_{rls} is the rate constant for H-abstraction, and [MeOH] is the gas-phase partial pressure of methanol.

The reason for the previously mentioned support effect in methanol oxidation is unclear, yet several explanations have been suggested. Wachs and coworkers hypothesized that the underlying metal oxide support affects the electronic properties of the vanadate. This conclusion was drawn by observing a correlation between the Sanderson metal cation electronegativity of the support with the methanol oxidation rate [9]. It is not clear, however, which aspect of the vanadate electronic property is altered, nor which step in the reaction mechanism is affected by this proposed change. Another hypothesis involves the presence of O-vacancies in the metal oxide surface adjacent to the vanadate species. The existence of these vacancies has been investigated using density functional theory (DFT) models of the active site for VO_x/TiO_2 catalysts, which resulted in activation energies and rate constants comparable to those observed experimentally [11]. More recent theoretical investigations by Metiu and coworkers suggest that when vanadia is supported on a metal oxide other than silica, the support facilitates the adsorbed methoxy H-abstraction step in the methanol oxidation to enhance the production of formaldehyde [12].

In order to determine the role of the support for methanol oxidation on supported vanadia catalysts, bilayered catalysts were used in the present study as a means to characterize both the support layer and surface vandate species. For these catalysts, the desired surface density of vanadia is deposited onto submonolayer coverages of MO_x (M = Ti, Zr, Ce) on silica. Advantages of these catalysts over bulk supported vanadia are the ability to vary the structure and surface density of the modifying element on silica, and the use of high surface area mesoporous silica, which allows for higher numbers of active sites while maintaining low surface densities of vanadia. By changing the surface density of the modifying element, the number and type of V-O-M (M = Ti, Zr, Ce) bonds can be determined and their effect on the rate of formaldehyde production determined. Also, the use of high surface area silica supports facilitates the investigation of surface V species with readily available spectroscopic techniques.

In chapter 2, the structure and redox properties of the TiO_2/SiO_2 support were investigated. In this study, the titania surface density was varied from 0.2 to 2.8 Ti nm⁻² on an MCM-48 support and the titania redox properties were shown to be a function of the cluster size on the silica surface. The effect of these supports on vanadia activity is investigated in chapter 3. In this chapter, the catalysts are studied both experimentally and theoretically using the O-vacancy theory to propose a mechanism by which the titania layer affects the reactivity.

The insights gained from investigating titania as a modifier were extended to zirconia in chapter 4. In this chapter, the distribution of vanadia sites is experimentally determined for these catalysts, as opposed to theoretically in ch. 3. For these catalyst, both VO_x/SiO_2 and VO_x/ZrO_2 sites were quantified, with the latter being responsible for the increase in reaction rate. Because of the inability to form O-vacancies in the underlying zirconia layer, an alternative mechanism in which the zirconia layer abstracts the adsorbed methoxy proton is proposed.

Finally, these insights are extended to catalysts with ceria as the modifying layer in chapters 5 and 6. First, in ch. 5, the impact of different ceria precursors on the resulting structure and redox properties is investigated for cerium (III) acetylacetonate, cerium (IV) *t*-butoxide, and cerium (IV) *i*-propoxide. Two-dimensional amorphous domains of ceria were achieved for cerium (IV) *t*-butoxide, which was used to support vanadia for the subsequent methanol oxidation study in ch. 6. The use of an amorphous ceria domain allowed for better comparisons to the previous chapters. The impact of these different ceria surface structures on the vanadia structure and reactivity toward formaldehyde are discussed and the results from the VO_x/CeO₂/SiO₂ catalysts are compared with results from VO_x/TiO₂/SiO₂ and VO_x/ZrO₂/SiO₂. Overall, the results suggest that the support participates in the reaction by facilitating the H-abstraction from the adsorbed methoxide species.



Figure 1.1. Schematic of methanol oxidation over isolated pseudo-tetrahedral VO_x/SiO₂ catalysts

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Chapter 2

A Study of oxygen vacancy formation and annihilation in submonolayer coverages of TiO₂ dispersed on MCM-48

Abstract

The reduction and reoxidation of submonolayer coverages of TiO_2 deposited onto MCM-48 were investigated. The deposited TiO₂ was characterized by Raman and UV-Visible spectroscopy. Raman spectra show that Ti atoms are bonded to the silica support by Ti-O-Si bonds and that crystalline TiO_2 is not formed. The results of the Raman and UV-Visible spectroscopy suggest that the dispersed TiO₂ is present as two-dimensional oligometric structures. Reduction in H_2 at 923 K produces Ti³⁺ cations observable by EPR (g = 1.932), suggesting the formation of oxygen vacancies. The fraction of Ti that could be reduced increased with TiO₂ surface concentration. This observation is attributed to the ease with which O atoms can be removed from the TiO₂ overlayer as the size of the titania patches increases. The amount of oxygen removed during reduction was quantified by pulsed reoxidation. It was observed that the temperature required for complete reoxidation decreased with increasing surface coverage of the silica support by TiO₂. This trend is explained with a proposed model of the reoxidation process, in which the rate limiting step is the migration of peroxide species through or between the deposited TiO₂ patches. A linear correlation was established between the intensity of the EPR signal for Ti^{3+} and the amount of oxygen removed from TiO_2/SiO_2 . This relationship was then used to determine the oxygen vacancy concentration present on the surface of TiO₂/SiO₂ after temperature-programmed oxidation of methanol.

2.1 Introduction

Crystalline anatase and rutile are good supports for both metal and metal oxide catalysts; however, such forms of TiO₂ are difficult to prepare with high surface area and have a tendency to sinter at low temperatures [1-6]. These shortcomings can be overcome by dispersing of TiO₂ on a high surface area support such as mesoporous SiO₂ [7,8]. By this means, the chemical properties of TiO₂ are combined with the high surface area and the high thermal stability of the SiO₂. Such TiO₂/SiO₂ materials exhibit catalytic activity and selectivity not possessed by bulk TiO₂. For example, TiO₂/SiO₂ is active for liquid-phase epoxidation of alkenes, whereas bulk TiO₂ is not [1,2,9,10]. Likewise, TiO₂/SiO₂ is active for the gas-phase oxidation of methanol to formaldehyde and methyl formate, whereas bulk TiO₂ promotes the condensation of methanol to dimethylether [3,11]. TiO₂/SiO₂ has also been used as a support for dispersed vanadia,[12,13] and VO_x/TiO₂/SiO₂ has been shown to have a considerably higher activity for methanol oxidation to formaldehyde than VO_x/SiO₂ [14,15].

It is well known that TiO_2 can lose oxygen, resulting in the formation of both bulk and surface vacancies [1,16-23]. The presence of such oxygen vacancies changes both the electronic and chemical properties of TiO_2 and consequently the performance of TiO_2 as both a catalyst and a catalyst support [1,24-29]. For example, oxygen vacancies have been shown to affect the photocatalytic activity of TiO_2 , [30,31] the preferential adsorption of water and alcohols, [32,33] and the anchoring of noble metal clusters, such as gold [34,35] or platinum [36]. Oxygen vacancies on TiO_2 have also been suggested to increase the catalytic activity of gold [34,37] and copper [38] nanoparticles supported on TiO_2 , and oxygen vacancies have been proposed to be responsible for the high activity of isolated vanadate species dispersed on TiO_2 for methanol oxidation to formaldehyde [14,39].

Studies of oxygen vacancy formation in bulk TiO₂ suggest that surface vacancies are more stable than bulk vacancies, and that vacancies can migrate from the bulk to the surface of the oxide [40,41]. However, only limited attempts have been made to quantify the surface concentration of O-atom defects. STM studies show that upon heating rutile in vacuum to 700-1100 K, the (110) surface of rutile can contain 2-10% O-vacancies [1,42-47]. Vacancies are also formed in bulk TiO₂ powders by heating in vacuum or an inert atmosphere, [48,49] or in a reducing gas [50,51]. By contrast, nothing is known about the formation of vacancies in two-dimensional structures of TiO₂ formed on SiO₂. Given the differences in the structure of dispersed and bulk TiO₂, it is reasonable to expect that significant differences could exist between the two types of materials with regard to the formation and annihilation of anionic vacancies. For example, whereas Ti has a sixfold coordination in anatase and rutile, [1] at low loading Ti cations in the dispersed Ti species on SiO₂ are believed to be predominantly fourfold coordinated with increasing numbers of 5 and 6-coordinated Ti cations at higher coverages [3,9]. Silicasupported TiO₂ monolayers also lack the subsurface transition metal oxide, which can delocalize charge.

Oxygen vacancies in bulk TiO_2 can be detected using EPR spectroscopy, as the electrons remaining in the vacancy move towards the neighboring Ti atoms forming two reduced Ti³⁺ cations, [39,52,53] according to:

$$Ti^{4+}-O-Ti^{4+} \to Ti^{3+}- -Ti^{3+} + \frac{1}{2}O_2$$
 (2.1)

The presence of Ti^{3+} cations is also readily discernable by the blue color of partially reduced TiO₂ [16,54,55]. In the current study, reduction-reoxidation studies in combination with EPR spectroscopy are used to investigate the reducibility of submonolayer coverages of TiO₂ dispersed onto MCM-48, a mesoporous silica, and the ease with which the oxygen vacancies can be removed. The maximum percentage of Ti atoms that can be reduced to the 3+ state is found to be a function of the Ti loading. The oxygen uptake varies with the reoxidation temperature, as the oxygen vacancies are partially kinetically stable at temperatures below 473 K. The temperature needed for complete reoxidation of the TiO₂/SiO₂ samples decreases with increasing Ti loading. The results of this study suggest that the formation of oxygen vacancies is facilitated when the O atom to be removed is surrounded by a large number of Ti-O-Ti bonds. It is also shown that oxygen vacancies are not completely removed upon reoxidation in O₂ and can persist during methanol oxidation.

2.2 Experimental Methods

2.2.1 Sample synthesis and characterization

The support used in the present studies, MCM-48, was prepared following the procedure given in Ref. 56. Submonolayer coverages of non-crystalline TiO₂ were dispersed onto the surface of the MCM-48 by grafting Ti($O^{i}Pr$)₄ from a solution of dry toluene [14]. MCM-48 support dried over night at 393 K under vacuum was brought into contact with a solution of Ti($O^{i}Pr$)₄ dissolved in about 60 ml of dry toluene at room temperature under inert atmosphere. After stirring the solution with the support for 4 h, the solution was removed and the sample was washed three times with ~60 ml of fresh toluene, before it was dried over night under vacuum at room temperature. The dried material was then heated to 573 K in helium and kept at this temperature for 1 h under synthetic air, before it was heated in synthetic air to 773 K and kept at this temperature for 4 h. Following this procedure, Ti loadings of up to 1 Ti/nm² could be achieved. For Ti loadings higher than 1 Ti/nm² the grafting process was repeated up to three times.

For comparison, an MCM-41 sample with Ti incorporated in the silica framework (denoted as Ti-MCM-41) was prepared following the procedures described in Refs. 57 and 58. The weight percent of Ti was comparable to that of a TiO₂/SiO₂ sample prepared with an apparent surface density of 0.2 Ti/nm². High surface area bulk anatase (99.7%, Aldrich) was used as a TiO₂ reference.

The BET surface area of all samples was measured by N_2 physisorption using an Autosorb-1 (Quantachrome). The weight loading of Ti in all samples was determined by Galbraith Laboratories using inductively-coupled plasma (ICP) analysis. The apparent surface density of Ti, expressed in Ti atoms per nm², was then calculated from the Ti loading and the BET surface area. The structure of the deposited titania was characterized by Raman spectroscopy using a Hololab Series 5000 spectrometer (Kaiser Optical) equipped with a 532 nm Nd: YAG laser operated at a power of 25 mW. Prior to acquiring the Raman spectrum, the sample was heated at 4 K/min to 773 K in 20% O_2 /He (UHP) and held at this temperature for 1 h. Diffuse reflectance UV-Vis spectra were recorded using a Harrick Scientific diffuse reflectance attachment (DRP) with a reaction chamber (DRA-2CR) and a Varian-Cary 6000i spectrophotometer. Prior to acquisition of the UV-Vis spectra, samples were pretreated in a flow of 20% O₂/He and heated at 4 K/min to 723 K and then held at this temperature for 1 h. Spectra were recorded at room temperature with 1-5 eV incident light. Conversion of reflectance data into absorption spectra was performed based on the reference reflectance of MgO using the Kubelka-Munk function $(F(R_{\infty}))$. Absorption edge energies were obtained as the intercept with the abscissa from a linear regression of $[(F(R_{\infty}))hv]^{1/2}$ data plotted versus hv. Temperature-programmed reaction (TPR_x) of methanol oxidation was carried out using about 25 mg of TiO₂/SiO₂ (2.8 Ti/nm²) placed in a $\frac{1}{4}$ -in O.D. guartz tubular reactor. The reaction temperature was measured with a thermocouple placed inside the catalyst bed, and a calibrated quadrupole mass spectrometer (Cirrus, MKS Instruments) was used for on-line gas analysis. The measurement procedure is described in detail in Ref. 11. As a pretreatment, the sample was heated in 60 cm³/min of 20 % O₂/He at a rate of 4 K/min to 773 K and then held at this temperature for 1 h. The reaction mixture was

composed of 6% CH₃OH/7.5% O₂/He. The flowrate was adjusted so that the condition of 1.4 cm^3 CH₃OH/min per Ti atom was maintained.

Temperature-programmed reduction (TPR) profiles of selected samples were performed in the same apparatus as that used for methanol TPRx. Reduction was carried out in 10 % H₂/He (UHP) flowing at 30 cm³/min. The sample was heated at the rate of 10 K/min starting from 323 K to 1073 K, while the concentrations of H₂ (Mass 2) and H₂O (Mass 18) were followed by mass spectrometry.

2.2.2 Reduction-reoxidation measurements

The reduction-reoxidation measurements were carried out in the apparatus described above using about 50 mg of sample. For the sample with the lowest Ti weight loadings $[TiO_2/SiO_2 (0.2 \text{ Ti/nm}^2) \text{ and Ti-MCM-41}]$, the sample weight was increased to 100 mg, but the residence time was held constant by doubling the flow rate. Prior to sample reduction, all samples were oxidized following the procedure described above (20% O_2/He , 4 K/min to 773 K, hold for 1 h) to ensure complete oxidation and removal of surface contaminants. The reduction was then carried out in 10% H₂/He flowing at 60 cm³/min, while the temperature was increased at 4 K/min from room temperature to 923 K. The final temperature of 923 K was kept for one hour, after which the sample was cooled in helium to the desired reoxidation temperature.

During pulsed reoxidation, the sample was constantly purged with 30 cm³/min UHP helium. A flow of 10 % O₂/He was passed through a pulse valve (VICI Valco Instruments), containing a pulse loop with a volume of 0.5 cm³, which was heated to 393 K. One pulse was dosed to the sample every 4 min by switching the pulse valve.

Assuming standard pressure and using the ideal gas law, each oxygen pulse was expected to contain 1.5 μ mol of O₂. Due to possible changes in temperature and pressure in the gas lines, or differences in the exact concentration in the gas in the manifold, the exact amount of oxygen per pulse was determined by dosing three oxygen pulses through the reactor bypass and into the mass spectrometer. The mass spectrometer signal was integrated to determine the concentration of O₂ in each pulse. The actual amount of O₂ per pulse varied between 1.4 and 1.8 μ mol. Each pulse reoxidation experiment was carried out until at least three pulses of equal height were measured with the mass spectrometer, indicating that no further oxygen uptake occurred.

2.2.3 EPR spectroscopy

X-band EPR measurements were performed on a Varian E-Line Century spectrometer equipped with a single microwave cavity operating at a frequency of 9.250 \pm 0.0005 GHz. Samples were cooled to near 12 K using liquid He. A microwave power of 25 μ W was chosen so that measurements were conducted under the condition that the intensity for all observed signals varied linearly with the square root of the power to ensure that no signal was saturated. Except for the gain, the same conditions were used for each EPR measurement. This allowed quantitative comparisons to be made among samples after all spectra were scaled to the same gain (3.2x10³). A DPPH standard was used to determine g values.

Samples were pretreated inside the EPR tubes. To mimic the reaction experiments, a 1/16-in OD stainless steel tube was inserted just above the sample in order to bring the flowing gas into contact with the sample. On both the upstream and the

downstream side, the EPR tube could be isolated with two ball valves. After oxidizing the sample according to the procedure described above (20% O_2 /He, 4 K/min to 773 K, held 1 h) and purging the reactor with helium, one of the following pretreatment procedures was carried out:

- Reduction in 10% H₂/He flowing at 60 cm³/min, while the sample was heated at 4 K/min to 923 K and then held at this temperature for 1 h.
- Heating in He flowing at 60 cm³/min, while the sample was heated at 4 K/min to 923 K and then held at this temperature for 1 h
- TPRx in 6% CH₃OH/7.5% O₂/He, while the sample was heated at 2 K/min to 823 K. The flowrate was adjusted so that the condition of 1.4 cm³ CH₃OH/min per Ti atom was maintained.

After each pretreatment the EPR tube was purged with helium, before the pressure in the EPR tube was reduced and the samples were sealed inside the tube by melting the glass.

2.3 Results and Discussion

2.3.1 Sample Characterization

The results of sample characterization by means of BET and ICP are summarized in Table 2.1. The samples used in this study had weight loadings of Ti of 0.2, 0.9, 1.5, 1.9, 2.6 and 2.8 Ti/nm². The BET surface area of MCM-48 was ~1500 m²/g, and is similar to values observed earlier [59]. With increasing loading of Ti, the BET surface area decreased from 1000 to 800 m²/g, following a pattern reported previously [14]. The surface area of the reference anatase was also measured after a reduction and reoxidation, because considerable sintering was expected during reduction at high temperature. The surface area did, in fact, decrease from an initial value of 100 m²/g to 58 m²/g after reduction and reoxidation.

Fig. 2.1 shows the Raman spectrum for the sample with a Ti loading of 2.8 Ti/nm². Similar spectra were observed for samples with lower Ti loadings but are not shown. The bands at 605 and 480 cm⁻¹ can be attributed to the D1 and D2 bands of the MCM-48 support, respectively, [60] confirming that the structure of the mesoporous silica was not destroyed during the deposition of TiO₂. The Raman bands at 922 and 1079 cm^{-1} can be assigned to Si-O-Ti bonds [3,61]. The presence of these bands indicates that the titania layer is bonded to the SiO₂ support. Ti-O-Ti bands would be expected in the vicinity of 460, 710, and 800-900 cm⁻¹, based on previous studies of TiO₂/Al₂O₃ [62]. The first two of these bands could not be observed because of the broad D1 and D2 bands for silica occurring at 605 and 480 cm⁻¹. A band was observed at 800 cm⁻¹, which may be due to Ti-O-Ti vibrations. No evidence for crystalline forms of titania was found for any of the samples, as evidenced by the absence of characteristic bands for rutile (143, 447, 612, 826 cm^{-1} , [63] or anatase (146, 197, 397, 516, 640, 800 cm⁻¹) [11]. The strongest of these features is the band at 145 cm⁻¹, which is a particularly sensitive detector of even very small amounts of crystalline TiO₂ [3]. The absence of any features in the region of the spectrum below 200 cm⁻¹ (not shown) confirms the absence of crystalline TiO₂ in the samples studies.

The edge energies obtained from the UV-Vis spectroscopic measurements are shown in Fig. 2.2 together with similar data from Ref. 15. The edge energies of the Ti-MCM-41 sample and the reference bulk TiO₂ (high-surface area anatase, Aldrich) are shown for comparison. For bulk TiO_2 , the number of 10 Ti surface atoms per nm² was estimated from geometric considerations of the anatase (101) surface. The decrease in the UV-Visible edge energy can be attributed to an increase in the domain size of TiO_2 , indicating larger "patches" or clusters of TiO_x -like structures on the surface at higher surface loading [15,64]. Values larger than 4.2 eV have been assigned to isolated, monomeric TiO₄ tetrahedra, whereas values smaller than 3.4 eV have been attributed to polymeric TiO_x-chains [15]. Based on the observed edge energies, only the two samples with the lowest Ti surface coverage in this study (Ti-MCM-41, and TiO₂/MCM-48 with 0.2 Ti/nm^2) clearly fall into the range of isolated TiO₄-species, whereas the samples with Ti surface densities of 0.9, 1.4, 1.9, 2.4 and 2.8 Ti/nm² have edge energies between those observed for isolated TiO₄ tetrahedra and polymeric chains. The UV-Visible edge energy is the same for all samples with TiO_2 surface concentrations between 0.9 and 2.8 Ti/nm². This observation suggests that the size of the TiO₂ domains does not increase with increasing TiO₂ surface concentration but, rather, the number of domains increases, while the distance between domains decreases. This interpretation is supported by the recognition that the edge energy is obtained from the position and shape of the low wavenumber side of the UV-Visible spectrum, so its value will be dominated by the properties of the largest clusters in the sample.

2.3.2 Sample reduction

Three peaks for water production were observed in the TPR spectra of samples with surface concentrations of 2.6 and 0.9 Ti/nm² (Fig. 2.3). The peak near 400 K (not shown in Fig. 2.3) can be assigned to desorption of water adsorbed in the pores of the mesoporous silica [65]. The steep increase of the water signal around 1000 K was caused by condensation of silanol groups on the surface of MCM-48, accompanied very likely by a collapse of the MCM-48 structure [65,66]. This peak was absent in bulk TiO₂. For 0.9 TiO₂/SiO₂, a small peak is observed between 800 and 973 K. This peak is higher for 2.6 TiO_2/SiO_2 and coincides with the release of water via silanol condensation. This peak is absent from the TPR spectra for pure MCM-48 and Ti-MCM-41. Therefore, the peak between 800 and 973 K is assigned to partial reduction of the titania deposited on SiO₂. Since no evidence was found for the reduction of Ti-MCM-41, it is concluded that the observed water peak is due to the loss of oxygen from titania oligomers, but not from isolated titanate groups. A similar peak at 840 K was observed for high surface area anatase, in agreement with previous studies of TiO_2 . The appearance of this peak at a temperature 55 K lower than that observed for TiO₂/SiO₂ indicates that the reduction of TiO_2 deposited on silica has a higher activation energy barrier than that for the reduction of anatase.

The amount of water formed by reduction of the SiO₂-supported TiO₂ was determined by integration of the peak near 900 K seen in Fig. 2.4 after subtraction of the baseline. For the TiO₂/SiO₂ sample with 0.9 Ti/nm², the release of water was calculated to be 2.28 μ mol H₂O, which is equivalent to 8.38 μ mol O₂ per gram of sample. Assuming one molecule of H₂O is formed for each oxygen vacancy together with two reduced Ti ions, i.e., [67]

$$Ti^{4+}-O-Ti^{4+} + H_2 \rightarrow Ti^{3+} - Ti^{3+} + H_2O$$
 (2.2)

then 1.9% of all Ti ions in this sample should be in the 3+ state after hydrogen reduction. It is noted that in Eq. (2.2), after the removal of the oxygen atom, the former Ti-O-Ti bond is assumed to contain a vacancy. It cannot be excluded, however, that one or both of the Ti atoms are bound to OH groups which might migrate and change to a bidentate configuration thereby increasing the coordination of the reduced Ti atoms.

We note that this measure of the extent of TiO_2 reduction may be subject to large errors caused by the sensitivity to the means by which the baseline is subtracted. Nevertheless, it is in reasonable quantitative agreement with the extent of TiO_2 reduction determined by pulse O_2 reoxidation. A similar estimate of the amount of water released upon reduction of anatase gave 1.65 µmol H₂O, equivalent to 8.21 mmolO₂/g, which, using the stoichiometry of reaction (2.2), shows that 3.40% of all surface Ti atoms were reduced to Ti³⁺. This value was calculated using the BET surface area measured after the reduction-reoxidation treatment and an assumed surface coverage of 10 Ti/nm². As will be shown below, this extent of reduction is in excellent agreement with results obtained from pulse reoxidation. Integration of the H₂O trace for the 2.6 TiO₂/SiO₂ sample was not possible, because the two water peaks could not be resolved.

2.3.3 Pulsed reoxidation

Plots of oxygen uptake for different reoxidation temperatures are shown in Fig. 2.4 for the TiO_2/SiO_2 sample with 2.8 Ti/nm^2 . With increasing reoxidation temperatures a larger number of pulses are needed to reach the saturation point, and the total oxygen uptake increases. However, no changes in the total uptake were observed for temperatures above 473 K. Complete reoxidation of the sample at temperatures above 473 K was confirmed by EPR spectroscopy: when a reduced sample containing 2.8 Ti/nm^2 was reoxidized pulsewise at 473 K in the EPR tube, only a very small residual signal of the Ti^{3+} species was observed (less than 0.1% of all Ti atoms in the sample). The slightly incomplete reoxidation inside of the EPR tube may have been caused by the less favorable flow conditions in the EPR tube compared to those in the reactor.

Assuming that each O_2 molecule reoxidizes 4 Ti³⁺ cations, [55] according to the reaction:

$$2 \operatorname{Ti}^{3+} - \operatorname{Ti}^{3+} + O_2 \rightarrow 2 \operatorname{Ti}^{4+} - O - \operatorname{Ti}^{4+}$$
 (2.3)

then the maximum oxygen uptake (observed for reoxidation temperatures of 473 K or above) of the TiO_2/SiO_2 sample with 2.8 Ti/nm^2 corresponds to 9.0% of all Ti cations, which were in a 3+ state prior to reoxidation. The incomplete reoxidation of the TiO_2/SiO_2 sample at temperatures below 473 K, suggests that a distribution of vacancy types exits, some of which are more difficult to reoxidize than others.

Figure 2.5 shows the oxygen uptake per Ti atom for different TiO_2/SiO_2 samples plotted as a function of reoxidation temperature. The error bars increase with decreasing TiO_2 loading because the uptake is plotted per Ti atom. It is noted that the maximum uptake of O₂ per Ti atom decreases with decreasing TiO_2 loading. These data then show that while 9.0% of the Ti atoms can be reduced in the TiO_2/SiO_2 sample with 2.8 Ti/nm^2 , only 1.4% of the Ti atoms can be reduced in the TiO_2/SiO_2 sample with 0.2 Ti/nm^2 . It is

also observed that the temperature required for complete reoxidation increases from 473 K for the TiO_2/SiO_2 sample with 2.8 Ti/nm^2 to 673 K for the TiO_2/SiO_2 sample with 0.2 Ti/nm^2 . Complete reoxidation of the samples was confirmed in several cases by EPR spectroscopy. Consequently, the maximum uptake of oxygen measured by pulsed reoxidation is equivalent to the amount of Ti^{3+} formed upon reduction. This conclusion is further supported by the observation of the expected 2:1 ratio between the amount of H_2O formed during the TPR measurement and the amount of O_2 that was consumed during pulse reoxidation. This ratio also indicates that Ti^{3+} is not formed by a reductive removal of OH groups,

$$Ti-OH + \frac{1}{2}H_2 \rightarrow Ti^{3+} + H_2O \qquad (2.4)$$

because in this case one H₂O would equal to only one Ti³⁺. The 2:1 ratio was also observed for reoxidation of anatase. The maximum uptake observed at 473 K equals to 7.93 μ mol O₂/g anatase, or 3.29% of all surface Ti atoms being reducible to the 3+ state. This is in excellent agreement with the extent of reduction as observed by TPR.

Noticeable changes of the catalyst structure, such as a sintering of the TiO_x species or migration of Ti into the SiO_2 structure, do not occur during reduction or pulsed reoxidation. For all samples, repeated measurements of reduction-reoxidation showed the same uptake. If major changes to the samples had occurred during the reduction or the reoxidation process, the uptake would decrease with repeated measurements.

The change in O_2 uptake as a function of the Ti loading is likely to be an effect of the number of Ti-O-Ti bonds in the samples. Ti-O-Ti bonds are expected to lose the oxygen atom more easily than Ti-O-Si bonds, which in turn are expected to lose their oxygen bridge more easily than Si-O-Si bonds. This is due to the lower defect formation energy of TiO₂ compared to SiO₂, [24,68] and because in case of Ti-O-Ti the two electrons left behind on removal of the oxygen atoms can be taken up by the two neighboring Ti atoms, to form two Ti³⁺. Si atoms, on the contrary, are not likely to change their oxidation state to 3+. Neither a MCM-48 sample without TiO₂ grafted on it, nor the Ti-MCM-41 showed any oxygen uptake at 773 K or 673 K, respectively, under the same reduction and reoxidation conditions applied to TiO_2/SiO_2 (results not shown). The absence of an EPR signal for MCM-48 and the observation of a Ti³⁺ signal hardly distinguishable from the baseline in case of Ti-MCM-41 after both the samples had been exposed to H₂ at 923 K confirms the irreducibility of Si-O-Si and Ti-O-Si bonds. The result for Ti-MCM-41 also confirms that Ti³⁺ is not formed by reductive removal of Ti-OH, since this process could, in principal, occur for Ti-MCM-41. Consequently, the results suggest that oxygen can be removed only from Ti-O-Ti bonds.

A model of the TiO₂ layer was developed to assess whether the achievable extent of reduction scales with the number of Ti-O-Ti bonds in the samples. Ti atoms corresponding to a certain surface coverage were randomly distributed on a 100 x 100 matrix, and the expected number of Ti-O-Ti bonds was then determined as a function of coverage. Full coverage was assumed to be 4 Ti/nm², according to the value given in Ref. 3. Figure 2.6 shows a plot of the number of Ti-O-Ti bonds in [mol/g] contained in the deposit (the left-hand ordinate) versus the Ti coverage in Ti/nm² and a plot of twice the oxygen uptake in [mol/g] (the right-hand ordinate) versus Ti coverage. The factor two is needed, because according to eq. (2.3) one O₂ molecule reoxidizes two Ti-O-Ti bonds.
As can be seen, the increase of the number of Ti-O-Ti bonds with coverage predicted from the model agrees qualitatively with the experimental data; however, the total number of Ti-O-Ti bonds is almost two orders of magnitude higher than the oxygen uptake, indicating that only about 2% of all Ti-O-Ti bonds can be reduced, suggesting that the Ti-O-Ti bonds are not all equal.

It is likely that only Ti-O-Ti bonds in larger clusters of TiO_x-species can be reduced because it is easier to distribute or delocalize the charges induced by the removal of the lattice oxygen atom. To test this hypothesis, the model was modified so that a Ti-O-Ti bond could be reduced only if the condition is fulfilled that both Ti atoms in this bond are fully surrounded by three more Ti-O-Ti bonds. Therefore, as soon as the central Ti-O-Ti bond is reduced, the surrounding 6 Ti atoms become irreducible. The results from this simulation are also plotted in Fig. 2.6, on the right axis, on the same scale with the experimental oxygen uptake. Almost quantitative agreement is achieved for the TiO₂/MCM-48 sample with the highest weight loading of titania (2.8 Ti/nm²), and the extremely low reducibility of the 0.2 Ti/nm² sample is also predicted well. However, the experimentally observed O_2 uptake during pulse reoxidation of the samples with intermediate Ti coverage $(0.9, 1.5 \text{ and } 1.9 \text{ Ti/nm}^2)$ is higher than the model suggests. This might be due to a higher than expected clustering of the deposited TiO₂ resulting in part from the tendency of titanium isopropoxide to graft onto silica in the form of dimeric titania species, [69] which, in turn, could aggregate into larger than expected twodimensional domains of titania.

The higher temperature needed for complete reoxidation of TiO_2/SiO_2 samples with lower Ti loading very likely reflects differences in the nature and spatial distribution of oxygen vacancies with TiO_2 surface density. At low TiO_2 surface densities, it is reasonable to expect that there may be only one vacancy per TiO_x patch, whereas at higher TiO_2 surface densities each patch might be larger and may contain several oxygen vacancies, or the TiOx patches are in closer proximity to each other. The mechanism by which vacancies are removed upon reoxidation can be envisioned to be as follows. O_2 adsorbs at a vacancy site to from an O_2^{-1} species, [55,70] probably as shown below:

$$Ti^{3+} - Ti^{3+} + O_2 \rightarrow Ti^{3+} - O_2^{-} - Ti^{4+}$$
 (2.5)

The superoxide species thus formed then dissociates to form a Ti-O-Ti structure and a peroxide structure:

$$Ti^{3+}O_{2}^{-}Ti^{4+}O^{2-}Ti^{4+} \to Ti^{4+}O^{2-}Ti^{4+}O_{2}^{-}Ti^{4+}$$
(2.6)

$$Ti^{3+}O_2^{-}Ti^{4+}O_2^{-}Si^{4+} \rightarrow Ti^{4+}O_2^{-}Ti^{4+}O_2^{-}Si^{4+}$$
 (2.7)

Reactions similar to (2.5) and (2.6) have been suggested to proceed in SiO₂, [71-74] and in the support of V/TiO₂ [39] and V/SiO₂ [75] catalysts. Depending on the size of the TiO_x patch and the location of the oxygen vacancy within it, the peroxide species could be located between two Ti⁴⁺ cations or between a Ti⁴⁺ cation and a Si⁴⁺ cation. Consumption of the peroxide species could then occur by Reactions (2.8) or (2.9) when peroxide species are proximate to an oxygen vacancy, viz.,

$$Ti^{4+}O_2^{2-}Ti^{4+} - Ti^{3+} \rightarrow Ti^{4+}O^{2-}Ti^{4+}O^{2-}Ti^{4+}$$
 (2.8)

$$\text{Si}^{4+}\text{-O}_2^{2-}\text{-Ti}^{4+}\text{-}\text{-Ti}^{3+} \rightarrow \text{Si}^{4+}\text{-O}^{2-}\text{-Ti}^{4+}\text{-}\text{O}^{2-}\text{-Ti}^{4+}$$
 (2.9)

Recent theoretical studies have shown that the activation barrier for migration of peroxide species through TiO_2 is significantly lower than through SiO_2 , [39,71,72,75] suggesting that peroxide migration via the Reaction 2.5 should occur more rapidly than by Reaction 2.6. While admittedly speculative, the proposed mechanism of peroxide formation and migration could explain the increasing ease of vacancy removal by reoxidation observed with increasing loading of TiO_2 deposited on SiO_2 .

2.3.4 EPR spectroscopy

After the pretreatment with 10% H₂/He at 923 K, the TiO₂/SiO₂ sample with 2.8 Ti/nm² was dark blue, indicating the presence of Ti³⁺ cations [42,55]. The EPR spectrum of this sample shows an intense, slightly anisotropic paramagnetic signal centered around g = 1.932 (Fig. 2.7). Even though this g value is lower than typical g values reported previously for Ti³⁺ in bulk TiO₂, [17,76,77] it compares very well to g values reported for surface Ti³⁺ on TiO₂, [55,78] V/TiO₂ [79], or TiO₂ colloids [80]. This observation is reasonable, since all Ti cations are located on the surface of our sample. Sub-surface or bulk TiO₂ is not present.

Figure 2.7 also shows the EPR spectra taken of the 2.8 Ti/nm² sample after it was reoxidized with O_2 pulses at different temperatures in the EPR tube. The EPR signal assigned to Ti³⁺ decreases progressively in intensity the higher the reoxidation temperature, but it does not disappear entirely at temperatures up to 373 K. This is in agreement with the incomplete reoxidation of this sample seen in Figs. 2.5 and 2.6.

Apart from the paramagnetic Ti^{3+} signal, all spectra of the partially reoxidized sample showed a second paramagnetic signal centered around g = 2.010. This feature is absent in the fully reduced, non-reoxidized sample, so it has to be related to the presence of oxygen. The g value is in agreement with values reported for oxygen radical species such as O_2^- or O^- on TiO₂ or Ti/SiO₂, [55,81-83] but signals of those species are expected to be anisotropic and to have components of the g tensor closer to 2.00 [55,81]. It is possible that some of the anisotropic components might overlap with the Ti³⁺ signal and thus be invisible. However, the O_2^- radical in particular would have the g_{zz} component with an absorbance profile at around g = 2.025, [55,81] which was not observed. Medium-polarized conduction electrons in reduced TiO₂ have been observed at a g value close to that of a free electron at 2.0023 [55,81]; however, the amorphous TiO_x species present in the samples studied here are not likely to have a conduction band. Thus, it seems that the most reasonable assignment of the signal at g = 2.010 is to an O⁻ species.

The amount of Ti^{3+} formed upon reduction of TiO_2/SiO_2 samples can be determined by pulsed reoxidation, as was shown earlier (see Figs. 2.5 and 2.6). It is, therefore, possible to correlate the strength of the observed EPR signal observed after sample reduction with the amount of Ti^{3+} in the sample determined by the amount of O_2 required to completely reoxidize the sample. For this purpose, it is very important to keep the EPR measurement conditions precisely the same for all measurements, including, for example, the sample volume, the shape and wall thickness of the EPR tube, the exact position of the sample in the cavity of the EPR spectrometer, and the temperature of the sample and the EPR laboratory [84]. For the measurements reported here, the sample mass was similar for all samples (17.0±0.3 mg). Due to similar packing densities of the different samples, the volume of the each sample was virtually the same. The EPR tubes

used are similar in shape and originate from the same package (WILMAD labglass, 707-SQ-250M). The sample was positioned inside the cavity with the sample center as close as possible to the cavity center, which is the recommended position for quantitative EPR spectroscopy [84]. Spectra for all samples were measured on the same day in an airconditioned laboratory, so the ambient conditions in the lab are assumed to be virtually the same for all samples. The sample temperature was adjusted to 12 ± 2 K.

The spectra obtained under the conditions described above were integrated twice - the first integration being necessary to account for the differential plot of EPR spectra and the signal area can be correlated to the amount of Ti^{3+} in the sample. The correlation thus obtained is presented in Fig. 2.8. It should be noted that the amount of Ti^{3+} was determined by reoxidation of the same sample at the same temperature in the flow reactor. Due to the numerous sources of error which have been identified for quantitative EPR spectroscopy, [84] the data points in Fig. 2.8 display a fairly large scatter, but it is obvious that a linear correlation between Ti³⁺ amount and signal area is obtained with a correlation factor of $R^2 = 0.984$. Two measurements were conducted to test the reproducibility of both the EPR measurements and the sample preparation. The 2.8 Ti/nm² sample reoxidized at 343 K was measured twice, the second time after removing it from the cavity and reinserting it. Both points are marked with the rectangle A in Fig. 2.8 and they almost coincide with each other, indicating the high accuracy of the EPR spectroscopic measurement. Furthermore, two reduced samples with 2.8 Ti/nm² were identically prepared in different tubes and the results with these two samples are marked by rectangle B in Fig. 2.8. Even though the difference between these two points is larger (the difference in the amount of Ti^{3+} in these samples is caused by a slightly different sample mass), the results indicate that the sample pretreatment method leads to generally consistent data.

2.3.5 Temperature-programmed oxidation of methanol

The temperature programmed oxidation of methanol was performed in order to study the state of reduction of the TiO_2/SiO_2 sample with 2.8 Ti/nm^2 under reaction conditions relevant for the catalytic process. Figure 2.9 shows the products formed during the oxidation of methanol on TiO_2/SiO_2 (2.8 Ti/nm^2) by temperature-programmed reaction. The principal product observed is formaldehyde. Some dimethyl ether (DME) and methyl formate (MF) are also produced, and at higher temperatures, decomposition of methanol to CO and H₂ occurs and some CO₂ is formed. The results are in agreement with reaction data reported in Ref. 3. As is expected from the absence of crystalline TiO_2 in all samples, DME is not formed in large quantities [3,11].

The correlation presented in Fig. 2.8 can be used to estimate the amount of Ti^{3+} in differently pretreated sample with an unknown extent of reduction. Fig. 2.10 curve b shows the EPR spectrum of the 2.8 Ti/nm² sample after it had undergone methanol oxidation in a temperature-programmed reaction (TPRx) experiment under conditions comparable to those used to obtain the data shown in Fig. 2.9. After 823 K was reached, the sample was purged with He and cooled to room temperature rapidly, before the pressure in the tube was reduced and the tube was sealed. This spectrum is compared with that obtained after reduction of the same sample of TiO_2/SiO_2 with H₂ (Fig. 2.10 curve a). Note that the intensity of the spectrum of the same scale as that used for

the sample taken after TPRx. The spectrum taken after TPRx exhibits both the paramagnetic signal of Ti^{3+} and the signal at g = 2.010. The amount of Ti^{3+} after TPRx is estimated by double integration of the Ti^{3+} signal and comparison of the area obtained with the correlation curve. By this means, it was established that about 0.22% of the Ti in this sample is present as Ti^{3+} after reaction.

It is possible that the reduction of TiO_2 observed after methanol oxidation in TPRx was caused when the sample was purged in He after reaction. Figure 2.10 curve c displays the EPR spectrum of the 2.8 Ti/nm² sample after it had been heated in He to 923 K and held at that temperature for one hour, a higher temperature and much longer time than those used for purging after TPRx. The high-temperature pretreatment of the sample in He resulted in a Ti³⁺ signal equivalent to 0.04% of the Ti in the sample, which is significantly less than that observed after TPRx. Thus, it is concluded that the level of TiO₂ reduction observed after methanol oxidation by TPRx is representative of the state of the catalyst at the highest reaction temperature.

2.4 Conclusions

Submonolayer deposits of TiO_2 have been prepared on mesoporous silica (MCM-48) by grafting. Raman spectroscopy shows that the deposited TiO_2 is bonded to the silica, where as UV-Visible and Raman spectroscopy suggest that the titania deposit is present in the form of two-dimensional clusters that exhibit an increasing number of Ti-O-Ti bonds with increasing Ti surface coverage. The deposited TiO_2 undergoes reduction in H₂ at temperatures near 900 K via the reaction

$$Ti^{4+}-O-Ti^{4+}+H_2 \rightarrow Ti^{3+}-Ti^{3+}+H_2O$$

The extent of reduction can be determined by the amount of water formed during H_2 reduction and by the amount of O_2 required to reoxidize the vacancies formed. The presence of surface Ti³⁺ cations formed upon reduction of TiO₂/SiO₂ are detected by the appearance of an EPR signal at g = 1.932. This feature disappears completely upon sample reoxidation. The maximum extent of reduction depends on the Ti loading, a larger amount of oxygen being removed the higher Ti surface coverage. It is also found that the temperature needed to fully reoxidize the titania deposit increases with decreasing titania coverage. A linear relationship was determined between the Ti³⁺ EPR signal and the extent of reduction of the deposited titania. Using this relationship, it was established that a small fraction of the Ti atoms in deposited titania remain as Ti³⁺ during the oxidation of methanol.

Sample	Ti loading	BET surface area	Average pore radius
	[nm ⁻²]	$[m^2 g^{-1}]$	[Å]
2.8 Ti/SiO ₂	2.8	923	10
2.6 Ti/SiO ₂	2.6	782	11
1.9 Ti/SiO₂	1.9	809	11
1.5 Ti/SiO ₂	1.5	825	11
0.9 Ti/SiO ₂	0.9	1018	10
0.2 Ti/SiO ₂	0.2	1396	10
Ti-MCM-41	0.13 ^{<i>a</i>}	1100	10.8
Anatase	10^b	100 (58.0 ^{<i>c</i>})	8.2^{c}

Table 2.1: Ti weight loading, BET surface area (single point) and average pore radius of samples used in this study.

^eestimated under the assumption of 100% exposed Ti atoms

^bestimated from geometry of anatase (101) surface

^{*c*}measured after reduction-reoxidation treatment



Figure 2.1. Raman spectrum of 2.8 TiO_2/SiO_2 . The sample was heated to 773 K and then cooled under flowing UHP He before the spectrum was acquired at ambient temperature.



Figure 2.2. UV-Visible edge energy as a function of the Ti surface coverage; TiO_2/MCM -48 samples (this work, red squares), Ti-MCM-41 (this work, pink diamond), TiO_2/SiO_2 (Ref. (15), blue triangles), TiO_2 (anatase) (this work, purple circle).



Figure 2.3. Mole fraction of H₂O formed during temperature-programmed reduction in 30 cm³/min 10% H₂/He; 2.6 TiO₂/SiO₂ (black), 0.9 TiO₂/SiO₂ (blue), MCM-48 (red), Ti-MCM-41 (green), high surface area anatase (purple).



Figure 2.4. Uptake of oxygen during pulsed reoxidation at different temperatures for 2.8 TiO₂/SiO₂; 673 K (purple), 473 K (red), 423 K (pink), 373 K (blue), 343 K (green), 313 K (black).



Figure 2.5. Maximum O_2 uptake during pulsed reoxidation as a function of temperature for 2.8 TiO₂/SiO₂ (black squares), 1.9 TiO₂/SiO₂ (blue triangles), 0.9 TiO₂/SiO₂ (red circles), 0.2 TiO₂/SiO₂ (green diamonds).



Figure 2.6. Comparison of the experimental O_2 uptake (black squares) with the theoretical number of Ti-O-Ti bonds (grey line) and the number of theoretically reducible Ti-O-Ti bonds for groups of eight (black line).



Figure 2.7. EPR spectra of 2.8 TiO_2/SiO_2 reoxidized with O_2 pulses at different temperatures in comparison with the spectrum of a fully reduced sample (grey); reoxidation temperature: 313 K (black, solid), 343 K (black, dashed), 373 K (black, dotted).



Figure 2.8. Correlation of signal area obtained from double integration of the Ti^{3+} signal to the amount of Ti^{3+} as determined from pulsed reoxidation; 2.8 TiO_2/SiO_2 and 1.9 TiO_2/SiO_2 samples reoxidized at different temperature used to generate the curve; rectangle A: 2.8 TiO_2/SiO_2 sample, reoxidized at 343 K, two measurements, after removing and reinserting sample from the cavity, rectangle B: 2.8 TiO_2/SiO_2 sample, fully reduced, two measurements of two samples pretreated in the exact same way.



Figure 2.9. Temperature-programmed reaction profiles of 2.8 TiO_2/SiO_2 , displaying the concentrations of CH₃OH (purple), H₂O (blue), formaldehyde (dark green), CO (cyan), CO₂ (bright green), H₂ (red), DME (gray) and MF (orange); reaction conditions: 6% CH₃OH/7.5% O₂/He, 1.4 CH₃OH cm³ min⁻¹ per Ti atom, temperature ramp - 2 K/min from 363 K to 823 K.



Figure 2.10. EPR spectra of 2.8 TiO_2/SiO_2 after different pretreatments; a) after reduction (10% H₂/He, 4 K/min to 923 K, hold 1 h), intensity divided by factor 100; b) after methanol oxidation TPRx (6% CH₃OH/7.5% O₂/He, 2 K/min to 823 K, then rapid cooling in He); c) after heating in He (4 K/min to 923 K, hold 1 h).

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Chapter 3

An Experimental and Theoretical Investigation of the Structure and Reactivity of Bilayered VO_x/TiO_x/SiO₂ Catalysts for Methanol Oxidation

Abstract

This study reports the results of a combined experimental and theoretical investigation of a bilayered $VO_x/TiO_x/SiO_2$ catalyst consisting of vanadia deposited onto silica containing a submonolayer of titania. Raman spectroscopy indicate that Ti atoms are bonded to the silica support via Ti-O-Si bonds, and Raman and EXAFS data indicate that the vandia is present as isolated vanadate groups bonded to the support through V-O-Si and V-O-Ti bonds. For a fixed vanadia surface density (0.7 V/nm²), the turnover frequency for methanol oxidation to formaldehyde increases with increasing Ti surface density (0.2 to 2.8 Ti/nm²) and the apparent activation energy decreases. These trends are well represented by a model of the active site and its association with Si and Ti atoms of the support. This model takes into account the distribution of Ti on the silica support, the fraction of active sites with 0, 2, and 3 V-O-Ti support bonds, and the rate parameters determined for each of these active sites determined from quantum chemical calculations and absolute rate theory.

3.1 Introduction

The selective oxidation of methanol to formaldehyde has been shown to be catalyzed by isolated vanadate groups supported on metal oxides, such as SiO₂, Al₂O₃, TiO_2 , ZrO_2 , and CeO_2 [1-8]. The structure of the active center has been deduced from evidence obtained by EXAFS and Raman spectroscopy; it consists of a central V atom bonded to the support through three V-O-M bonds (M = Si, Al, Ti, Zr, Ce) and a single V=O vanadyl bond [7,8]. The activity of these sites strongly depends on support composition [1,2,5,7,8]. For example, the turnover frequency (TOF) for methanol oxidation on VO_x/TiO₂ is roughly 10^3 higher than that for VO_x/SiO₂ at the same reaction conditions. Previous studies have concluded that the activity of the vanadate sites increases with decreasing Sanderson electronegativity of the support metal cation [2,5,9]. While this interpretation leads to a good correlation of catalyst activity with Sanderson electronegativity, it is not supported by compelling theoretical arguments. For instance, if the Sanderson electronegativity of the support metal cation were the sole reason for the increased activity, then the thermodynamics of the adsorption step would vary greatly because it is the only step involving the metal support atom. Since the adsorption energy of methanol on different metal oxide supports is comparable [5], a large variation in entropy must then exist, which is unlikely for the same reaction. By contrast, a recent theoretical study aimed at understanding the higher activity of VO_x/TiO₂ relative to VO_x/SiO_2 has shown that O-vacancies in TiO₂ can increase the reaction rate by lowering the activation energy of the rate-determining step [10]. Sub-monolayer quantities of titania dispersed on silica have also been found to increase the activity of dispersed vanadia by over an order of magnitude [11-14]. The aim of the present work was to develop a deeper understanding of the origins of enhanced activity of isolated vanadate species supported on silica containing submonolayer quantities of titania. To this end, theoretical and experimental studies were carried out to understand the role of Ti atoms in bilayered VO_x/TiO_x/SiO₂ catalyst. Samples were characterized by X-ray absorption near-edge spectroscopy (XANES), extended X-ray absorption fine structure (EXAFS), and Raman spectroscopy. The rate parameters involved in the oxidation of methanol were determined using density functional theory (DFT) and absolute rate theory.

3.2 Experimental Methods

A mesoporous silica support with high surface area, MCM-48, was prepared as described previously [7]. The BET surface area was measured by N_2 physisorption with an Autosorb-1 instrument. Prior to N_2 adsorption/desorption measurements each sample was treated under vacuum for 12 h at 393 K. The single point BET method was used to determine the surface area, and the total pore volume was calculated from the desorption isotherm using the method of Barrett, Joyner, and Halenda (BJH). The concentration of silanols on the MCM-48 support was determined by reacting Mg(CH₂Ph)₂•2THF with the Brønsted acid sites and monitoring the evolved toluene by ¹H NMR using a known quantity of ferrocene as an internal standard [15].

Prior to each metal grafting step, the MCM-48 support was heated to 393 K under dynamic vacuum (< 27 Pa) to remove any physisorbed water. Titanium was grafted under a N₂ atmosphere onto the MCM-48 via impregnation with a solution of Ti($O^{i}Pr$)₄ dissolved in approximately 60 cm³ of anhydrous toluene. The mixture was stirred for 4 h at ambient temperature, and then rinsed 2-3 times with ~60 cm³ anhydrous toluene per rinse before drying under vacuum. The as-prepared catalyst was then transferred to a furnace under inert atmosphere, where it was treated in He flowing at a rate of 50 cm³/(min g-catalyst) and heated at 2 K/min from 298 to 573 K. Dry air flowing at 50 cm³/(min g-catalyst) was then passed over the sample as the temperature was ramped at 2 K/min from 573 to 773 K, where it was held for 4 h. Subsequent Ti grafting steps were performed in the same manner to increase the surface coverage of Ti. Vanadium was grafted onto the previously prepared TiO_x/SiO₂ sample via impregnation with a solution of O=V(OⁱPr)₃ in 60 cm³ anhydrous toluene in a manner analogous to that used to graft Ti onto the support.

Catalyst metal weight loadings were determined by inductively coupled plasma (ICP) at Galbraith Labs. The surface densities of Ti and V were calculated based upon the surface area of the catalyst determined by N_2 physisorption after metal grafting.

Raman spectra were recorded with a 532 nm frequency-doubled Nb:YAG laser using 25 mW power measured at the sample. The catalyst was pressed into a 20 mg pellet at 28 MPa and was then pretreated in flowing air at 60 cm³/min from 298 to 773 K. Heating at 773 K was continued for at least 1 h to reduce the fluorescence background. Samples were mounted onto a holder and were rotated at 150 Hz in a quartz Raman cell to prevent sample damage by the laser. Spectra were recorded at a resolution of 2 cm⁻¹ with a collection time of 2 s at room temperature after pretreatment.

X-ray absorption spectroscopy (XAS) measurements were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) on beam lines 2-3 and 10-2 using a

Si (111) crystal. Data were acquired at the V and Ti K-edges and the energy was calibrated using a metal foil placed between two ionization chambers located after the sample. The metal edge was calibrated to the first inflection point of the main peak for V and Ti and set to 5465 and 4966 eV, respectively. Sample weights were calculated to obtain an absorbance of ~2.5 in order to obtain the optimal signal to noise ratio [16], and boron nitride was added to make a self-supporting pellet. Samples were placed in a controlled-atmosphere cell that could be heated up to 823 K in the presence of flowing gas [17]. The cell was evacuated to 6 x 10^{-4} Pa at ambient temperature and cooled to 84 K before collecting the XAS data. XANES measurements were taken under flowing gases at reaction temperature.

The XAS data were analyzed with the software IFEFFIT and its complementary GUIs Athena and Artemis [18, 19]. The edge energy of the sample was defined as the first inflection point after the pre-edge feature. The data were normalized by subtracting a pre-edge line fit to the data from -150 to -30 eV relative to the edge energy, then a quadratic polynomial was fit with a k-weight of two to the data from 150 to 950 eV for EXAFS and 100 to 300 eV for XANES, both relative to the edge energy. A cubic spline was then fit to the data from 0 to 15.6 Å⁻¹ with background frequencies below 0.9 Å minimized and subtracted from the data to obtain the EXAFS signal. Finally, the EXAFS data were Fourier transformed with a Hanning window over a range from 2 to 11 Å to optimize the signal to noise ratio. The oxidized samples were fit with k-weights of 1, 2, and 3 in the range 0.9 < R < 3.4 Å.

Temperature programmed reaction (TPR_x) measurements were performed after treating the catalyst to 773 K under UHP 20% O₂/balance He for 1 h. Ultra high purity (UHP) He and O₂ were flowed through a methanol saturator held at a constant temperature of 273 K to maintain a reactant mixture of 0.04:0.07:0.89 MeOH:O₂:He at a total pressure of 101 kPa. The temperature was ramped from 373 to 773 K at 2 K/min, and the composition of the effluent gas was monitored with a Cirrus quadrupole mass spectrometer. The intensities of the peaks recorded for each product were normalized using He (mass 4) as the internal standard. Species concentrations were obtained by inverting the raw data using matrix deconvolution and a calibration matrix.

3.3 Theoretical Methods

Density functional theory (DFT) was used to determine optimized geometries, vibrational frequencies, and thermodynamic properties for all species. All DFT calculations were performed within QChem 3.0 [20]. The B3LYP functional and 6-31G* basis sets were used for all atoms, except for Ti and V, which were treated using an effective core potential and LANL2DZ basis sets. All atoms were allowed to relax during geometry optimization calculations. The calculated vibrational frequencies were scaled by 0.9614 to account for the overestimation predicted at the B3LYP/6-31G* level of theory [21].

The growing string method (GSM) [22, 23] was used to determine an initial guess of the transition state geometry. The transition state estimate was then refined by performing a transition state search using the eigenvector following (EF) algorithm in QChem 3.0. Each transition state search consisted of three parts: (1) an initial analytical Hessian calculation, (2) a transition state optimization, and finally (3) a frequency calculation to verify the presence of one imaginary frequency corresponding to the motion of atom(s) associated with the transition state. The broken symmetry approach [24, 25] was used to calculate the activation energy for reactions involving a biradicaloid electronic structure with multiple spin states, as described in previous work [10,26,27]. The Landau-Zener probabilities for spin-surface crossing reactions [28-30] were calculated, as done previously [31]. The rate constant for spin-surface crossing was ~10⁶-10⁷ times greater than the rate constant for the rate-limiting step at 550 K for all cases. To obtain more accurate estimates of the reaction and activation energies, single-point calculations were performed on all optimized reactant, product, and transition state geometries. All basis sets were augmented to include diffuse and polarization functions; for instance all non-metal atoms were treated using the 6-311++G** basis sets.

The Gibbs free energy for all structures was calculated using the standard equations from statistical mechanics [32,33]. The translational, rotational, and vibrational partition functions were computed explicitly, as done in previous work [10, 27]. The standard state for all Gibbs free energies reported in this work was 550 K and has been denoted as ΔG° . The standard state used for gas-phase species was taken to be 1 atm, and a mole fraction of 1 was used for all vanadia species.

3.4 Results and Discussion

3.4.1 Catalyst Characterization

The single point BET surface area ranged from 1522 to 1567 m²/g for MCM-48 before grafting. These surface area measurements are consistent with values reported in the literature for samples up to 1600 m²/g [34, 35]. Total pore volumes of the silica support ranged from 0.84 to 0.87 cm³/g, consistent with previously reported values [7]. The concentration of silanols on the support was 1.69 OH/nm², which is similar to values reported for silica heated to 723 K [36]. The surface area decreased to ~1000 m²/g after grafting V and Ti, for all but the lowest Ti weight loading, as shown in Table 3.1. Similar values for the surface area have been reported previously [34].

The metal weight loadings for all catalysts are shown in Table 3.1. Five catalysts with varying Ti coverages were synthesized, including a reference sample without Ti. The vanadium surface coverage for each sample was held constant at 0.7 V/nm² to ensure isolated vanadate sites [7], except in the sample without Ti present, as trace amounts of V_2O_5 were detected on VO_x/SiO_2 from Raman spectroscopy at that coverage.

The Raman spectra in Figure 2.1 of the MCM-48 support show broad peaks centered at 607 and 458 cm⁻¹ indicative of the D_1 and D_2 bands of silica, respectively [36]. The spectrum of the TiO_x/SiO₂ supports show additional peaks at 918 and 1080 cm⁻¹, indicative of Si-O-Ti vibrations [37, 38]. Peaks were not observed at 146, 197, 397, 516, 640, 800 cm⁻¹ or 143, 447, 612, 826 cm⁻¹, characteristic of anatase [8] or rutile [35], respectively. For this reason it is concluded that all of the Ti is atomically dispersed on the surface of MCM-48.

As seen in Figure 2.1, the Raman spectrum taken after grafting vanadium onto the support shows a vanadyl band at 1037-1039 cm⁻¹. The frequency of this band is consistent with what has been reported for vanadium supported on SiO₂ [7] and TiO_x/SiO₂ [39] and matches the vanadyl frequency shown for 0.3 VO_x/SiO₂. Broad bands at 500-800 cm⁻¹ and 200-300 cm⁻¹ corresponding to V-O-V vibrations were not

observed nor were bands at 998, 702, 529, or 287 cm⁻¹, characteristic of V_2O_5 [40]. No evidence of crystalline TiO_x was seen upon V grafting, indicating that by the absence of anatase or rutile in the sample. The peak at 607 cm⁻¹ is attributed to 3-ring siloxane bridges and shifts towards a broad peak centered at 659 cm⁻¹ upon V grafting, which could indicate V-O-Ti bonds [41].

EXAFS and XANES data were acquired at both the V and Ti K-edges. Examination of the edge energy of Ti in each sample indicates that it is predominantly in the 4+ oxidation state. Farges et al. [42] have shown that the height and energy of the pre-edge feature can indicate the coordination of Ti⁴⁺ species. Figure 3.2 shows that the pre-edge energy of 4979.7 eV is consistent with 4-coordinated Ti [42], but the height of the pre-edge feature for $0.9 \text{TiO}_x/\text{SiO}_2$ and $1.4 \text{TiO}_x/\text{SiO}_2$ is lower than that found typically for a fully allowed transition. A reference scan of anatase was used to align the energy with the data of Farges *et al.* [42]. These authors propose that a smaller than expected pre-edge peak could be indicative of a mixture of 4- and 5-coordinated or 4- and 6coordinated Ti. A lower pre-edge height, however, can also be attributed to a distorted tetrahedral geometry from HO-Ti(OSi-)₃ that one would expect to see upon grafting and activation on the surface of the silica support [43], as a consequence of lower 3d-4p Ti orbital hybridization and less overlap with the 2p O orbitals than could be observed for the purely tetrahedral case. Most likely, both factors contribute to the reduction in the pre-edge peak, with coordination effects resulting in a lower peak for $1.4 \text{ TiO}_x/\text{SiO}_2$ than $0.9 \operatorname{TiO}_{x}/\operatorname{SiO}_{2}$.

After grafting V onto the 0.9 $\text{TiO}_x/\text{SiO}_2$ samples, the Ti K-edge energy did not change but the pre-edge feature decreased from 0.49 to 0.26, indicating an interaction between V and Ti after grafting and activation. Interestingly, the pre-edge feature decreased in the higher Ti loading sample to 0.37, but the decrease was less than that for the 0.9 $\text{TiO}_x/\text{SiO}_2$ sample. This result is expected, since for a given quantity of V-O-Ti interactions, the 1.4 Ti sample would have a smaller fraction of Ti interacting with V than the 0.9 Ti sample, and hence, the average effect on the XANES would be less pronounced. Therefore, the smaller decrease in pre-edge intensity for 0.7 $\text{VO}_x/1.4$ $\text{TiO}_x/\text{SiO}_2$ relative to 0.7 $\text{VO}_x/0.9$ $\text{TiO}_x/\text{SiO}_2$ is most likely a result of a smaller fraction of the Ti interacting with V.

Examination of the V K-edge indicates that most of the vanadium is in the 5+ oxidation state, since the edge energy, 5484.34 eV, is consistent with the edge energies of both V₂O₅ and NaVO₃, 5484.58 eV and 5482.78 eV, respectively, as shown in Figure 3.3. In addition, the height of the pre-edge feature, which reflects the hybridization of the metal 3d and 4p orbitals, is consistent with a 5+ oxidation state. The V K-edge XANES for the other VO_x/TiO_x/SiO₂ samples and 0.3 VO_x/SiO₂ are the same as for 0.7 VO_x/0.9 TiO_x/SiO₂ and are not shown.

The fit of the V K-edge EXAFS data for $0.7 \text{ VO}_x/0.9 \text{ TiO}_x/\text{SiO}_2$, shown in Figure 3.4, indicates that there are two oxygen shells at 1.58 ± 0.01 Å and 1.77 ± 0.01 Å. The shorter V-O bond distance is consistent with a vanadyl oxygen, while the longer bond is indicative of a V-O single bond [7] possibly connected to a Si or Ti atom. A Si shell was fit with a V-Si distance of 3.32 ± 0.19 Å from the absorbing vanadium. A backscattering Ti atom was fit to the data at a distance of 3.34 ± 0.05 Å, which could be indicative of either a V or Ti backscattering atom because of the closeness in the atomic numbers of the two atoms, but is more likely attributable to Ti because of the appearance of a Raman

peak at 659 cm⁻¹, characteristic of V-O-Ti vibrations [40], and the reduction in Ti preedge intensity in the Ti XANES. These measurements are summarized in Table 3.2, and more details of the fit can be found in the supporting information for this catalyst. The bond distances obtained from fitting the EXAFS data for the other VO_x/TiO₂/SiO₂ samples were similar to those obtained for the 0.7 VO_x/0.9 TiO_x/SiO₂ sample.

3.4.2 Catalysis

The results of TPR_x studies for each of the VO_x/TiO_x/SiO₂ catalysts are qualitatively similar. The TPR_x results from the 0.9 Ti grafted sample are shown as a representative case in Figure 3.5. For each catalyst sample, CH₂O and H₂O are formed in a 1:1 ratio at the onset of methanol oxidation. As the temperature rises, CH₂O decomposes to form CO and H₂, which rapidly reacts to form water, and a small fraction of the CO undergoes oxidation to CO₂. The primary difference between VO_x/SiO₂ and the samples of VO_x/TiO_x/SiO₂ is the temperature at which CH₂O first appears. The peak temperature shifts from 700 K for VO_x/SiO₂ to 573 K for all samples except the lowest Ti weight loading, even though the production of formaldehyde begins at the same temperature for all samples with Ti.

Figure 3.6 shows an Arrhenius plot with the apparent activation energy for each catalyst. These results may then be compared to those reported by Bronkema *et al.* on titania-supported vanadium [7, 8]. The apparent activation energy measured for the $VO_x/TiO_x/SiO_2$ samples ranges from 21 kcal/mol (for the 0.7 $VO_x/0.2 TiO_x/SiO_2$ sample) to 18 kcal/mol (for the 0.7 $VO_x/2.8 TiO_x/SiO_2$ sample). These values fall between those for VO_x/SiO_2 (23 kcal/mol) and VO_x/TiO_2 (16 kcal/mol), demonstrating that the activation energy of the reaction decreases as the loading of Ti increases.

3.4.3 Theoretical Representation of VO_x/TiO_x/SiO₂

Based on the experimental results indicating the presence of isolated V sites, the titania-silica support was represented by a model similar to that used to represent isolated vanadate sites on silica [26, 27] and titania [10], as shown in Figure 3.7. In this model, the support is represented as a silsesquioxane structure (cubic $Si_8O_{12}H_8$ with terminating H atoms), containing either all Si or Ti atoms. The silsesquioxane model was found in previous work [27] to provide a very good estimate of experimentally measured bond lengths, bond angles, D_1 and D_2 breathing modes, and coordination environment of Si. The vanadate species is then introduced by removing one of the corner Si or Ti atoms and replacing it with a V=O unit. The optimized geometries of such cluster representations of VO_x/SiO_2 and VO_x/TiO_2 were shown to agree closely with experimental measurements, and yielded estimates of the reaction energetics and the rate parameters for methanol oxidation that corresponded closely to those measured experimentally [10, 27]. Although these DFT calculations considered 4-coordinated Ti cluster models, the geometry, vibrational frequencies, and adsorption energies for small molecules were shown to be in good agreement with more extensive slab calculations and with experimental values, where surface Ti atoms are generally 5-coordinated [10].

The cluster model used previously to describe VO_x/SiO_2 was modified by systematically increasing the number of Ti atoms by replacing Si atoms in order to increase the number of V-O-Ti support bonds from zero to three. Active sites with and without an O-vacancy were considered for species with one or more V-O-Ti support

bonds. O-vacancies have been shown to play a role in the enhanced activity of VO_x/TiO_2 [10] and have recently been observed on TiO_x/SiO₂ samples identical to those used for this study (see Supporting Information). All sites comprised of three V-O-Si support bonds were assumed to be free of O-vacancies because formation of an O-vacancy from a Si-O-Si bond in silica is energetically much less favorable than from a Ti-O-Si bond or a Ti-O-Ti bond in titania. For instance, the defect formation energy on SiO₂ is 196 kcal/mol (8.5 eV), [44] compared to 98 kcal/mol (4.27 eV) on the anatase phase of TiO₂ [45] and 46 kcal/mol (1.98 eV) on V₂O₅ [45]. O-vacancies next to isolated V atoms are excluded because DFT calculations introducing such a vacancy result in the rearrangement and loss of the vanadyl oxygen in the active site, thereby forming a V^{3+} species. Likewise, since the energy to form a vacancy at a Si-O-Ti bond is higher than that for the formation of a vacancy at a Ti-O-Ti bond, only vacancy formation involving the latter type of bond vas considered. The seven different optimized active site geometries are shown in Figure 3.7 and are denoted by the number of V-O-Ti support bonds (zero to three) and the presence or absence of an O-vacancy (represented by d) as species 0, 1, 1d, 2, 2d, 3, and 3d. The replacement of terminal H atoms with terminal – OH groups resulted in no change in the optimized geometries or reaction energies for the active sites.

The geometries and frequencies of the seven active sites are in good agreement with the EXAFS and Raman measurements observed experimentally, as seen in Table 3.2. Where multiple bond lengths or vibrational frequencies are listed, these correspond to the lower and upper values for all active sites shown in Figure 3.7. A single theoretical value is listed when the bond length or vibrational frequency is identical for all seven species. The theoretical and experimental V=O and V-O bond lengths are in good agreement and differ by less than 0.2 Å; indeed, the calculated V-Si and V-Ti lengths differ by no more than 0.06 Å from experimental values. The differences between the cubic cluster model of the active site and the structure of the actual catalyst site may be the cause of the small elongation in the V-Si and V-Ti distances. Lastly, the calculated V=O stretch and the symmetric and asymmetric Si-O-Ti stretches agree well with experimental results. The calculated V=O, V-O-Si, and V-O-Ti stretching frequencies do not change significantly as the number of V-O-Ti support bonds is increased. The good agreement between theory and experiment in Table 3.2 suggests that the species shown in Figure 3.7 should provide a reasonable representation of the active sites on the bilayered support.

3.4.4 Theoretical Modeling of Methanol Oxidation Kinetics

Methanol adsorption on the active sites shown in Figure 3.7 can be achieved by cleaving a V-O-Si or V-O-Ti support bond to form a V-OCH₃ species and a Si-OH or Ti-OH species. Previous theoretical calculations have shown that while formation of a V-OH species and a Si-OCH₃ or Ti-OCH₃ species are possible, they are not preferred energetically [10, 27]. Experimental work has also shown that V-OCH₃ species are precursors for the formation of formaldehyde [1, 5-8].

The adsorption energy for methanol, ΔE_{ads} , was calculated for each of the seven active sites and is shown in Table 3.3. Cleavage of both the V-O-Si and V-O-Ti support bonds was considered for all cases. ΔE_{ads} was found to be insensitive to the number of V-O-Ti support bonds and to sites with and without an O-vacancy, ranging from -15.5 kcal/mol for an all SiO₂ support (species **0**) to -15.4 kcal/mol for species containing 3 V-

O-Ti support bonds (species **3** and **3d**). The small range of calculated values of ΔE_{ads} suggests that the support has little intrinsic electronic effect during methanol adsorption.

For all sites that do not contain an O-vacancy and have at least one V-O-Si support bond (species **0**, **1**, and **2**), the V-O-Si bond is the preferred bond to break upon methanol adsorption. However, the reverse is observed for sites that contain an O-vacancy and at least one V-O-Si support bond (**1d**, **2d**), in which cae the V-O-Ti bond is broken preferentially by 1.0 to 1.5 kcal/mol. Despite the small difference in MeOH adsorption energy across either the V-O-Ti or V-O-Si bonds, the overall rate for methanol oxidation on sites containing an O-vacancy is one to two orders of magnitude higher than on sites not containing an O-vacancy.

The rate-limiting step in methanol oxidation involves abstraction of one of the three methoxy H atoms to the vanadyl O atom. The broken symmetry approach was used to calculate the activation energy for this step $(\Delta E_{rls}^{\ddagger})$ because the oxidation state of V changes from V⁵⁺ with zero *d* electrons in the reactant to V³⁺ with two unpaired *d* electrons in the product [26]. The activation energies for each of the active sites in Figure 3.7 are shown in Table 3.3. For sites without an O-vacancy, $\Delta E_{rls}^{\ddagger}$ decreases slightly with increasing number of V-O-Ti support bonds – from 39.8 kcal/mol for species **0** to 38.6 kcal/mol for species **3**. For sites with an O-vacancy, $\Delta E_{rls}^{\ddagger}$ decreases with increasing number of V-O-Ti support bonds more dramatically – from 38.6 kcal/mol for species **3d**. The reason for the large decrease in $\Delta E_{rls}^{\ddagger}$ for sites with an O-vacancy is the increased flexibility of the support and the strong H-bond stabilization in the transition state.

The apparent activation energy ($\Delta E_{app}^{\ddagger}$) and apparent rate constant at 550 K (k_{app}) are defined by Equations (3.2) and (3.3), respectively [10, 26, 27]. The equilibrium constant for methanol adsorption, K_{ads} , is calculated using Equation (3.4). The rate constant for the rate-limiting H-abstraction step, k_{rls} , is determined using Equation (3.5).

$$\Delta E_{app}^{\ddagger} = \Delta E_{ads} + \Delta E_{rls}^{\ddagger} \tag{3.2}$$

$$k_{app} = K_{ads} k_{rls} \tag{3.3}$$

$$K_{ads} = \sigma_{ads} \frac{q_{MeOH \bullet S}}{q_{MeOH} q_S} \exp\left(\frac{PV}{RT}\right) \exp\left(\frac{-\Delta E_{ads}}{RT}\right)$$
(3.4)

$$k_{rls} = \sigma_{rls} \kappa(T) \frac{k_B T}{h} \frac{q_{cH_2 o \cdot s}}{q_{MeOH \cdot s}} \exp\left(\frac{-\Delta E_{rls}^{\ddagger}}{RT}\right)$$
(3.5)

In Equation (3.4), σ_{ads} is the symmetry factor, which is equal to the number of equivalent V-O-M bonds that can be broken during the adsorption of methanol. The partition functions q_{MeOH} , q_s , and $q_{MeOH\bullet s}$ are for methanol, the active site, and the

active site with adsorbed methanol, respectively. In Equation (3.5), σ_{rls} is the symmetry factor for the rate-limiting step and is equal to three, because of the three equivalent methoxy H atoms that can be abstracted. The transmission coefficient for tunneling, $\kappa(T)$, is calculated using Wigner's approximation [46] and is included in the rate constant because the transition state involves transfer of a H atom. The partition function $q_{CH,O*S}^{\dagger}$ is for the transition state leading to the formation of formaldehyde.

Values for $\Delta E_{app}^{\ddagger}$ and k_{app} at 550 K are calculated for each of the active sites and are shown in Table 3.3. The value of $\Delta E_{app}^{\ddagger}$ decreases more significantly for sites with an O-vacancy than for sites without an O-vacancy as the number of V-O-Ti support bonds increases, as can be seen in Figure 3.8. For example, $\Delta E_{app}^{\ddagger}$ decreases by 1.1 kcal/mol progressing from species **0** to **3**, whereas the decrease is > 7 kcal/mol progressing from species **1d** to **3d**. The experimental values of $\Delta E_{app}^{\ddagger}$ for VO_x/SiO₂ [7] and VO_x/TiO₂ [8] are also shown and are in good agreement with the range of values on $\Delta E_{app}^{\ddagger}$ for sites on VO_x/TiO_x/SiO₂ containing an O-vacancy. The value of k_{app} changes by less than 20% as the number of V-O-Ti support bonds increases from zero to three for sites without an Ovacancy; however, the value of k_{app} increases by over a factor of 60 for sites with an Ovacancy, as shown in Figure 3.9. Thus, the number of V-O-Ti support bonds strongly influences the activity of methanol oxidation for sites containing an O-vacancy.

An alternative pathway for methanol oxidation is the adsorption of methanol onto an active site containing a surface Ti-OH group, thereby forming a HO-V=O and H₃CO-Ti-OH species. One of the three methoxy H atoms is then abstracted by the vanadyl O to form a HO-V-OH and H₂CO-Ti-OH species. The weakly bound formaldehyde species rapidly desorbs, and water is released, reforming a V-O-Ti support bond. For this pathway, the change in energy for methanol adsorption is $\Delta E_{ads} = -8.6$ kcal/mol and the activation energy for H-abstraction is $\Delta E_{rls}^{\ddagger} = 34.1$ kcal/mol. Using Equations (3.3)-(3.5), the value of k_{app} at 550 K for this pathway is 1.00 x 10⁻⁵ atm⁻¹·s⁻¹, which is two orders of magnitude smaller than the value of k_{app} on non-defect sites, as shown in Table 3.3, and therefore, this reaction pathway was not considered further.

3.4.5 Model for the Distribution of Active Sites

To compare the theoretical calculations with the experimental results, it is necessary to define the distribution of active sites on the surface. This was done by determining the distribution of Ti on SiO₂, and then V on TiO_x/SiO₂. Experimental work by Scott and coworkers [47] has shown that Ti grafts preferentially as Ti-O-Ti dimers ([(\equiv SiO)Ti(OⁱPr)₂]₂O) onto a silica support when Ti(OⁱPr)₄ is used as the Ti precursor, the same precursor used in the present study. This work suggests that upon calcination, Ti may exist primarily as O_xTi-O-TiO_x species on the MCM-48 support. Correspondingly, V was assumed to have a low probability of bonding to only one Ti.

The distribution of V on the TiO_x/SiO_2 surface was determined in a manner similar to that for Ti. In this analysis, it was assumed that the V atoms are mobile on the surface during calcination, but that the Si and Ti atoms are immobile. Calculations were

performed to determine whether an energetic preference exists for V to graft to certain sites on the surface. From these calculations, V was found to prefer sites with three similar bonds, with V coordinated to three V-O-Ti support bonds favored by 2.03 kcal/mol relative to V coordinated to three V-O-Si support bonds. Active sites with one or two V-O-Ti support bonds were found not to be preferred energetically to sites with zero or three V-O-Ti support bonds because of the increased strain imparted to the cluster model by the difference in size between Ti and Si atoms. The trend in the relative energetic stability was used to determine the statistical distribution of these sites.

The preferential anchoring of VO_x species at TiO_x sites supported on SiO_2 deduced from the above analysis is supported by recent work by Lee and Wachs [14] on multilayered metal oxide supports, which shows that transition metals coordinate preferentially to surface metal oxide modifiers deposited on SiO_2 . This observation further supports our previous assumption that there are a negligible number of active sites that contain one V-O-Ti support bond (species 1 and 1d).

The fraction of V sites that contain x Ti support bonds, P(xTi|V), can be determined using Bayes' probability theorem [48]. Briefly, P(xTi|V) depends on the distribution of Ti and V atoms on the surface and the V surface coverage for isolated, non-interacting V sites. The overall distribution of active sites is explained in further detail in the Supplementary Material. The distribution of sites with zero, two, and three V-O-Ti support bonds (P(0Ti|V), P(2Ti|V), and P(3Ti|V), respectively) are plotted versus Ti surface coverage up to one monolayer (4 Ti/nm²) in Figure 3.10. As can be seen, the fraction of sites with three V-O-Ti support bonds increases greatly at low Ti surface coverage, consistent with the large increase in activity observed experimentally.

3.4.6 Surface O-Vacancy Concentration

We have used a thermodynamic model to determine the distribution of active sites that contain an O-vacancy, consistent with previous work on VO_x/TiO₂ [10]. An equilibrium was assumed to exist between active sites with an O-vacancy, represented as $[V - D]_x$, and an active site without an O-vacancy, represented as $[V - O]_x$. A $[V - D]_x$ site can be formed from a $[V - O]_x$ site by migration of an O-vacancy contained between either a Ti-Ti or Ti-Si surface bond, as shown in Equation (3.6), where D and O stand for the presence and absence of an O-vacancy, respectively.

$$K_{def}$$
(3.6)
[V-O] + [D] \longleftarrow [V-D] + [O]

Separate equilibrium constants were determined for the exchange of an O-vacancy in a Ti-Ti bond $(K_{def,x,Ti})$ or a Ti-Si bond $(K_{def,x,Si})$ with an O atom near an isolated vanadate species containing x V-O-Ti support bonds at 550 K. The value of these equilibrium constants are comparable for species with the same number of V-O-Ti support bonds, although there is a slight preference for the exchange of an O-vacancy in a Ti-Ti bond compared to that in a Ti-Si bond.

These calculations show that O-vacancies present on the surface of $VO_x/TiO_x/SiO_2$ prefer to be near vanadate species, since all values of $K_{def.x.Ti}$ and

 $K_{def,x,Si}$ are greater than one, especially for active sites with three V-O-Ti support bonds. This conclusion is in good agreement with the distribution of surface O-vacancies calculated for VO_x/TiO₂ [10]. The relationship between the fraction of vanadate species with x V-O-Ti support bonds containing an adjacent O-vacancy, $\frac{[V-D]_x}{[V-D]_x + [V-O]_x}$, and the fraction of possible surface O-vacancies per Ti atom, $\frac{[D]}{[Ti]}$, are plotted in Figure 3.11. The determination of $K_{def,x,Ti}$ and $K_{def,x,Si}$, and the system of equations solved to generate Figure 3.11 are discussed further in the Supplementary Material.

3.4.7 Overall Kinetics

The apparent first-order rate constant (k_{app}) at 550 K and the apparent activation energy ($\Delta E_{app}^{\ddagger}$) can be calculated using the distribution of active sites discussed above, either with or without an O-vacancy. The value for k_{app} was determined by considering the contribution of each active site to the total rate constant, as shown in Equation (3.7). Since it was previously assumed that Ti grafts to the SiO₂ surface as Ti dimers, consistent with prior experimental work [47], the sum in Equation (3.7) is over all sites with zero, two, or three V-O-Ti support bonds with and without an O-vacancy. This includes sites **0**, **2**, **2d**, **3**, and **3d** in Figure 3.7, and omits sites **1** and **1d**, which only contain 1 V-O-Ti support bond.

$$k_{app} = \sum_{x=0,2,3} \left\{ k_{app,x,0} \theta_{x,0} + k_{app,x,D} \theta_{x,D} \right\}$$
(3.7)

The values for $k_{app,x,O}$ and $k_{app,x,D}$, where x equals the number of V-O-Ti support bonds, are shown in Table 3.3. The fraction of each active site can be determined from the distribution shown in Figure 3.10 and the concentration of surface O-vacancies shown in Figure 3.11. It is noted further that not all O-vacancies are oxidized on the catalyst surface during methanol oxidation, despite the presence of O₂ [10, 51]. The value of k_{app} at 550 K is plotted in Figure 3.12 as a function of Ti surface coverage for assumed percentages of surface O-vacancies of 1, 2, and 5%. The theoretical results correctly capture the dramatic increase in activity measured experimentally. For a constant vanadia surface coverage, the TOF, and hence the value of k_{app} , increases systematically with Ti loading, as previously indicated by Wachs and coworkers [12]. Figure 3.12 shows that sites containing an O-vacancy (species **2d** and **3d**) contribute to over 80% of the total observed rate.

Similar agreement between theoretical and experimental work is also seen in a plot of $\Delta E_{app}^{\ddagger}$ versus Ti surface coverage, as shown in Figure 3.13. The theoretical results indicate that there is a sharp decline in $\Delta E_{app}^{\ddagger}$, as confirmed by the experimental work in the present study. It should be noted that for Ti surface coverages below 0.5 Ti/nm², $\Delta E_{app}^{\ddagger}$ is lower when there is a higher fraction of surface O-vacancies; however, this trend

reverses above 0.5 Ti/nm², in which case $\Delta E_{app}^{\ddagger}$ is lower when there is a lower fraction of surface O-vacancies. This trend is unexpected because having more active sites with an O-vacancy (species **2d** and **3d**) increases the apparent rate constant, as seen in Figure 3.12, and should lower $\Delta E_{app}^{\ddagger}$. However, the activation energy becomes more sensitive to Ti surface coverage as the fraction of O-vacancies decreases, and as a consequence the ordering of the 1% and 5% curves in Figure 3.13 reverses.

3.5 Conclusions

 $VO_x/TiO_2/SiO_2$ catalysts have been synthesized with a constant V surface coverage of 0.7 V/nm² and Ti surface coverages ranging from 0.2 to 2.8 Ti/nm². The Ti atoms are bonded directly to the support through Ti-O-Si bonds and V atoms are present as isolated vanadate species bonded to the support through a combination of V-O-Si and V-O-Ti bonds. For a fixed surface density of V atoms, the activity of $VO_x/TiO_2/SiO_2$ catalysts for methanol oxidation increases rapidly with increasing surface density of Ti, and the apparent activation energy decreases from 23 kcal/mol for $0.3VO_x/SiO_2$ to 18 kcal/mol for $0.7VO_x/2.8TiO_2/SiO_2$. The active site on $VO_x/TiO_2/SiO_2$ is well represented by a cluster model. The introduction of an oxygen vacancy between to two Ti atoms adjacent to the active site decreases the apparent activation energy and increases the apparent rate coefficient for the oxidation of methanol. The experimentally observed variation in the apparent rate coefficient and the apparent activation energy with Ti surface coverage are well described by a theoretical model that takes into account the distribution to Ti atoms on the surface of silica, the fraction of active sites with 0, 2, and 3 V-O-Ti support bonds, and the rate parameters determined for each of these active sites.

	Surface	Avg. pore	Vanadium	Titanium
Catalyst	Area	size	loading	loading
	(m^2/g)	(Å)	(V/nm^2)	(Ti/nm ²)
$0.3 \text{VO}_{\text{x}}/\text{SiO}_2$	1335	21	0.3	
0.6VO _x /0.2TiO _x /SiO ₂	1201	20	0.6	0.2
0.7VO _x /0.9TiO _x /SiO ₂	1045	19	0.7	0.9
0.7VO _x /1.4TiO _x /SiO ₂	1059	18	0.7	1.4
0.7VO _x /2.8TiO _x /SiO ₂	923	20	0.7	2.8

Table 3.1: BET surface area, pore volume, and metal surface coverages for each catalyst.

Table 3.2: Comparison between theoretical and experimental measurements of the active site. The theoretical values are similar for each of the active sites shown in Figure 3.7. The experimental values for bond lengths are obtained from the EXAFS fit in Figure 3.4, and the vibrational frequencies are from Raman spectroscopy.

	Theory	Experiment
r(V=O)	1.57 Å, 1.58 Å	1.58±0.01 Å ^a
r(V-O)	1.76 Å, 1.77 Å	1.77±0.01 Å ^a
r(V-Si)	3.28 Å	3.32±0.19 Å ^a
r(V-Ti)	3.40 Å	3.34±0.05 Å ^{a,b}
v(V=O)	$1030 \text{ cm}^{-1}, 1033 \text{ cm}^{-1}$	1037-1039 cm ^{-1 a}
v(Si-O-Ti)	924 cm ⁻¹ , 1073 cm ⁻¹	918 cm ^{-1a,c} , 1080 cm ^{-1 a,c}

^a Present work. ^b Cannot discern between V-Ti and V-V backscattering, but assumed to correspond to V-Ti bond length from Ti XANES and Raman. ^c Reference 39.

Table 3.3: Values for ΔE_{ads} , ΔE_{rs}^{\ddagger} , $\Delta E_{app}^{\ddagger}$, and k_{app} for each of the active sites in Figure 3.7. The top half of the table is for sites without an O-vacancy, and the bottom half is for sites with an O-vacancy (denoted as *d*). Also shown are the values for VO_x on TiO₂. The support bond that is broken during methanol adsorption is indicated in parentheses. All energies are listed in kcal/mol. The value of k_{app} is reported for 550 K in units of atm ⁻¹·s⁻¹.

Active Site	ΔE_{ads}	ΔE^{\dagger}_{rls}	ΔE_{app}	k _{app} (atm ⁻¹⋅s⁻¹)
0 , SiO ₂ ^a	-15.5 (V-O-Si)	39.8	24.3	8.93x10 ⁻³
1	-15.0 (V-O-Si)	39.1	24.1	9.52x10 ⁻³
2	-15.7 (V-O-Si)	39.0	23.3	9.80x10 ⁻³
3	-15.4 (V-O-Ti)	38.6	23.2	1.07x10 ⁻²
TiO₂ [♭]	-15.7 (V-O-Ti)	38.5	22.8	1.17x10 ⁻²
1d	-15.4 (V-O-Ti)	38.6	23.2	2.40x10 ⁻²
2d	-15.6 (V-O-Ti)	35.7	20.1	6.81x10 ⁻¹
3d	-15.4 (V-O-Ti)	34.3	18.9	1.35
TiO₂-d ⁵	-15.9 (V-O-Ti)	31.8	15.9	1.48

^a Reference 27. ^b Reference 10.



Figure 3.1: Raman spectra for SiO₂, 0.9TiO_x/SiO₂, 0.3VO_x/SiO₂, and 0.7VO_x/0.9TiO_x/SiO₂. Samples were pretreated in 20% O₂/balance He at 773 K. Scans were taken at ambient temperature in UHP He following pretreatment.



Figure 3.2: Pre-edge peak heights obtained from Ti K-edge normalized XANES for $x \operatorname{TiO}_x/\operatorname{SiO}_2$ and $y \operatorname{VO}_x/x \operatorname{TiO}_x/\operatorname{SiO}_2$. Samples were pretreated in 20% O₂/balance He at 773 K. Scans were taken at LN2 temperature under vacuum.



Figure 3.3: V K-edge XANES data for $0.7VO_x/0.9TiO_x/SiO_2$ () after pretreatment at 773 K in UHP 20% O₂/balance He, NaVO₃ (••••), V₂O₅ (••••), VO₂ (•••••), and V₂O₃ (•••••). Scans taken at room temperature. The inset shows a close-up of the pre-edge feature. XANES data for the other catalysts are similar and not shown for clarity.



Figure 3.4: Real space Fourier transformed k³-weighted $\chi(k)$ for 0.7 VO_x/0.9 TiO_x/SiO₂ treated in synthetic air up to 773 K and the corresponding fit to the data. Scans were taken at 84 K and < 6 x 10⁻⁴ Pa. The data was fit over the range from 0.9 to 3.4 Å for k-weights of 1, 2, and 3.



Figure 3.5: TPR_x data for methanol oxidation on $0.7VO_x/0.9TiO_x/SiO_2$. The temperature was ramped at 2 K/min in a mixture of 0.04 MeOH/0.07 O₂/balance He.



Figure 3.6: Arrhenius plot and apparent activation energies in kcal/mol for $0.7VO_x/y$ TiO₂/SiO₂ obtained from TPR_x experiments carried out with 0.04 MeOH/0.07 O₂/balance He with a temperature ramp of 2 K/min.





Figure 3.7: Active sites with 0, 1, 2, and 3 V-O-Ti support bonds. The species 1d, 2d, and 3d in the second row contain an O-vacancy.



Figure 3.8: Values of $\Delta E_{_{app}}^{\ddagger}$ for active sites with a different number of V-O-Ti bonds.^a Reference 7 (SiO₂). ^b Reference 8 (TiO₂).


Figure 3.9: Values of k_{app} for active sites with a different number of V-O-Ti bonds. ^a Reference 7 (SiO₂). ^b Reference 8 (TiO₂).



Figure 3.10: The fraction of active sites with 0, 2, and 3 V-O-Ti support bonds (left axis) and the average number of V-O-Ti support bonds per active site (right axis) plotted versus Ti surface coverage.



Figure 3.11: Percent of active sites with an O-vacancy versus the total surface O-vacancies at 550 K. The curves are for active sites containing 2 or 3 V-O-Ti support bonds and 2.8 Ti/nm². Active sites containing 0 V-O-Ti (3 V-O-Si) support bonds have been assumed to have no O-vacancies. The plot for the case of 2.8 Ti/nm² is shown.



Figure 3.12: The apparent first-order rate constant at 550 K for methanol oxidation plotted versus the surface coverage of Ti. The surface was assumed to consist only of active sites with 0 (species 0) 2 (species 2, 2d) and 3 (species 3, 3d) V-O-Ti support bonds. The curves calculated from theoretical calculations are shown assuming 1, 2, and 5% surface O-vacancies. ^a Reference 7. ^b Reference 39 (0.29, 1.47, 3.617 Ti/nm²).



Figure 3.13: The apparent activation energy for methanol oxidation plotted versus the surface coverage of Ti. The surface was assumed to consist only of active sites with 0 (species 0), 2 (species 2, 2d) and 3 (species 3, 3d) V-O-Ti support bonds. The curves calculated from theoretical calculations are shown assuming 1, 2, and 5% surface O-vacancies. ^a Reference 7 (SiO₂). ^b Present work (0.2, 0.9, 1.4, 2.8 Ti/nm²).

3.6 Supporting Information



Figure S3.1. Illustration of model used for EXAFS fits shown in Table S3.1.

Table S3.1. V K-edge EXAFS fit parameters for $0.7VO_x/0.9TiO_x/SiO_2$. The V K-edge EXAFS fit was performed on the structure below by first fixing the number of atoms to those shown in the structure, then fixing the amplitude reduction factor and allowing the number of Ti atoms to vary. The paths, parameters, and best fit are shown in the table below.

		Number of	Mean-	Change in		Change in	
	Amplitude	Scatterers	squared	Edge	Initial Atomic	Atomic	
	Reduction	(set except	disorder	Energy	Distance (R _{eff} ,	Distance	Final Interatomic
Path	Factor (set)	Ti)	$(\sigma^2, \text{\AA}^{-2})$	$(\Delta E_0, eV)$	Å)	$(\Delta \mathbf{R}, \mathbf{A})$	Distance (R, Å)
$V=O_4$	0.931	1	0.00326	-4.29078	1.5753	0.00316	1.578 ± 0.010
V-O ₁	0.931	3	0.00326	-4.29078	1.7639	0.00316	1.767 ± 0.010
$V-O_1-O_4$	0.931	6	0.00653	-4.29078	3.0337	0.00632	3.040 ± 0.030
$V-O_4-V-O_4$	0.931	1	0.00653	-4.29078	3.1506	0.00632	3.156 ± 0.040
V-O ₁ -O ₃	0.931	4	0.00653	-4.29078	3.2047	0.00632	3.211 ± 0.030
V-O ₃ -O ₂	0.931	2	0.00653	-4.29078	3.2048	0.00632	3.211 ± 0.030
V-Si ₁	0.931	2	0.03076	-4.29078	3.2667	0.05321	3.319 ± 0.186
V-Si ₁ -O ₁	0.931	4	0.03403	-4.29078	3.3469	0.05637	3.403 ± 0.206
V-O ₂ -Si ₂ -O ₂	0.931	2	0.03729	-4.29078	3.4263	0.05953	3.485 ± 0.216
V-O ₂ -V-O ₂	0.931	3	0.00653	-4.29078	3.5288	0.00632	3.535 ± 0.040
V-Ti	0.931	0.3 ± 0.44	0.00138	-4.29078	3.2768	0.06528	3.342 ± 0.045

R-factor for all k-weights (1, 2, and 3) = 0.0123



Figure S3.2. EPR spectra of TiO₂/SiO₂ (2.8 Ti/nm²); (a) after reduction, 10% H₂/He, 4 K/min to 923 K, hold 1h; (b) after temperature programmed reaction (TPRx), 6% MeOH/7.5% O₂/He, 2 K/min to 823 K, then cool in He. EPR – conditions: frequency 9.250 \pm 0.0005 GHz, power 25 μ W, temperature 12 K. The additional peak in the TPRx spectrum is most likely due to oxygen or carbon radicals.

3.6.1 Probability Distribution

For a given surface coverage of Ti, the fraction of active sites that have 0 (species **0**), 2 (species **2**, **2d**), and 3 (species **3**, **3d**) V-O-Ti supports can be determined. Active sites with 1 V-O-Ti support bond (species **1**, **1d**) were assumed not to be present because Ti has been shown to graft as Ti-O-Ti dimer species. Since the catalyst preparation consists of separate grafting and calcination steps for the Ti-precursor $Ti(O^iPr)_4$ and the V-precursor $O=V(O^iPr)_3$, it is necessary to look at the distribution of Ti and V atoms on the surface in a sequential manner.

First, the distribution of Ti on the SiO₂ surface was investigated. Calculations were performed to determine the energetic preference of forming Ti-O-Ti species compared to Ti-O-Si species. The reactant species consisted of a silsesquioxane model $(Si_8O_{12}H_8)$ for SiO₂ and an identical model in which four Si atoms were replaced with Ti atoms $(Si_4Ti_4O_{12}H_8)$, thus having three Ti-O-Ti bonds. The product species were formed by systematically interchanging one or more of the Si atoms in Si₈O₁₂H₈ with an equal number of Ti atoms from Si₄Ti₄O₁₂H₈, thereby forming Ti-O-Si bonds. The overall change in energy for each of the three reactions was less than 1 kcal/mol, indicating that there is no strong energetic preference for Ti to form a Ti-O-Si bond compared to a Ti-O-Ti bond. Thus, in this work it has been assumed that Ti is dispersed in a probabilistic distribution on the surface.

The probability of finding x Ti neighbors on the surface is given by Eq. (SM-3.1), where $x = 0, 2, \text{ and } 3, \theta_{Ti}$ is the Ti surface coverage, and σ_x is the number of equivalent ways of forming a given configuration. For instance, σ_0 and σ_3 are equal to one because there is only one way to have neighboring atoms be all Si, P(0Ti); or all Ti, P(3Ti).

$$P(xTi) = \frac{\sigma_x \theta_{Ti}^x (1 - \theta_{Ti})^{3-x}}{\sum_{x=0,2,3} \sigma_x \theta_{Ti}^x (1 - \theta_{Ti})^{3-x}}$$
(SM-3.1)

Second, the distribution of V on the TiO_x/SiO₂ surface was investigated in a similar manner. Calculations were performed to determine whether there is an energetic preference for V to graft to certain sites on the surface. The Si atoms involved in the V-O-Si bonds in species **0** were systematically interchanged with Ti atoms in Si₄Ti₄O₁₂H₈ to form species **2** and **3**. The results of these calculations show that V prefers to be coordinated to the metal oxide surface with three equivalent support bonds. As a result of the energetic preference of V to prefer certain surface arrangements, it has been assumed in this work that V achieves an equilibrium Boltzmann distribution on the surface during calcination. Thus, the conditional probability for a V atom to graft to a site given x Ti support bonds, P(V | xTi), is described by the Boltzmann distribution in Eq. (SM-3.2). The value for $\Delta E_{0\to x}$ is equal to the change in energy for sites with 0 V-O-Ti support bonds and sites with x V-O-Ti support bonds. The case of x = 0 was taken to be the zero of energy, such that $\Delta E_{0\to 0} = 0$ kcal/mol. The remaining values for $\Delta E_{0\to x}$ were calculated to be $\Delta E_{0\to 2} = 3.4$ kcal/mol and $\Delta E_{0\to 3} = -2.0$ kcal/mol.

$$P(V \mid xTi) = \frac{\exp\left(\frac{-\Delta E_{0 \to x}}{RT}\right)}{\sum_{x=0,2,3} \exp\left(\frac{-\Delta E_{0 \to x}}{RT}\right)}$$
(SM-3.2)

The V atoms are able to achieve a Boltzmann distribution because they are mobile on the surface, whereas the Si and Ti atoms are not. This assumption is supported by comparing the Tamman temperature for the different metal oxides, which is a measure of the mobility of surface species and equal to half the melting temperature. In the present work, the calcination temperature is 773 K, which is greater than the Tamman temperature for V₂O₅ (482 K) but below that for SiO₂ (962 K) and TiO₂ (1064 K). For this reason, T = 773 K in Eq. (SM-3.2).

The fraction of V sites that contain x Ti support bonds, P(xTi|V), can be determined using Bayes' theorem from Bayesian probability, given in Eq. (SM-3.3). Bayes' theorem states that the conditional probability of having x Ti support bonds given a V atom, P(xTi|V), is equal to the product of the conditional probability of finding a V atom given x Ti support bonds, P(V|xTi), multiplied by the prior probability of finding x Ti atoms on the surface, P(xTi), and divided by the prior

probability of V on the surface, P(V). P(V) is equal to the fractional surface coverage, defined as the number of V atoms on the surface divided by the maximum number of V atoms on the surface for monolayer coverage. Also note that the prior probabilities P(xTi) and P(V) do not depend on each other because the catalyst contains isolated, non-interacting V sites.

$$P(xTi|V) = \frac{P(V|xTi)P(xTi)}{P(V)}$$
(SM-3.3)

The distribution of sites with 0, 2, and 3 V-O-Ti support bonds, P(0Ti|V), P(2Ti|V), and P(3Ti|V), respectively, are calculated using Eq. (SM-3.3). Lastly, the average number of V-O-Ti support bonds, $\langle V - O - Ti \rangle$, at a given Ti surface coverage are calculated using Eq. (SM-3.4).

$$\langle V - O - Ti \rangle = \sum_{x=0}^{3} x P(xTi | V)$$
 (SM-3.4)

The theoretical values of $\langle V - O - Ti \rangle$ are in reasonable agreement with the experimental values determined from fitting the EXAFS results for both samples, which further suggests that the theoretically calculated distribution of active sites is consistent with experimental observables.

3.6.2 Calculation of Surface O-Vacancies

The system of equations listed below is used to generate Figure 3.11 and determine $K_{def,x,Ti}$ and $K_{def,x,Si}$, where x is the number of V-O-Ti support bonds.

Balance on V:
$$[V]_{tot} = \sum_{x=0,2,3} [V]_x = [V]_0 + [V]_2 + [V]_3 = 0.7 \text{ V/nm}^2$$
 (SM-3.5)

Balance on O:
$$[O]_{tot} = [O] + [D] = 10.8 \text{ O sites/nm}^2$$
 (SM-3.6)
= 7.37 O sites/nm² not associated with a Si-O-Si bond
= 1.4 O sites/nm² capable of forming a defect

Equilibrium Condition:
$$K_{def,x} = \frac{[V - D]_x[O]}{[V - O]_x[D]}$$
(SM-3.7)
$$K_{def,x,Ti} = \frac{[V - D]_x[O]}{[V - O]_x[D]}$$
 where [D] are from Ti-O-Ti bonds only
$$K_{def,x,Si} = \frac{[V - D]_x[O]}{[V - O]_x[D]}$$
 where [D] are from Ti-O-Si bonds only

If an O-vacancy is created by removal of an O atom from a Ti-O-Ti bond, then $K_{def,2,Ti} = 2.49$ and $K_{def,3,Ti} = 7.26$ at 550 K. However, these equilibrium constants are slightly

reduced if an O-vacancy is created by removal of an O atom from a Ti-O-Si bond, in which case $K_{def,2,Si} = 1.76$ and $K_{def,3,Ti} = 5.13$ at 550 K.

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Chapter 4

Investigation of the structure and activity of VO_x/ZrO₂/SiO₂ catalysts for methanol oxidation to formaldehyde

Abstract

High surface area silica-supported bilayered $VO_x/ZrO_2/SiO_2$ catalysts were prepared with a constant vanadium surface density of 0.5 V nm⁻² and zirconium surface coverages ranging from 0.0 to 2.1 Zr nm^{-2} . In all cases the zirconia layer was predominantly amorphous in nature. The vanadia existed as isolated tetrahedral O=V(-OM)₃ (M = Si, Zr) regardless of zirconia surface density. At least two distinct tetrahedral vanadia environments were identified by 51 V NMR on the support: O=V(O-Si)₃ and $O=V(O-Zr)_3$, with up to 35% of all V in the latter site at the highest Zr loading. The fraction of V bound to Zr as determined by ⁵¹V NMR agrees with an independent determination of the fraction of sites reduced by methanol at 600 K, a temperature too low for significant reduction of vanadia on silica. The turnover frequency for methanol oxidation increased by nearly two orders of magnitude as the Zr loading was increased. When normalized by the number of $O=V(O-Zr)_3$ sites determined from ⁵¹V NMR and UV-Visible, the turnover frequency for methanol oxidation to formaldehyde was constant with zirconia surface coverage. It is proposed that the much higher activity of O=V(O-Zr)₃ compared to O=V(O-Si)₃ sites is attributable to differences in the mechanism by which H-abstraction from V-OCH₃ groups in the rate-limiting step lead to formaldehyde formation associated with the two types of sites.

4.1 Introduction

The activity of vanadate species for the oxidation of methanol to formaldehyde strongly depends on the composition of the oxide to which these species are bonded [1-3]. Vanadate species dispersed on titania and zirconia, for example, are more than an order of magnitude more active than similar species dispersed on silica, and even higher rates are possible if ceria is used as the support [1,3,4]. Similar effects of support composition have been observed for vanadate species dispersed on silica containing submonolayer coverages of titania or zirconia [4-7]. While a number of proposals have been made to explain the origin of the observed support effects, a consensus concerning the primary cause(s) has not yet emerged [1-5,8-12]. To achieve this goal, it is necessary to characterize, thoroughly, the composition and surface structure of the support. Structural characterization of the supported vanadate species is equally important, since a part of the observed difference in catalytic activity with support composition could be attributable to differences in the structure of vanadate species dispersed on different supports. A particularly fruitful approach for gaining insights into the factors affecting the activity of dispersed vanadate species involves the preparation of two-dimensional submonolayer oxides on silica, and subsequent deposition of isolated vanadate species on such supports. This approach is well illustrated by studies of Wachs and coworkers [6] and our own [4]

for vanadate species dispersed on submonolayer deposits of titania grafted to silica, in which V-O-Ti bonds were shown to be responsible for the rate increase through stabilization of the transition state in the rate determining step. In the present study, we have extended our efforts to isolated vanadate species deposited onto submonolayers of zirconia deposited onto silica. The structure of the deposited zirconia layer was characterized by Raman and UV-Visible spectroscopy and by XANES and EXAFS. These techniques, as well as ⁵¹V MAS-NMR were used to characterize the dispersed vanadate species. An important finding of our work is that the activity of VO_x/ZrO_x/SiO₂ catalysts prepared with a fixed surface concentration of vanadia increases with increasing surface coverage of silica by zirconia. This increase is attributed to the fraction of the vanadate species bonded to zirconia.

4.2 Experimental Methods

MCM-41, high surface area mesoporous silica, was synthesized according to previously reported methods [13-15]. Briefly, dodecyltrimethylammonium bromide (DTMABr) and isopropyl alcohol were added to a flask and stirred at 313 K until fully dissolved. This mixture was then added to tetraethylorthosilicate (TEOS) in a Teflon container and stirred rigorously at ambient temperature for 30 min. A mixture of tetramethylammonium hydroxide (TMAOH) and de-ionized water was added to the TEOS mixture drop-wise and stirred for 2 h. The resulting mixture had a molar ratio 1:0.75:0.26:84.4 of TEOS:DTMABr:TMAOH:H₂O. The milky-white mixture was heated to 358 K for 4 h and de-ionized water was added to maintain the liquid level. This mixture was sealed into the Teflon container and placed into an oven at 373 K for 7 days without stirring and was then filtered and rinsed with de-ionized water. The wet powder was heated to 823 K at 2 K min⁻¹ in high-purity synthetic air and held at this temperature for 5 h.

The surface areas of MCM-41 and the final catalysts were determined by nitrogen physisorption (Quantachrome Autosorb-1 instrument) using the single point BET method.

Zirconium was grafted onto the silica support using zirconium 2-methyl-2butoxide (Gelest) as the precursor. The amount of precursor needed to obtain a desired surface coverage was mixed with approximately 60 cm³ of anhydrous toluene, after which the solution was added to dry MCM-41 and stirred for 4 h at ambient temperature. The solid was filtered from the suspension and then heated in 50 cm³(g min)⁻¹ high purity synthetic air at 4 K min⁻¹ to 773 K for 1 h. Multiple grafting steps were used to obtain zirconium surface coverages greater than 0.8 Zr nm⁻². Vanadium was grafted onto the samples, after zirconium grafting and air treatment, in a single grafting step, using VO(OⁱPr)₃ (Alpha, 96% pure) as the vanadium precursor. The procedure for carrying out the grafting of vanadium was analogous to that used to graft zirconium. The weight loadings of Zr and V were determined by inductively-coupled plasma emission analysis at Galbraith Laboratories, and the surface densities of Zr and V were determined on the basis of the bare support surface area. Monolayer coverage is approximately 7 M nm⁻² (M = V, Zr) based on the number of V atoms that can be placed per nm² on bulk crystalline oxides.

Raman spectra were acquired using a JobinYvon-Horiba spectrometer equipped with a confocal microscope and a 532 nm Nb/YAG laser. The laser line at 532 nm was

removed from the backscattered light using an edge filter and the filtered radiation was detected by a CCD detector (Andor) after passage dispersion by a grating. Prior to the acquisition of Raman spectra, samples were treated at 773 K in 60 cm³ min⁻¹ of 20% O_2 /He for 1 h, cooled in He (99.999%) flow, and then sealed in quartz tubes. Ten scans of 1 s each were acquired at room temperature using 15 mW of laser power at the sample.

⁵¹V nuclear magnetic resonance (NMR) spectra were obtained using an Avance 500 MHz (11.75 T) magnet in the solid-state NMR facility at the University of California, Davis. The samples were pretreated at 773 K for 1 h in 20% O₂/He flowing at 60 cm³/min. After which it was cooled and loaded into a 7 mm ZrO₂ rotor under anhydrous conditions. The measured 90° pulse length was 3 μ s, and a 1.5 μ s pulse length was used to achieve a 45° tip angle. All chemical shifts were referenced to the chemical shift of V₂O₅, -609 ppm [16]. Spectra were acquired using a magic angle spinning (MAS) speed of 7 MHz. Spectra were also recorded at the University of California, Berkeley using a 300 MHz (7 T) magnet in order to establish that the spectral shapes reflected true chemical shifts and not quadrupolar broadening effects due to vanadium [17].

V K-edge and Zr K-edge XAS measurements were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamlines 4-3 and 4-1 using Si(111) and Si(220) monochromator crystals, respectively. All scans were taken in transmission mode using ionization chambers filled with N_2 and a reference foil placed after the sample for energy calibration. The sample mass was adjusted to obtain an absorbance of 2.5 and boron nitride was added, as needed, to form a self-supporting pellet. The sample cell has been described previously [18]. The catalysts were treated in high purity synthetic air at 773 K for 1 h before cooling in He to ambient temperature. All scans were taken at ambient temperature.

The XAS data were analyzed with the IFEFFIT software and its complementary GUI, Athena [19,20]. The edge energy was defined as the first inflection point after any pre-edge feature. The data were normalized by subtracting a pre-edge line fit to the data from -150 to -30 eV relative to the edge energy and a quadratic polynomial (k weight = 2) fit to the data from 150 to 783 eV relative to the edge energy. A fourth order polynomial spline was fit to the data from 0 to 15.96 Å⁻¹ and subtracted to obtain the EXAFS data, minimizing background signals below 1 Å. Finally, the EXAFS data were Fourier transformed from 2-11 Å⁻¹.

Diffuse reflectance UV-Visible spectra were recorded using a Harrick Scientific diffuse reflectance attachment (DRP) with a reaction chamber (DRA-2CR) and a Varian-Cary 6000i spectrophotometer. The spectra of oxidized samples were acquired at ambient temperature after treating the catalysts in 20%O₂/N₂ at 723 K for 1 h. The edge energy was calculated using Tauc's law for indirect transitions in amorphous and crystalline semiconductors [21]. In this expression, a straight line is fit through a plot of $[F(R_{\infty})hv]^{1/2}$ versus hv, where $F(R_{\infty})$ is the Kubelka-Munk function and hv is the incident photon energy. The x-intercept of this linear fit is the edge-energy.

Measurements to determine the fraction of vanadium active for MeOH oxidation were performed in the UV-visible, using a fully oxidized sample as the reference. A reaction mixture of 8% $O_2/4\%$ MeOH/He flowing at 60 cm³ min⁻¹ was passed over the catalyst at 600 K for 10 min before the reaction mixture was switched to 4% MeOH/He and scans taken every 2 min. The absorbance at 15,000 cm⁻¹ was used to indicate the degree of reduction of the V centers on the catalyst. The extent of reduction was

determined by comparison to a calibration curve in a manner identical to that done previously [22]. The calibration curve was determined by reducing an equivalent mass of catalyst in the UV-Visible spectrometer at 623 K in 10% H₂/He flowing at 100 cm³ min⁻¹ and recording the change in its absorbance at 15,000 cm⁻¹. The number of reduced V centers formed was quantified in a separate apparatus using the following technique. A mass of catalyst equivalent to that used for the UV-Visible measurements was reduced at 623 K in 10% H₂/He flowing at 100 cm³ min⁻¹ and then by pulse reoxidized in 3%O₂/He flowing at 30 cm³ min⁻¹. Each O₂ adsorbed was assumed to provide 4 e⁻. The calibration curve was generated by plotting the signal of the UV-visible spectra of these samples with the corresponding time point for total e⁻ adsorbed per V reoxidized pulse-wise in the mass spectrometer. The fraction of V reduced was assumed to correspond to the e⁻/V ratio determined from the experiment.

Temperature programmed reaction (TPR_x) experiments were performed using a mixture of approximately 25 mg of catalyst and 25 mg of bare MCM-41 to provide sufficient catalyst bed depth. The mixture was placed in a quartz reactor and supported with quartz wool. The sample was heated at 4 K/min to 773 K in a flow of high purity O_2 in He (20%O₂/He) flowing at 60 cm³/min and then held at 773 K for 1 h. Next, the sample was cooled in the synthetic air mixture to 363 K, after which a mixture of 4%MeOH/7.5%O₂/He was flowed over the catalyst for 10 min at 363 K before the reactor temperature was increased at 2 K min⁻¹ to 823 K. The reactor effluent was analyzed with a MKS Cirrus mass spectrometer. The concentrations of species formed were analyzed using a matrix-deconvolution method with calibrated response factors.

4.3 Results and Discussion

4.3.1 Catalyst Characterization

Table 4.1 lists the properties of the materials prepared for this study. The BET surface area of MCM-41 was 1353 m²g⁻¹. The maximum zirconium loading obtained for a single grafting was 9.45 wt%, corresponding to 0.8 Zr nm⁻². Higher Zr loadings were obtained with repeated grafting steps, and the highest loading, 2.1 Zr nm⁻², was obtained after three graftings. Vanadium surface coverages of 0.3-0.6 V nm⁻² were obtained from a single grafting step. A low vanadium surface coverage was used intentionally in order to prevent the agglomeration of the vanadia, which is known to form V₂O₅ for coverages greater than 0.7 V nm⁻² on silica [3,23].

Figure 4.1 shows Raman spectra of the catalysts after treatment in 20% O₂/He at 773 K. The broad band centered near 485 cm⁻¹, and the peaks at 600 cm⁻¹ and 800 cm⁻¹ are all indicative of the bare silica support [24]. The shoulder at 1060-1080 cm⁻¹ can be attributed to Si-O vibrations [25]. Upon grafting of vanadium onto ZrO_2/SiO_2 , a peak appears around 1035 cm⁻¹ indicative of the V=O stretch for isolated tetrahedral vanadium species on silica [3]. As the weight loading of Zr was increased, the position of the vanadyl peak shifted from 1040 to 1033 cm⁻¹. This trend is similar to that reported previously for VO_x/ZrO₂/SiO₂, in which the vanadyl stretching frequency decreased from 1041 cm⁻¹ to 1039 cm⁻¹ with increasing zirconium loading [26]. The red shift in the V=O stretch for VO_x/ZrO₂ is lower than that for VO_x/SiO₂ [3,27,28]. The appearance of a band at 995

 cm^{-1} , indicative of V₂O₅, was not observed [29], further indicating that the vanadium is well dispersed and in a tetrahedral coordination on the surface of the support.

At the Zr loading of 1.3 Zr nm⁻², a broad peak appeared at 924 cm⁻¹, which has been attributed to formation of V-O-M (M = V, Zr) bonds in similar systems [26,27]. This band is not observed in the Raman spectra ZrO₂/SiO₂ catalysts regardless of zirconium weight loadings and is present only upon grafting of V. We believe that this peak could be due to V-O-V bonds formed by inadvertent exposure of the sample to moisture during V grafting. No peaks associated with monoclinic or tetragonal zirconia are observed for most Zr surface coverage indicating that the Zr atoms are well dispersed on the support. The small shoulder at 650 cm⁻¹ seen in the spectrum for the highest loading Zr sample (2.1 Zr nm⁻²) could be indicative of small tetragonal ZrO_2 clusters on the support, [30-33] formed during the V grafting process, because this peak is not present in the spectrum of $2.1 \text{ ZrO}_2/\text{SiO}_2$. The large silica peak makes it difficult to determine if additional peaks for t-ZrO₂ at 280, 316, or 462 cm⁻¹ are present [26]. The amount of tetragonal ZrO₂, if present, is small, however, given the peak size in the Raman spectrum. No bands were observed at 780 cm⁻¹ indicative of ZrV_2O_7 units [27] in the final catalysts. Therefore, for all catalysts studied the Zr and V atoms are well dispersed.

Zr K-edge XANES spectra are shown in Figure 4.2. All spectra show the same edge at 18,015 eV indicating that Zr is present in the 4+ oxidation state regardless of the Zr coverage [34,35]. The small shoulder around 18.001 keV, which is more visible in the inset, is indicative of hybridization between the oxygen p- and zirconium d-orbitals, which occurs for non-centrosymmetric species, and represents a transition from the 1s to 4d orbital [33,34]. The intensity of this peak increases with decreasing Zr surface density. Furthermore, as the zirconium surface coverage decreases, the peaks at 18.020 keV and 18.070 keV shift towards higher energy. Both the decrease in intensity of the shoulder at 18.001 keV and the shift in the position of oscillations to lower energy indicate that as the coverage increases the zirconia agglomerates to form domains with increasing oxygen coordination of zirconium to form centrosymmetric structures with a lengthening of the Zr-O bonds [34-37]. Detailed understanding of the Zr bonding environment does not exist in the literature; however, most studies of zirconia-silica gels and supported zirconia indicate that the zirconium atoms have 5 or greater oxygen bonds [7], yet coordination numbers of 5 have been observed in EXAFS for weight loadings less than 17% [38]. Therefore, the observed changes in the Zr K-edge XANES could indicate a shift from 5coordinate Zr atoms at the lowest loadings to 6 or higher Zr-O coordinations at the highest.

After V grafting, the Zr K-edge shows minor changes that are best illustrated by comparing the derivatives of the normalized Zr K-edge XANES spectra with and without grafted V. As seen in Figure 4.3, the greatest changes in the spectra occur for the lowest surface coverage of Zr, which is consistent with larger fractions of Zr on the surface interacting with the grafted V. The highest weight loading of Zr, 2.1 Zr nm⁻², showed the smallest change because it had the highest Zr/V ratio. The decrease in the peak intensity at 18.001 keV indicates that zirconium increases its coordination as a result of V grafting, possibly becoming centrosymmetric, as discussed above. The changes in the Zr K-edge spectra with Zr surface coverage indicate that some of the V interacts with Zr atoms

bonded to the silica surface. A similar effect was observed in Ti K-edge spectra of $VO_x/TiO_2/SiO_2$ catalysts containing isolated vanadate species [4].

The Zr K-edge EXAFS spectra in Figure 4.4 show a large peak centered at 1.35 Å, associated with backscattering from neighboring oxygen atoms approximately 2 Å from the Zr atoms. This peak decreases with increasing Zr surface density, which is most likely a result of two or more Zr-O path lengths whose backscattering destructively interferes and reduces the overall intensity. For the lowest Zr surface density, Zr is fully dispersed and likely contains a single shell of oxygen atoms with similar Zr-O bond distances; however, as the Zr loading increases, Zr begins to form higher coordinated structures. A similar reduction intensity is observed in tetragonal ZrO₂, which contains two Zr-O path lengths at 2.08 and 2.36 Å [35]. The backscattered waves from these two paths interfere causing the decrease in the intensity of the Zr-O peak observed in the EXAFS data shown in Figure 4.4. The broadening in the sample spectra with increasing Zr surface density also implies that multiple O backscattering at increasing distances is the cause of the decrease in intensity, and the O peak position shifts in the direction of the Zr-O backscattering for m-ZrO₂, also shown in Figure 4.4. For all samples except that with the highest Zr surface density, the EXAFS spectra reveal weak Zr-Zr backscattering at slightly below 3 Å corresponding Zr-Zr path length of ~3.3 Å. At the highest Zr surface density, a signal appears consistent with backscattering from Zr atoms separated by 3.6 Å, as observed in t-ZrO₂. Attempts to fit the spectra were unsuccessful because of the variety of Zr environments and the limited data range.

The V K-edge XANES spectra (see supplementary information) for all the catalysts investigated, as well as a reference spectrum of VO_x/SiO_2 , are qualitatively similar, exhibiting a large pre-edge feature and an edge energy at 5,483 eV characteristic of V⁵⁺. [3,4] The V K-edge pre-edge feature at 5,470 eV results from excitation of a vanadium 1s electron into a hybrid O-p and V-d orbital present in tetrahedral and pseudo-tetrahedral V oxides [39]. Examination of the derivative spectra presented in Figure 4.5 reveals subtle changes with Zr loading. The shoulder at 5,468 eV of the pre-edge feature decreases at the same time that the intensity of the main pre-edge peak increases with increasing Zr loading. This trend has been observed previously and has been attributed to a narrowing of V-O bond length differences [39].

The V K-edge EXAFS data are shown in Figure 4.6. All samples show a large peak associated with nearest neighbor oxygen backscattering that shifts slightly to smaller distances with increasing Zr surface coverage and in the direction of the V-O path found in ZrV_2O_7 . A weak peak around 3 Å could indicate V-Zr interactions as seen in ZrV_2O_7 ; however, attempts to obtain information beyond the first shell through fitting were unsuccessful due to the variety of environments in which V are bound to the support.

The UV-visible absorption edge energies determined for $VO_x/ZrO_2/SiO_2$ are shown in Figure 4.7. Since bulk and silica-supported ZrO_2 has an edge energy above 4 eV the optical transition is due to the ligand to metal charge transfer involving V [26,40,41]. All samples have edge energies that are higher than that observed for bulk V_2O_5 (2.05 eV), but smaller than that for $OV[OSi(O^tBu)_3]_3$ (3.65 eV) [42]. The observed edge energies are also consistent with the edge energy found for isolated $O=VO_3$ tetrahedra bound on silica [42]. The peak maxima for these samples of $VO_x/ZrO_2/SiO_2$ occur below 265 nm, consistent with what has been observed for isolated, tetrahedral $O=VO_3$ species as well [29]. The absence of a significant change in the edge energy with increasing Zr surface coverage also indicates that the electronic environment of vanadium remains essentially unchanged with increasing Zr loading.

⁵¹V NMR spectra of the fully oxidized catalysts are shown in Figure 4.8. The speed at which the sample rotated (7 kHz) was not sufficiently high to observe spinning sidebands for these samples. VO_x/SiO_2 shows a single peak at around -485 ppm characteristic of isolated vanadate species on silica [43,44]. Upon grafting Zr onto the sample, the -485 ppm peak broadens requiring a new gaussian at -300 ppm to fit the data. This feature is most likely due to the presence of tetrahedral V sites weakly bound by one V-O-Zr bond [27,16]. A new peak is also observed at -750 ppm, characteristic of tetrahedrally coordinated V bound to the support by 3 V-O-Zr bonds. Replacing Si with the less electronegative Zr will result in more electron density on the neighboring O and more negative chemical shifts [16]. This interpretation is supported by ⁵¹V NMR spectra of ZrV₂O₇, which exhibit a large peak at -775 ppm [16,27,45]. As the surface density of Zr increases, an additional peak appears at approximately -650 ppm. A similar peak has been observed for vanadia supported on anatase, and has been attributed to strongly bound vanadium in an octahedral environment involving with a short V=O bond and a strong interaction with the support [16].

Gaussian peaks centered at -300, -485, -630, -750, and -930 ppm were fitted to each spectrum. The peak at -930 ppm is present in all samples and, with the peak at -300 ppm, suggests some octahedral V moieties on the surface [16,43]. Because the relative intensity of the peaks -630 and -750 ppm increased with increasing Zr loading, the areas of these peaks were divided by the total V signal to obtain a fraction of vanadium associated with zirconium. The ⁵¹V spectrum of 0.3VO_x/1.4ZrO₂/SiO₂ catalyst was also taken using a 300 MHz (7 T) magnet, and the resulting spectrum (see supporting information) is the same as that taken at the higher field, indicating that the appearance of these signals is due to a true chemical shift and not to quadrupolar effects arising from V [46]. The results of the ⁵¹V NMR peak fits are shown in Figure 4.9. The NMR peak fitting indicates that the fraction of vanadium associated with zirconium increases with increasing zirconium surface coverage up to the point where ~35% of all V atoms are associated with Zr. The fraction for the 1.3 Zr nm⁻² sample is significantly higher than the other samples, but this is likely due to the uncertainty in the fit of that spectrum. The 95% confidence interval for the fit is shown as error bars in Figure 4.9, confirming the larger error for the $0.6VO_x/1.3ZrO_2/SiO_2$ sample. This particular sample also exhibited a very intense Raman peak at 924 cm⁻¹ indicative of V-O-M bonds. The appearance of an unusually intense Raman peak near 924 cm⁻¹ may be due to an anomaly in the synthesis procedure, as noted above. In fact, the other two samples synthesized with a similar Zr surface coverage in Table 4.1 showed V-Zr fractions similar to what would have be expected based on the trends with the remaining samples.

The spectroscopic results indicate that the $VO_x/ZrO_x/SiO_2$ catalysts prepared for this study consist primarily of $O=V(O-Si)_3$ and $O=V(O-Zr)_n(O-Si)_{3-n}$ (n = 1-3) units. The position of the chemical shift and the Zr agglomeration evidenced in the Zr K-edge XAS suggests that the total number of V with 1 or 2 V-O-Zr bonds is small and that the dominant V structures on the catalyst are $O=V(O-Si)_3$ and $O=V(O-Zr)_3$; however, species with n = 1, 2 cannot be ruled out. In both cases, the vanadium atoms occur in pseudotetrahedral structures. It is notable, though, that while no differences could be observed in the electronic properties between the two types of sites by either UV-Visible spectroscopy or V K-edge XANES, the presence of $O=V(O-Si)_3$ and $O=V(O-Zr)_3$ species could be detected by ⁵¹V NMR. As discussed below the structural and electronic similarities between the two V environments have implications for the mechanism by which methanol oxidation occurs.

4.3.2 Studies of Methanol Oxidation

For low conversions of methanol to formaldehyde, the rate of methanol oxidation over supported vanadium catalysts was described by the following rate expression [1,4,5,47]

$$\frac{r_{app}}{[V]_{total}} = k_{app}[MeOH]$$
(4.1)

Here r_{app} is the rate of formaldehyde formation, k_{app} is the apparent rate constant, $[V]_{total}$ is the total number of V atoms, and [MeOH] is the gas-phase concentration of methanol. Using equation (4.1), the apparent rate constant was determined from temperature-programmed-reaction (TPRx) experiments. Representative TPRx results for sample $0.6VO_x/0.8ZrO_2/SiO_2$ are shown in the Supporting Information.

Figure 4.10 shows that the apparent rate constant at 543 K increases by over an order of magnitude as the Zr surface coverage increases from 0 to 2.1 Zr nm⁻². This pattern is similar to that observed previously for VO_x/TiO₂/SiO₂ [4]. The apparent activation energy for methanol synthesis was determined from an Arrhenius plot of the rate of formaldehyde formation versus temperature. Figure 4.11 shows that the apparent activation energy is 23 kcal/mol for VO_x/SiO₂ [3] but then decreases to 16 kcal/mol for a Zr coverage of 0.2 Zr/nm² and remains approximately constant for higher Zr coverages. It is also noted that apparent activation energy is essentially the same for all samples of VO_x/ZrO₂/SiO₂ and nearly identical to the value for ZrV₂O₇. The activation energies for VO_x/ZrO₂/SiO₂ are also similar to values reported earlier for ZrO₂-supported vanadia [1,28].

The data presented in Figures 4.10 and 4.11 suggest that the vanadate species are distributed between two classes – those that are bonded exclusively to silica and those that are bonded exclusively to the zirconia overlayer deposited on the surface of silica. The former are described by the structure $O=V(O-Si)_3$, whereas the latter are described most generally by $O=V(O-Zr)_n(O-Si)_{3-n}$ (n = 1-3). Since the surface structural data available for the latter species are insufficient to precisely determine the number of V-O-Zr bonds, we will assume that n = 3 for the balance of the discussion presented here, since the dominant structure is most likely $O=V(O-Zr)_3$ as discussed previously. Therefore, the apparent rate coefficient for methanol oxidation can be described by the relationship:

$$k_{app} = x k_{SiO2}^{0} \exp\left(-\frac{E_{SiO2}}{RT}\right) + (1 - x) k_{ZrO2}^{0} \exp\left(-\frac{E_{ZrO2}}{RT}\right),$$
(4.2)

where x is the fraction of vanadate sites bonded exclusively to SiO₂ and (1-x) is the fraction of sites bonded to ZrO_x exclusively, $k_{SiO_2}^0$ and $k_{ZrO_2}^0$ are the apparent preexponential factors for vanadate species bonded to SiO₂ and ZrO_x, respectively, and

 E_{SiO2} and E_{ZrO2} are the apparent activation energies for vanadate species bonded to SiO₂ and ZrO_x, respectively.

The intrinsic activity of the $O=V(O-Zr)_3$ species was obtained by dividing the values of k_{app} for $VO_x/ZrO_2/SiO_2$ reported in Figure 4.10 by the fraction of V bound to Zr determined from the ⁵¹V NMR spectra. In so doing, it was assumed that the contribution of $O=V(O-Si)_3$ species to the value of k_{app} is small, which, as will be shown below, is fully justified [3]. Figure 4.12 shows that the apparent first-order rate coefficient attributed $O=V(O-Zr)_3$ species is nearly constant with Zr surface coverage. It is also noted that the magnitude of this apparent rate coefficient is two orders of magnitude higher than that for $O=V(O-Si)_3$ species, fully justifying the assumption made in preparing Figure 4.12.

The number of $O=V(O-Zr)_3$ species was quantified independently using UVvisible spectroscopy by counting the number of reduced vanadia centers after reduction in methanol at 600 K. This temperature coincides with the peak in formaldehyde productivity for the catalysts prepared with Zr present but not for VO_x/SiO_2 , which only becomes active at higher temperatures [see Supporting Information]. Since formaldehyde production proceeds in the absence of O₂, treatment in methanol at 600 K should only reduce the sites active for formaldehyde production given the lack of significant side reactions. Therefore, only the reduced sites determined by UV-visible spectroscopy are considered to be active for methanol oxidation at 600K on $VO_x/ZrO_2/SiO_2$ in the presence of O_2 . The conversion from the measured oxygen uptake to the number of reduced V was made assuming 4 e^{-} per O₂ consumed and that all reduced V was in the 4+ oxidation state. Justification for this assumption is given below. Figure 4.9 shows that the fraction of all V sites that are catalytically active determined on the basis of UV-visible spectroscopy in combination with pulsed reoxidiation (see Experimental Section) is consistently lower than that determined independently from ⁵¹V NMR. However, given the significant errors associated with both methods of site determination, the differences may not be physically significant. The important thing to note is that the fraction of active sites determined by UV-visible spectroscopy also shows an increase with increasing Zr surface coverage, which further supports the claim that vanadia to bonded zirconia is responsible for the observed increase in catalytic activity. Consistent with the preceding discussion, it is seen in Figure 12 that the value of the apparent rate coefficient attributable to $O=V(O-Zr)_3$ species determined from analysis of UV-Visible data is nearly a factor of two higher than that determined from analysis of ⁵¹V NMR data.

The preexponential factor, k_{Zr02}^0 , was calculated using both the NMR and UV-Visible method for determining the fraction of V present as $O=V(O-Zr)_3$ species. In the first approach, the values for the preexponential factor and activation energy for VO_x/SiO_2 were obtained from Bronkema, et al. [28] and the activation energy for the VO_x/ZrO_2 sites was taken to be 16 kcal/mol, as measured in this study. The resulting preexponential factor was $6x10^6$ and $3x10^6$ (atm•s)⁻¹ based on the site fractions determined from the UV-Visible and the ⁵¹V NMR data, respectively. The second method assumed the contribution to the rate by VO_x/SiO_2 sites was negligible. The resulting preexponential factor, with an activation energy of 16 kcal/mol, were $6x10^6$ and $3x10^6$ (atm•s)⁻¹ for UV-Visible and ⁵¹V NMR site fractions, respectively. Regardless of the method used, the pre-exponential factors obtained were comparable to those reported previously for isolated vanadate species present on $VO_x/ZrO_2 [7x10^6 (atm \cdot s)^{-1}]$ [28]. This analysis suggests that the primary contribution to the higher rate of formaldehyde production on $O=V(O-Zr)_3$ sites relative to $O=V(O-Si)_3$ sites is the lower activation energy on the former type of site.

It is useful to review what is known about the mechanism of methanol oxidation and the influence of support composition before discussing possible reasons for the differences in the activity of $O=V(O-Si)_3$ species and $O=V(O-Zr)_3$ species. Both experimental and theoretical studies suggest that for isolated vanadate species supported on silica (i.e., $O=V(O-Si)_3$ species) methanol oxidation occurs via the mechanism shown in Figure 4.13A [3,9,48]. Reaction begins with the adsorption of CH₃OH across a V-O-Si bond to form V-OCH₃ and Si-OH groups (Reaction 1). This process is quasi-equilibrated and is followed by the rate-limiting step in which an H atom is transferred from the methyl group of V-OCH₃ to the V=O bond (Reaction 2), resulting in the formation of adsorbed CH₂O, which quickly desorbs, and a V-OH group. In the next step H₂O is formed via the condensation of the Si-OH and V-OH groups (Reaction 3). This leaves the V in the +3 oxidation state. Rapid reoxidation then restores V to the +5 state. Theoretical analyses of the elementary steps shown in Figure 4.13a have confirmed that Reaction 1 is quasi-equilibrated, that Reaction 2 is the rate-limiting step, and that the reoxidation of V is much more rapid than V reduction. These studies have also shown that the rate parameters obtained for the proposed mechanism are in close agreement with those determined experimentally [3,9].

Several attempts have been made to explain the observed dependence of the rate of methanol oxidation on support composition. Wachs and co-workers have proposed that the Sanderson electronegativity of the support metal cation affects the rate of methanol oxidation by influencing the adsorption of methanol (Reaction 1 in Figure 4.13A) [49]. While the turnover frequency for methanol oxidation is found to increase with decreasing Sanderson electronegativity, both experimental and theoretical studies show no significant effect of support composition on the heat of methanol adsorption [1,4,5]. For methanol oxidation on $VO_x/TiO_2/SiO_2$, it has been proposed that larger domain sizes and greater electron delocalization of the titania layer result in a higher TOF towards formaldehyde; however, the manner in which electron delocalization affects the reaction kinetics was not defined [10].

Theoretical studies have suggested that the high activity of isolated vanadate species supported on titania may be due to the influence of O vacancies present at the support surface or to a change in the reaction mechanism relative to that shown in Figure 4.13A. In the first of these two proposals, it is proposed that O vacancies occur adjacent to a few percent of the vanadate species supported on titania [4,5]. While the presence of the vacancy has minimal effect on the calculated equilibrium constant for methanol adsorption, the activation barrier for H-abstraction from V-OCH₃ groups (Reaction 2 in Figure 4.13A) decreases by 7 kcal/mol relative to that for vanadate species that are not adjacent to an O vacancy. The reason for the decrease in activation energy is that the defect provides the active site with more flexibility thereby allowing for a larger degree of H-bonding in the product between Ti-OH and V-OH ligand species. The rate parameters determined on the basis of the O-vacancy hypothesis agree well with those measured for titania-supported vanadia. The proposed interpretation is supported by EPR measurements of small concentrations of Ti³⁺ cations present on TiO₂ [50] and VO_x/TiO₂

[5], and by the observation of a correlation between the turnover frequency for methanol oxidation and the energy required to form an O-vacancy in the support [5].

A second explanation for the high activity of titania-supported vanadia is possibility that the rate limiting step for methanol oxidation occurring on VO_x/TiO₂ and VO_x/SiO₂ are not the same. Recent theoretical studies of methanol oxidation on rutilesupported vanadate species suggest that the rate-limiting step is H-abstraction from V-OCH₃ via reaction with Ti-OH [11]. This elementary reaction is illustrated in Figure 4.13B. The same authors have also examined the adsorption of methanol on rutilesupported VO_x and found that CH₃OH addition across the V-O-Ti bond to form V-OCH₃/Ti-OH and on the V=O to form HO-V-OCH₃ are equally possible [12]. In the latter case, the H-abstraction would produce a Ti-OH group on the surface during the rate determining step. While a detailed microkinetic analysis of methanol oxidation for rutilesupported vanadate species was not carried out, it is plausible that the rate-limiting step for the pathway shown in Figure 4.13B is operative for VO_x/TiO₂ and explains the higher activity of vanadate groups supported on titania relative to silica.

We now turn to a discussion of possible reasons for the higher activity of $VO_x/ZrO_x/SiO_2$ compared to VO_x/SiO_2 . None of the evidence presented in this study shows any indication for intrinsic differences in the electronic properties of $O=V(O-Si)_3$ and $O=V(O-Zr)_3$ species. However, the latter species can be identified by difference in shielding caused by Si versus Zr, as demonstrated by the ⁵¹V NMR spectra presented in Figure 4.8. This observation and the greater ease of methanol reduction of $O=V(O-Zr)_3$ species clearly demonstrates that there are two types of vanadate groups on $VO_x/ZrO_x/SiO_2$. Attempts to identify oxygen vacancies formed upon reduction of the ZrO₂/SiO₂ supports used in the present study showed no evidence for O-vacancy formation, as was observed for TiO_2/SiO_2 [15]; therefore, we do not expect O-vacancies to contribute to the higher activity of vanadates species grafted to zirconia. Likewise, no evidence was seen in the present work for increased electron delocalization with increasing ZrO₂ domain sizes, which would have been evidenced by a decreasing edge energy in the UV-visible [51]. This leads us to suggest that the differences in activity between VO_x/ZrO_x/SiO₂ are due difference in the rate-limiting step in methanol oxidation occurring on the two types of catalyst. We propose that the methanol oxidation proceeds via the mechanism shown in Figure 4.13A for $O=V(O-Si)_3$ species present on VO_x/SiO_2 and $VO_x/ZrO_x/SiO_2$, and via the mechanism shown in Figure 4.13B for $O=V(O-Zr)_3$ species present on $VO_x/ZrO_x/SiO_2$. In the latter case, we envision that the Zr-OH groups participating in the rate-limiting step occur on Zr atoms adjacent to the $O=V(O-Zr)_3$ species. We note further that in the mechanism shown in Fig. 4.13B, vanadium is reduced to the +4 state upon formation of formaldehyde and water, which is consistent with the assumption used to define the number of active vanadium sites associated with zirconia determined by the UV-Visible methods discussed above.

4.4 Conclusions

Characterization of $VO_x/ZrO_x/SiO_2$ prepared with Zr surface coverages between 0.0 and 2.1 Zr nm⁻² demonstrates that zirconia is dispersed on the silica support primarily in two-dimensional structures exhibiting increasing Zr-O-Zr coordination with increasing Zr surface coverage. By contrast, vanadium exists as well dispersed pseudo-tetrahedral

 $O=V(O-Zr)_3$ or $O=V(O-Si)_3$ species. For a fixed vanadium loading, the fraction of vanadium bound to zirconia increases from 0% to approximately 35% with increasing Zr A similar fraction of V sites was found to be active for production of loading. formaldehyde at 600 K, a temperature too low for significant activity on VO_x/SiO₂. Therefore, the active site on these catalysts is proposed to consist of tetrahedral $O=V(OZr)_3$ species. The formaldehyde production rate for $VO_x/ZrO_x/SiO_2$ catalysts is constant with Zr surface density when normalized to the number of these sites determined from either ⁵¹V NMR or UV-Visible spectroscopy, indicating that the increase in the reaction rate is due to an increase in concentration of highly active species on the surface. The apparent preexponential factor for methanol oxidation at $O=V(O-Si)_3$ and $O=V(O-Si)_3$ Zr)₃ species is essentially the same, but the apparent activation barrier is 7 kcal/mol smaller for the latter sites. Thus the nearly hundred-fold higher turnover frequency for methanol oxidation on $O=V(O-Zr)_3$ versus $O=V(O-Si)_3$ is due to lower activation barrier associated with the former sites. We propose that this is due to a difference in the intrinsic activation barrier for the rate-limiting step on the two catalysts as described in Fig. 4.13.

				Surface		
				area after V		
			MCM-41	& Zr		
			surface	grafting,	V coverage,	Zr coverage,
Sample Name	V, wt%	Zr, wt%	area, m ² g ⁻¹	$m^2 g^{-1}$	$V \text{ nm}^{-2}$	$Zr nm^{-2}$
0.5VO _x /0.2ZrO ₂ /SiO ₂	4.08	2.68	1350	1040	0.46	0.17
0.5VO _x /0.4ZrO ₂ /SiO ₂	3.85	5.55	1350	960	0.47	0.38
0.6VO _x /0.8ZrO ₂ /SiO ₂	4.16	9.45	1350	800	0.61	0.78
0.6VO _x /1.3ZrO ₂ /SiO ₂	4.07	15.4	1350	800*	0.60	1.30
0.3VO _x /1.4ZrO ₂ /SiO ₂	2.25	17.9	1350	860	0.31	1.40
0.4VO _x /1.3ZrO ₂ /SiO ₂	3.04	16.7	1350	820	0.44	1.30
0.6VO _x /2.1ZrO ₂ /SiO ₂	3.65	23.2	1350	720	0.60	2.13

Table 4.1. Surface area of MCM-41 before and after Zr and V grafting on a metal-free basis and vanadium and zirconium weight and surface coverages for the surface area after metal grafting.

* Surface area approximated based on other samples.



Figure 4.1. Raman spectra of $VO_x/ZrO_2/SiO_2$ samples and MCM-41 after treating in high purity 20% O_2/He at 773 K for 1h. Scans taken at ambient temperature.



Figure 4.2. Zr K-edge XANES after heating to 773 K in 10% O_2 /He for 1 h at 4 K min⁻¹. Scans taken at ambient temperature in He. Inset is an enlargement of the pre-edge feature at 18005 eV.



Figure 4.3. Zr K-edge derivative spectra for samples with V (solid lines) and without V (dashed lines). Scans were taken at ambient temperature after heating to 773 K for 1 h in 10% O_2 /He at 4K min⁻¹.



Figure 4.4. Magnitude of Fourier-transformed Zr K-edge EXAFS spectra of selected samples (A) and simulated spectra of t-ZrO₂ and m-ZrO₂ (B). Samples were treated in 10% O₂/He at 773 K for 1 h before cooling in He and acquiring the spectra at ambient temperature. Spectra offset for clarity.



Figure 4.5. Derivative of V K-edge Normalized XANES. Samples were heated to 773 K in 60 cm³ min⁻¹ 10% O_2 /He for 1 h at 4 K min⁻¹, then cooled in 60 cm³ min⁻¹ He to ambient temperature before taking scans. See supporting information for normalized spectra.



Figure 4.6. Magnitude of Fourier-transformed k^3 weighted V K-edge EXAFS. Samples were heated to 773 K in 60 cm³ min⁻¹ 10% O₂/He for 1 h at 4 K min⁻¹, then cooled in 60 cm³ min⁻¹ He to ambient temperature before taking scans. The ZrV₂O₇ spectrum was simulated.



Figure 4.7. UV-vis edge energies of $VO_x/ZrO_2/SiO_2$ catalysts after treating in 20% O_2/N_2 to 723 K for 1 h. Samples cooled to ambient temperature in He before taking scan. ^aReference values obtained from ref. [42].



Figure 4.8. ⁵¹V MAS NMR of VO_x/ZrO₂/SiO₂ catalysts after treatment in 20% O₂/He at 773 K for 1 h and cooled to ambient temperature in He. Spectra were acquired on a 11.75 T magnet. V_2O_5 was used as the reference and set to -609 ppm.



Figure 4.9. Fraction of V-Zr sites on catalyst as determined by ⁵¹V NMR peak fitting (blue trangles) and fraction of active sites as determined by UV-vis (red squares). The errors indicate the 95% confidence interval from the fit.



Figure 4.10. Apparent rate constant for methanol oxidation over $VO_x/ZrO_2/SiO_2$ at 543 K as a function of Zr surface density.



Figure 4.11. Apparent activation energy for methanol oxidation on VO_xZrO_2/SiO_2 catalysts as a function of Zr surface coverage. ^{a,b}VO_x/SiO₂ and VO_x/ZrO₂ from refs. 3 and 28, respectively.



Figure 4.12. Apparent rate constant as a function of Zr surface coverage normalized by the fraction of V strongly bound to Zr as determined by ⁵¹V NMR peak fits (blue triangles) and normalized by the fraction of V reduced by MeOH at 600 K as determined by UV-Visible (red squares). Dashed lines are to guide the eye.



Figure 4.13. Proposed schematic for methanol oxidation on VO_x/SiO₂ sites (A) and on VO_x/ZrO₂ sites (B).

4.5 Supporting Information



Figure S4.1. Normalized V K-edge XANES offset for clarity. The samples were treated to 773 K in $10\%O_2$ /He and held for 1 h before cooling in He. Scans were taken at ambient temperature.



Figure S4.2. ⁵¹V NMR data for $0.3VO_x/1.4ZrO_2/SiO_2$ catalyst on 7.05 T and 11.75 T magnets. Data were acquired without spinning and a quadrupolar echo experiment with an excitation pulse of 1.6 μ s.



Figure S4.3. Temperature programmed reaction data for $0.6VO_x/0.8ZrO_2/SiO_2$. The reaction conditions were 4%MeOH/7.5%O₂/He at 60 cm³ min⁻¹ over 25 mg catalyst mixed with 25 mg MCM-41.



Figure S4.4. Formaldehyde mole fraction for $0.6VO_x/0.8ZrO_2/SiO_2$ and $0.4VO_x/SiO_2$ as a function of temperature while flowing 4% MeOH/ 7% O₂/He over catalysts at 4 K min⁻¹.



Figure S4.5. Calibration curves for UV-visible reduction in H₂.

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Chapter 5

Synthesis of different CeO₂ structures on mesoporous silica and characterization of their reduction properties

Abstract

An investigation was performed to establish the effects of precursor composition on the structure of ceria deposited onto mesoporous silicas, MCM-41 and SBA-15. The structure of the deposited ceria was characterized by XRD, TEM, Raman and UV-Visible spectroscopy, and by XANES and EXAFS. Using $Ce(acac)_3$ as the precursor resulted in formation of 3-nm diameter ceria particles located predominantly in the mouths of the support pores. Amorphous agglomerates, but with domains of comparable size to those obtained using $Ce(acac)_3$, were obtained using $Ce(O^iPr)_4$. Much smaller domains and a high degree of dispersion was obtained using $Ce(O^{t}Bu)_{4}$ as the precursor. The structure of the deposited ceria affects its reduction-reoxidation properties. Reduction and reoxidation is almost fully reversible for the nanoparticles. Only surface reduction is observed up to 723 K, whereas partial bulk reduction takes place at higher reduction temperatures. In case of the well dispersed, layer-like Ce species on the silica surface, an extent of reduction similar to that of the nanoparticles is achievable, but upon heating the samples in 10% H₂/He to 923 K the reduction becomes partially irreversible. The latter effect might be explained by a formation of cerium silicates that prevent the complete reoxidation of the cerium species.

5.1 Introduction

Dispersion of a transition metal oxide on a high surface area support such as Al_2O_3 or SiO_2 , makes it possible to combine the catalytic properties of the transition metal oxide with the high surface area and thermal and mechanical stability of the support [1]. Good illustrations of the manner in which the transition metal oxide is introduced onto the support and the physical properties of the deposited oxide are given for the cases of TiO_x [1-9], VO_x [5,9-14] or MoO_x [10,11,15-21] dispersed on high surface area supports. A notable consequence of this approach is the formation of catalytically active sites which are not present on either the support or the bulk transition metal oxide. For example, neither TiO2 nor SiO2 is active for the liquid-phase epoxidation of alkenes, but TiO₂/SiO₂ exhibits high activity and selectivity for this reaction [6,22-24]. The appearance of such novel catalytically active sites has been attributed to the formation of a two dimensional oxide overlayer whose physical properties differ from those of the corresponding bulk oxide. Dispersed transition metal oxides have also been shown to stabilize the dispersion of small metal particles and to enhance the activity of supported metal oxo species. For example, Au particles have been shown to be much more stable on TiO_x/SiO₂ than SiO₂ [25] and isolated vanadate species dispersed on TiO_x/SiO_2 exhibit turnover frequencies that are up to 60-fold higher than when dispersed on SiO_2 [7].

CeO₂ is a highly reducible oxide exhibiting oxygen storage and release properties that are important for the operation of three-way, automotive exhaust catalysts [26]. It can also stabilize the dispersion of noble metal particles [27] and CeO₂-supported vanadia is much more active for methanol synthesis than vanadia dispersed on other supports [10,28]. Since it is hard to prepare bulk CeO_2 with a high surface area, interest has arisen in dispersing ceria onto high surface area supports. While there have been numerous attempts to disperse ceria on SiO_2 or Al_2O_3 [29-49], or to incorporate cerium atoms into the walls of mesoporous silica [50-52], these efforts have largely led to the formation of small crystallites of CeO₂ because ceria has a strong tendency to sinter at elevated temperatures [53-55]. While there have been some reports of non-crystalline CeO₂ species grafted on SiO₂ [39,45,55-58], the deposited material has not been well characterized. What is known, though, is that the structure of CeO₂ deposited on inert supports depends on the composition of the cerium precursor and the deposition In general, alkoxide precursors and cerium acetylacetonate lead to the conditions. formation of smaller CeO_2 particles on SiO₂ than deposits produced using cerium nitrate or cerium ammonium nitrate as the precursor [32,41,42,45,55].

The aim of the present work was to establish the influence of precursor composition and support structure on the deposition of ceria on silica. Mesoporous silicas – MCM-41 and SBA-15 – were used as the supports. Previous work has shown that high dispersion of V [59], Pt [60] and Ti [61] species can be deposited by using organometallic complexes with spatially demanding ligands. Based on these findings, cerium precursor molecules with bulky ligands were selected for the deposition of ceria layers on silica. Due to the generally superior performance of alkoxide precursors for grafting transition metals on silica, cerium isopropoxide and cerium t-butoxide were investigated in this study. The use of cerium *t*-butoxide for the grafting of ceria on silica has not been reported previously. Cerium acetylacetonate was also used because it grafts differently to the surface than the alkoxide precursors. It will be shown that the use of these three precursors allows the controlled synthesis of layer-like structures, uniform ceria nanoparticles, and partially amorphous agglomerates on MCM-41 and SBA-15. The different structures were identified and characterized by XRD, TEM, Raman and UV-Visible spectroscopy, and by XANES and EXAFS. The reduction and reoxidation properties of the samples were also characterized and compared.

5.2 Experimental Methods

MCM-41 was prepared following previously reported procedures [62,63]. The resulting material had a surface area of almost 1100 m²/g and an average pore diameter of 18 to 20 Å. SBA-15 was synthesized following a modification of the method described in Ref. [64], using Pluronic P123 ($<M_W> = 5,800$) as the structural template. The template was suspended in water and stirred for 1.5 h before it was fully dissolved by adding 120 ml of 2 M HCl and stirred for another 2 h. TEOS was added dropwise at 308 K and the mixture was stirred for 24 h. It was then heated to 373 K and kept for 24 h under static conditions (without stirring). The precipitate was filtered and washed six

times with deionized water and once with about 50 ml of acetone. The filtrate was dried overnight in air, heated at 2 K/min from room temperature to 773 K, and then held at this temperature for 4 h. The resulting SBA-15 had a BET surface area between 700 and 800 m^2/g and an average pore diameter of 45 to 60 Å.

Prior to grafting ceria, about 2 g of MCM-41 or SBA-15 was dried overnight under vacuum at 383 K. Three different precursors were used for the grafting of cerium species on the silica surface: cerium-III-acetylacetonate-hydrate ($Ce(C_5H_7O_2)_3 \cdot xH_2O$, from Sigma-Aldrich), cerium-IV-isopropoxide isopropanol complex ($Ce(OC_3H_7)_4 \cdot C_3H_7OH$, from Gelest, Inc.) and cerium-IV-*tert*-butoxide ($Ce(OC_4H_9)_4$ from Gelest, Inc.). All precursors were obtained as powders. $Ce(O^iPr)_4$ and $Ce(O^tBu)_4$ are highly sensitive to moisture and were stored in a glove box. $Ce(acac)_3$ is hygroscopic and was stored in a desiccator prior to use.

For the grafting of $Ce(acac)_3$ the compound was dissolved in 70 mL of toluene under inert atmosphere. The concentration was adjusted according to the desired coverage for the amount of support used. To completely dissolve $Ce(acac)_3$, the toluene solution was heated to 348 K, resulting in the formation of a bright orange-red solution. The MCM-41 or SBA-15 support was heated to 363 K, before it was brought in contact with the toluene solution of $Ce(acac)_3$ under stirring. After 2 h, the color of the solution changed from red to a pale yellow, and the sample color changed from white to a reddish brown. The precursor solution was removed and the sample was washed three times with 30 cm³ of fresh toluene. The sample was dried at room temperature under vacuum over night and then heated to 573 K in He, after which the gas was switched to synthetic air and the sample was heated to 773 K for 4 h. For selected samples, the grafting procedure was repeated to achieve a higher coverage of ceria.

Under inert atmosphere, the moisture-sensitive compounds $Ce(O^{1}Pr)_{4}$ and $Ce(O^{t}Bu)_{4}$ were dissolved in toluene that had been dried over CaH_{2} . These precursors dissolved rapidly at room temperature, yielding a bright yellow solution in the case of $Ce(O^{t}Bu)_{4}$ and a honey-colored solution in the case of $Ce(O^{t}Pr)_{4}$. The precursor solution was brought in contact with the support at room temperature and was stirred for 2 h before the suspension was allowed to settle at 328 K overnight. The formerly yellow solution of $Ce(O^{t}Bu)_{4}$ was colorless in the morning. In the case of $Ce(O^{t}Pr)_{4}$, the solution did not lose its color in contact with the support at 328 K overnight, so another sample with similar starting conditions was refluxed for 4 h in contact with the support, after which the solution was colorless as well. Samples with different Ce coverages on the SiO₂ surface were prepared by adjusting the concentration of the $Ce(O^{t}Bu)_{4}$ precursor solution. Higher loadings were achieved by repeating the grafting procedure with $Ce(O^{t}Bu)_{4}$ twice. The drying and the calcination steps were identical to those using $Ce(acac)_{3}$ as the precursor (see above).

The BET surface area of all supports, and selected samples, was measured by N_2 physisorption using a Quantachrome Autosorb-1. The weight percentage of cerium in the different samples was determined by Galbraith Laboratories using inductively coupled plasma (ICP) analysis. An apparent Ce surface coverage could be calculated from the weight loading and the support surface area.

Diffuse reflectance UV-Vis spectra were recorded using a Harrick Scientific diffuse reflectance attachment (DRP) with a reaction chamber (DRA-2CR) and a Varian-Cary 6000i spectrophotometer. Samples were measured both in a "wet" state right after

placing it in the chamber and in a "dry" state, after heating them at 4 K/min to 723 K and holding them at this temperature for 1 h. Spectra were recorded at room temperature with 1-5 eV incident light. MgO was used as the reference spectrum in the Kubelka-Munk function ($F(R_{\infty})$).

For the measurement of the Raman spectra, samples were pretreated and sealed in glass tubes as described in detail in Ref. [8]. This allowed the pretreatment of samples without contacting them with air. Raman spectra of the sealed samples were acquired using a Jobin Yvon Horiba Labram spectrometer equipped with a confocal microscope. A NbYAG laser with an excitation wavelength of 532 nm and 15 mW power was used as the probe.

Transmission electron microscopy was performed using a FEI Tecnai 12 Transmission Electron Microscope with an accelerator voltage of 120 kV. X-ray powder diffractograms were obtained using a Siemens Diffractometer D 5000 with CuKa radiation ($\lambda = 1.5418$ Å) at 20 kV and 5 mA. Angles (2 θ) between 20° and 70° were scanned.

X-ray absorption spectra (EXAFS and XANES) were acquired at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 4-3. A detailed description of the experimental procedure used to acquire these data can be found in Ref. [7]. XANES data were acquired in transmission mode at the Ce L_{III} -edge while the samples were reduced *in situ*. Three ionization chambers were used with the sample placed in between the first two and a reference foil, used for energy calibration, placed after the sample and between ionization chambers two and three. Samples were heated in a flow of 5% H₂/He to 723 K and held at that temperature for one hour. Prior to and after sample heating, EXAFS data were collected to investigate the structure of oxidized and reduced state of each sample. IFEFITT and its GUI Athena were used to process the data [65,66]. The edge energy was defined as the first inflection point of the main absorption edge. Data were normalized by subtracting a pre-edge line fit from -150 to -30 eV below the edge and a k² weighted quadratic polynomial fit from 150 to 376 eV above the edge.

Pulse reoxidation of reduced samples was carried out using a procedure similar to that described in Ref. [8]. In brief, after oxidizing the samples (20% O_2 /He, 4 K/min to 773 K, hold 1 h), the samples were reduced in 10 % H₂/He, heating them with a ramp of 4 K/min to either 723 or 923 K and then holding at this temperature for one hour, before the samples were cooled in He to the desired reoxidation temperature. Pulses of 1.6 µmol O_2 were passed over the sample until three pulses of equal height were observed by mass spectrometry. The amount of oxygen consumed was calculated by integrating the oxygen pulses.

5.3 Results and Discussion

5.3.1 Grafting process

Ce can oligomerize either in the grafting solution or on the surface of the support during the process of grafting. For example, the red color of the solution of Ce(acac)₃ in warm toluene can be attributed to formation of Ce(acac)₄·10H₂O, which based on stoichiometry suggests the formation of a hexamer complex with the possible composition of $[Ce_6(acac)_{12}O_4(OH)_4]$ [67]. It is, therefore, possible that parts of the cerium precursor pre-aggregated in solution. Furthermore, acetylacetonate precursors of transition metals are known to bind only weakly by hydrogen bonding interactions to the surface of SiO_2 when they are grafted from solution and, hence, surface migration may further contribute to high degrees of agglomeration of these species during the grafting [68,69,70]. On the other hand, alkoxide precursors of transition metal ions are known to react with hydroxyl groups on oxide surfaces, thereby facilitating higher dispersion [1,3,6]. However, the formation of dimers of the cerium isopropoxide-isopropanol complex in benzene has been observed [71], and it is reasonable to think that a similar process may occur in toluene. Thus, the grafting process of both Ce alkoxide precursors may not eliminate the formation of oligomeric species that could lead to the formation of crystalline domains.

5.3.2 Cerium loading

The properties of the CeO₂/SiO₂ samples investigated are summarized in Table 5.1. The cerium surface coverage for each sample was calculated from the measured weight percent of cerium in the samples and the surface area of the support. The sample labels consist of the two digits of the weight loading of Ce after the decimal point, followed by two letters indicating the precursor used in the synthesis (Ac for Ce(acac)₃, tB for Ce(O^tBu)₄ and iP for Ce(OⁱPr)₄) and one letter for the support (M for MCM-41 and S for SBA-15). For example, the sample with the label 43CetBM has a weight loading of 0.43 Ce/nm² obtained by grafting Ce(O^tBu)₄ onto MCM-41. A number "2" inserted after the letters for the precursor indicates that the sample was obtained by two graftings of the corresponding precursors.

The observed surface coverage of ceria for the singly grafted samples prepared on MCM-41 using Ce(acac)₃ as the precursor is close to that expected based on the amount of precursor in solution. Therefore, Ce(acac)₃ grafted almost completely in the first grafting step. For the second grafting step, the precursor solution was adjusted to increase the coverage of the once grafted sample by about 1.0 Ce/nm², but the coverage only increased by 0.45 Ce/nm². The inability to graft more ceria during the second grafting is probably due to an insufficient concentration of exposed Si-OH groups, the anchoring points on the silica surface. For the Ce(acac)₃ sample on SBA-15, a slight discrepancy exists between the actual and the expected surface coverage. This result is surprising, because the pores should be more accessible since they are larger than those in MCM-41.

For both the Ce(O^tBu)₄ and Ce(OⁱPr)₄ grafted on MCM-41 and SBA-15, the surface coverage achieved is lower than that expected, with the exception of 51CeiPM, which was refluxed during the grafting process. This indicates incomplete grafting of the precursor, even though the yellow color of the solution disappeared completely in case of Ce(O^tBu)₄. For the *t*-butoxide precursor the difference between observed and expected coverage increases with increased Ce loading. The highest loading that could be achieved in one grafting step on MCM-41 was 0.43 Ce/nm², with a concentration of the precursor in solution equivalent to 1.0 Ce/nm², and corresponds to approximately 1/3 of surface hydroxyl groups expected under the grafting conditions [72]. As can be seen for 35CetB2M, distributing a similar amount of precursor in two grafting steps did not lead to an increased loading and the surface coverage was even slightly lower than was obtained for the singly grafted sample. This indicates that no more anchoring sites are accessible for Ce(O^tBu)₄ when a coverage of about 0.4 Ce/nm² has been reached, due

either to pore blockage or a lack of Si-OH anchoring sites. For SBA-15, the maximum coverage that could be achieved in one grafting step (using a precursor concentration equal to 1.0 Ce/nm²) was 0.55 Ce/nm², in accordance with the observation that SBA-15 usually contains a higher surface density of hydroxyl groups [73].

51CeiPM prepared by refluxing the Ce(OⁱPr)₄ solution in contact with the support had a slightly higher coverage than expected, possibly due to errors in the ICP analysis or the BET surface area measurement of the support. The complete grafting for this precursor under reflux might indicate that higher temperatures facilitate Ce(OⁱPr)₄ agglomeration and, thus, the attainment of higher surface coverages.

5.3.3 Surface area and pore diameter

The BET surface area and average pore diameters of selected samples prepared by grafting $Ce(acac)_3$ on MCM-41 and SBA-15 are given in Table 5.2, and results for the samples prepared by grafting of $Ce(O^tBu)_4$ are shown in Table 5.3. The surface areas were calculated on a cerium-free basis, taking into account the weight loading of Ce as obtained from ICP [43,74,75]. Both the average pore diameter and the pore diameter corresponding to the maximum in the pore size distribution determined by the method of Barrett, Joyner and Halenda (BJH) [76] are given. Small amounts of microporosity were observed in the bare silica support in accordance with previous reports for MCM-41 [77,78] and SBA-15 [79,80].

For all samples obtained by grafting $Ce(acac)_3$, the surface area decreased to a limited degree with increased ceria loading, and it even increased slightly in the case of samples with low Ce loading (Table 5.2). This indicates that the pores of mesoporous silica are not clogged, except for the highest loading of $Ce(acac)_3$ on MCM-41 (0.88 Ce/nm² apparent surface density). Table 5.2 also shows that for all samples prepared using Ce(acac)_3 the diameter of the silica pores remained unchanged. Therefore, ceria species formed during the grafting of Ce(acac)_3 are situated predominantly on the outer surface of the silica particles, and not in the pores for both the narrow pores of the MCM-41 material and the larger pores of the SBA-15.

For any loading of $Ce(O^tBu)_4$ on the silica surface, however, the surface area is lower than in case of ceria-free SBA-15 or MCM-41 (Table 5.3). At the same time, the average pore diameter increases for all samples, while the peak maximum of the pore size distribution shifts to smaller diameters. These observations suggest that the ceria formed from $Ce(O^tBu)_4$ narrows the mesopores and clogs the micropores of SBA-15 or MCM-41. A decrease in surface area with a concomitant increase in the average pore radius has been observed previously for CeO_2 nanoparticles deposited on SBA-15 [41], and was attributed to a decrease in the wall thickness during deposition. However, in that study, the deposition was performed in an aqueous, urea-containing solution, which is more likely to damage the SBA-15 support than the moisture-free toluene used here.

The BET surface areas of the samples prepared using $Ce(O^{1}Pr)_{4}$ after grafting were not determined, because the ceria domains were not as well defined as those prepared with the other two precursors, as will be shown below.

5.3.4 X-ray diffraction

XRD patterns for selected CeO₂/MCM-41 samples are presented in Fig. 5.1. Peaks observed at $2\theta = 28.6$, 32.8, 47.5 and 53.6 degrees are attributable to the (111),

(200), (220) and (311) reflections of cubic CeO₂ [81,82]. While these features are very weak and broad in the case of samples with surface coverages of ≤ 0.4 Ce/nm², they are much sharper in case of the twice grafted sample, indicating an enhanced degree of crystallinity and/or bigger crystals of CeO₂. The average crystallite size determined from the Scherrer formula and the full-width-at-half-maximum (FWHM) of the (220) peak is 3.2 nm for the 0.43 Ce/nm² sample and 3.5 nm for the 0.88 Ce/nm² sample. Particles of this size are too big to fit into the pores of MCM-41, which have an average pore diameter of 1.8 to 2 nm, suggesting that most of the ceria must be located on the outer surface of the silica particles. This deduction is consistent with the observation of an unchanged pore diameter and surface area before and after grafting of Ce(acac)₃ on MCM-41.

No peaks were observed in any diffraction pattern of samples prepared by grafting $Ce(O^{t}Bu)_{4}$ on MCM-41, except for the broad peak around $2\theta = 25^{\circ}$ originating from the MCM-41 support and/or the sample holder. Fig. 5.1 displays the diffraction pattern of 29CetBM as an example. The absence of diffraction peaks due to CeO_{2} or $Ce_{2}O_{3}$ indicates that ceria is either well dispersed on the silica surface or amorphous. The XRD pattern of 29CeiPM, obtained by grafting $Ce(O^{t}Pr)_{4}$ without refluxing toluene, also showed no diffraction peaks. By contrast, the XRD pattern of 51CeiPM prepared by grafting of $Ce(O^{t}Pr)_{4}$ under toluene reflux (Fig. 5.1) was very similar to the XRD patterns of the samples prepared using $Ce(acac)_{3}$, which suggests that the formation of crystalline CeO_{2} particles occurred during the sample preparation.

Figure 5.2 displays selected XRD patterns for $CeO_2/SBA-15$. Here, too, the samples that were prepared using $Ce(acac)_3$, show characteristic peaks for CeO_2 in the fluorite structure. The average particle size of the ceria particles are 3.2 nm for 25CeAc2S and 3.3 nm for 33CeAcS. These diameters are very similar to the values obtained for the samples prepared by grafting $Ce(acac)_3$ onto MCM-41.

As was seen for the MCM-41 support, no new diffraction peaks were observed for samples obtained using $Ce(O^tBu)_4$ on SBA-15 independent of the cerium loading. Therefore, it is concluded that crystalline particles of ceria were not produced on either support using $Ce(O^tBu)_4$ as the precursor.

5.3.5 Transmission Electron Microscopy (TEM)

Figure 5.3 presents TEM images of selected CeO₂/MCM-41 samples. The bare MCM-41 support is displayed in Fig. 5.3A. The typical MCM-41 structure, consisting of a parallel array of straight channels, can be seen in the particle on the right side of Fig. 5.3A. The absence of an obvious MCM-41 structure for some of the particles is attributable to non-parallel or non-perpendicular alignment of the channels with respect to the electron beam, resulting in the observation of a uniform texture. However, it is also possible that some amorphitization of the mesoporous silica occurred under the influence of the electron beam. The same texture and channel structure is also seen in Figs. 5.3B and 5.3C, which display the TEM pictures of sample 43CetBM and 29CeiPM, respectively. There is no indication for the presence of ceria in these images, indicating that the ceria is well dispersed over the support surface. This finding is in line with the XRD results, which show no evidence for crystalline CeO₂. The absence of dark spots in Fig. 5.3B and 5.3C indicates that larger amorphous agglomerates of CeO₂ are not present.

TEM images of the other samples obtained before and after grafting $Ce(O^tBu)_4$ on MCM-41 (not shown) are very similar to that of 43CetBM displayed in Fig. 5.3B.

A TEM image of 43CeAcM is presented in Figure 5.3D. Small crystallites indicated by darker spots are observed. The TEM image resembles that of 2.2 nm CeO₂ crystallites on quartz shown in Ref. [83]. Most of the particles seen in Fig. 5.3D are \sim 2 to 3 nm in diameter. Two larger dark spots are observed at the top the TEM image, but similar spots can be observed in case of the pure support (Fig. 5.3A). Therefore, these spots are assumed to be small support particles lying on top of or below larger support particles and they are not attributed to ceria. A particle size distribution was obtained from measurements of 200 particles in the TEM images of sample 43CeAcM. The particle size distribution is displayed in Fig. 5.4. In agreement with the picture displayed in Fig. 5.3D, most particles have diameters between 2 and 3 nm, with an average particle diameter of 2.66 nm. This diameter is in reasonable agreement with the results from XRD obtained with the Scherrer formula (3.2 nm). These observations confirm the deduction presented earlier that most of the particles are too big to fit into the pores of the MCM-41, and hence are located on the outer surface of this support.

Figure 5.5 displays representative TEM images of selected CeO₂/SBA-15 samples. The channels of SBA-15 are wider than those of MCM-41 and, hence, readily observable. As in the case of Ce(O^tBu)₄ grafted onto MCM-41, no differences can be detected between the images of the bare support (Figure 5A) and the sample with CeO₂ grafted onto it (Figure 5.5B, sample 55CetBS), indicating that here, too, the CeO₂ is well dispersed over the support surface with no evidence for separate ceria domains.

Figures 5.5C and 5.5D display TEM images of 33CeAcS obtained by grafting Ce(acac)₃ onto SBA-15. As in case of Ce(acac)₃ grafted onto MCM-41, nanoparticles overlaying the silica structure can be distinguished. The contrast is slightly worse than in the case of the MCM-41 sample, due probably to the thicker walls of the SBA-15. Therefore, it is more difficult to tell the exact size and shape of the particles, and consequently a particle size distribution could not be determined. It is not obvious from Figure 5.5C where the ceria particles are located. In the TEM image displayed in Figure 5.5D a large number of ceria particles can be seen on the outer part of the support particle (right side and bottom of the image), while the interior of the particle (left side and top of the image) appears to be free of ceria nanoparticles. This pattern suggests that the deposition of ceria starting with Ce(acac)₃ was spatially inhomogeneous. However, ceria particles located away from the edge of the support might not be as readily visible due to the higher thickness of the support in that region.

5.3.6 Raman spectroscopy

Raman spectra of selected CeO₂/MCM-41 samples are displayed in Figure 5.6. In the spectrum of a physical mixture of bulk, crystalline CeO₂ with MCM-41, adjusted to contain 10 wt% Ce, the characteristic band of the CeO₂ lattice is observed at 458 cm⁻¹. Crystalline CeO₂ with fluorite structure has only one Raman mode around 465 cm⁻¹ originating from the symmetric "breathing" vibrations of the oxygen anions around the cerium cation [84]. All other bands in this spectrum (483, 600 and 793 cm⁻¹) can be assigned to silica [85,86], originating from either the MCM-41 support, or from the quartz tube into which the samples were sealed. In the sample with 0.43 Ce/nm² grafted from Ce(acac)₃ corresponding to a cerium weight loading of ~10 wt%, the CeO₂ lattice

band is observed at 452 cm⁻¹. The observation of a band for crystalline CeO₂ is consistent with the evidence from XRD and TEM for nanoparticles of ceria. Compared to the physical mixture, the band of CeO₂ nanoparticles on SiO₂ is weaker and shifted to lower wavenumbers. The red shift of this vibrational band has been observed previously [54,87] and has been attributed to a quantum size effect for small CeO₂ nanoparticles [87].

The spectrum of the 0.43 Ce/nm² sample obtained by grafting Ce(O^tBu)₄ (Figure 5.6) does not show the peak for the CeO₂ lattice vibration. The absence of a Raman signal cannot be ascribed to insufficient ceria since this sample also contains ~10 wt% ceria, giving further indication that the ceria in all of these samples is not crystalline. It should be noted, though, that the band of crystalline CeO₂ could not be observed in the spectrum of the sample 51CeiPM, either, even though the presence of nanoparticles has been evidenced by XRD.

Figure 5.7 displays the Raman spectra of the samples obtained by grafting $Ce(O^{t}Bu)_{4}$ on SBA-15. Spectra of samples from $Ce(acac)_{3}$ grafted on SBA-15 are not displayed, as they were qualitatively similar to the spectra of samples obtained by grafting $Ce(acac)_{3}$ onto MCM-41. The Raman band for crystalline CeO_{2} was weaker for the SBA-15 supported samples, probably because of their lower cerium weight loading. For the samples obtained by $Ce(O^{t}Bu)_{4}$ grafted onto SBA-15, however, a sharp band appeared at 479 cm⁻¹ that cannot be attributed to either the support or bulk CeO_{2} . This feature cannot be attributed to ceria nanoparticles, since it is blue shifted relative to the frequency of bulk CeO_{2} . Consequently, the origin of this peak cannot be defined at this time.

5.3.7 UV-Vis spectroscopy

Figure 5.8 displays the UV-Vis spectra of samples obtained from different precursors together with the spectrum of bulk CeO₂. All samples were heated in 20%O₂/He to 723 K inside the UV-Vis cell prior to acquisition of the spectrum. The exact value of F(R) differed considerably among different samples, because of differences in ceria loading and differences in sample packing density in the diffusereflectance cell. Consequently, the spectra were scaled to a similar height. The UV absorbance of bulk CeO₂ originates from a charge transfer transition from O2p to Ce4f, and the spectrum (Figure 5.8, grey line) displays two overlapping absorption peaks attributable to indirect and direct transitions [88]. By contrast, the spectra of all CeO_x/SiO_2 samples exhibit only one peak. The absorption edge energy and the peak maximum in the spectra of the CeO_x/SiO_2 samples differ, but can generally be grouped into two classes: one comprising the samples prepared using $Ce(O^{t}Bu)_{4}$ which have a high edge energy, an onset of the absorption peak around 26,000 cm⁻¹, and a peak maximum of around 40,000 cm⁻¹; and the other set comprised of samples prepared with either $Ce(O^{1}Pr)_{4}$ or $Ce(acac)_{3}$ which have a much lower edge energy, an onset of the absorption peak around 24,000 cm⁻¹, and a varying peak maximum. All of the UV-Vis spectra for samples using $Ce(O^tBu)_4$ are not shown because all of the spectra had exactly the same peak shape and position, indicating very good reproducibility for both supports. For the samples prepared with $Ce(acac)_3$ the spectra differed slightly, as can also be seen in Figure 5.8, but were similar in appearance. The UV-Vis spectra for samples prepared using $Ce(O^{1}Pr)_{4}$ depended on the preparation conditions. The spectrum of the sample obtained without refluxing has the same edge energy as the samples prepared using $Ce(acac)_3$, but the peak for this spectrum occurred at a higher wavenumber. The spectrum of the refluxed sample had exactly the same appearance (edge energy, onset and peak position) as the spectrum of the $Ce(acac)_3$ samples,.

It has been observed previously that small CeO₂ crystallites show only one transition in the UV range [89]. However, there has been some debate as to whether this is a direct or an indirect transition, so usually the absorption edge energy is calculated both under the assumption of a direct and an indirect transition [88,90,91]. The general procedure is to obtain the edge energy as the intercept with the abscissa from a linear regression of $[(F(R_{\infty}))hv]^{1/n}$ data plotted versus hv, with $n = \frac{1}{2}$ for a direct transition and n = 2 for an indirect transition [88,91,92]. For the samples in this study, especially those without crystalline CeO₂, the band theory is not strictly valid. As a consequence it is not possible to distinguish between a direct or an indirect transition and, hence, to determine which value of n is most appropriate [92,93]. The edge energies were, therefore, calculated both under the assumption of a direct and an indirect transition, as shown in Figure 5.9.

For both cases, classes of samples can be distinguished on the basis of the precursor used to introduce Ce. Samples prepared using $Ce(O^tBu)_4$ have the highest edge energies with values around 4.1 eV for E_{dir} and around 3.4 eV for E_{ind} , while samples prepared using either $Ce(O^iPr)_4$ or $Ce(acac)_3$ have much lower edge energies, ranging between 3.8 and 3.5 eV for E_{dir} , and 3.3 to 3.1 eV for E_{ind} . For E_{ind} the scatter of the edge energies is much larger in each class. In particular, the value of E_{ind} for 35CetB2M, prepared using two graftings of $Ce(O^tBu)_4$, is much lower, while the value of E_{dir} is in perfect agreement with the values of the other samples.

For suspensions of crystalline CeO₂ nanoparticles of uniform size, it has been reported that an inverse relationship exists between particle size and absorption edge energy attributable to quantum size effects [88,91,94]. The same relationship is observed here for the samples prepared using Ce(acac)₃. The samples with higher loading, which have slightly higher average particle diameters, show smaller edge energies. The samples obtained using Ce(OⁱPr)₄ fit into the correlation obtained for samples prepared using Ce(acac)₃, indicating that the ceria domains in these samples show characteristics of crystalline CeO₂, even though the presence of the latter was not unambiguously shown by other methods (XRD, TEM, Raman). It is possible that the ceria domains obtained using Ce(OⁱPr)₄ are not fully crystalline. Due to the lack of a well-defined ceria structure in these samples, they were not characterized further.

No previous data could be found on UV-Vis edge energies of non-crystalline CeO_x, and the edge energies reported here are larger than those reported previously for crystalline CeO₂ [88,91,94]. However, in cases of non-crystalline TiO_x and VO_x species on SiO₂, a higher UV-Vis edge energy has been attributed to a lower domain size of the supported transition metal oxide due to quantum size effects [95]. The electronic states are more localized in smaller clusters, leading to higher absorption edge energy [96]. Applying this concept to the CeO₂/SiO₂ samples, we conclude that for any loading, the samples prepared with Ce(O^tBu)₄ have the smallest CeO₂ domains. From the variation of E_{ind} with Ce loading it might be deduced that the CeO_x domains grow slightly with increasing Ce loading for both supports, especially when cerium was grafted in two steps (35CetBM), but E_{dir} suggests that a similar domain size is obtained for all samples supported on MCM-41.

While the smaller observed ceria domain size obtained using $Ce(O^tBu)_4$ relative to $Ce(acac)_3$ is in agreement with the suggested chemical processes during the grafting procedure as described above, the large domains obtained from $Ce(O^iPr)_4$ are unexpected. It is possible that an agglomeration of $Ce(O^iPr)_4$ in toluene might occur.

5.3.8 Oxygen uptake of reduced CeO_x/SiO₂

Figure 5.10 shows the amount of oxygen adsorbed as a function of temperature for samples of 43CeAcM and 43CetBM that had been reduced at 923 K. For both samples, temperatures well above room temperature were required to achieve complete reoxidation. The maximum uptake is also a function of the precursor used for sample preparation. For 43CeAcM the maximum uptake is 101 μ mol/g, and a plateau in the oxygen uptake is reached for temperatures of 673 K or higher. Assuming complete reoxidation, this O₂ uptake is equal to 59.0% of Ce⁴⁺ being reduced to Ce³⁺ in 10%H₂/He at 923 K. The O₂ uptake of 43CetBM, measured at 773 K, is only 22.8 μ mol/g, which is equivalent to reoxidation of 12.9% of the cerium cations in the sample. For this sample, the amount of reoxidation is lower at all temperatures than that for 43CeAcM. It is noted that for calcination temperatures up to 773 K, saturation with oxygen did not occur for the sample 43CetBM. This may possibly be a consequence of the formation of cerium silicates upon reduction, which are resistant to oxidation under the conditions used in this study.

To study the influence of temperature, reduction was carried out at either 723 K or 923 K. For these experiments pulsed reoxidation was performed at 723 K. Multiple reduction/reoxidation cycles were performed to study the stability of the different ceria structures. The results are shown in Figure 5.11. For reduction at 723 K and reoxidation at the same temperature, the oxygen uptake of all samples is comparable, and equal to roughly 40% of the total amount of cerium ions in the sample being reoxidized from Ce^{3+} to Ce^{4+} . The oxygen uptake increases for the samples prepared using $Ce(acac)_3$ after they have been reduced at the higher temperature. This result is expected, since the ceria should be more easily reduced at higher temperature. On the other hand, the O_2 uptake for the samples prepared using $Ce(O^{t}Bu)_{4}$ decreases with each reduction/reoxidation cycle, even after reduction at higher temperature. This observation might be attributed to either a loss of cerium during reduction or to high temperature driven structural rearrangements that make parts of the reduced cerium cations inaccessible for reoxidation. The first of these possibilities can be ruled out, since ICP analysis of 34CetBS after reduction indicates a comparable quantity of Ce both before (6.07 wt%) and after (5.85 wt%) multiple treatments in H₂. Therefore, the lower oxygen uptake of sample 43CetBM and 33CetBS compared to 43CeAcM and 43CetBM plotted in Figure 10 and 11 was not due to a decrease in the amount of cerium.

A possible explanation for the loss in oxygen uptake following repeated reduction of samples at 923 K could be the formation of cerium silicates. The formation of cerium silicates has been observed previously for a variety of samples containing CeO₂ and SiO₂ [97-99] and is reported to be more facile under reducing conditions than oxidizing conditions [99,100]. Consistent with the latter observation, most known cerium silicates, such as Ce₂SiO₅, Ce_{9.33}(SiO₄)₆O₂ or Ce₂Si₂O₇, contain cerium in the 3+ state, the only exception being CeSiO₄ [99,100]. So far, the formation of cerium silicates has not been observed for temperatures below 1173 K, but the amorphitization and spreading of CeO₂ nanoparticles (diameter ~5 nm) deposited on silica has been observed at temperatures as low as 770 K during prolonged heating in hydrogen [101]. In the related system CeO₂/Al₂O₃, the formation of cerium aluminate has already been observed at 873 K when Ce is well dispersed on the alumina surface, while temperatures of 1073 K were necessary in the case of CeO₂ nanoparticles [102]. Therefore, it is reasonable to hypothesize that the formation of cerium silicates could be facilitated by high dispersion of ceria onto the surface of silica.

The extent of ceria reduction in samples prepared using $Ce(acac)_3$, is similar regardless of the support. Since these samples contain ceria nanoparticles, it is not surprising that the structure of the support does not affect the extent of reduction. The oxygen uptake for the different reduction temperatures can be explained in terms of surface vs. bulk reduction processes. Previous studies have demonstrated that the reduction of ceria particles at temperatures below 723 K is limited to the surface, whereas reduction at temperatures above 800 K proceeds in the bulk [53]. It is, therefore, likely that in the case of CeO_2 particles supported on SiO_2 only the surface of the particles is reduced to Ce₂O₃ upon reduction at 723 K. To test this hypothesis, the number of surface CeO₂ units on 43CeAcM was estimated by the total volume of ceria in the sample, obtained from the cerium weight loading (9.55 wt%) and the density of ceria (7.28 g/cm³ [91]), and by the estimated volume of a 3 nm diameter hemispherical nanoparticle. All nanoparticles were assumed to expose the hexagonal $CeO_2(111)$ surface, the most stable facet of CeO_2 [29,103-105]. Using these approximations, the number of exposed CeO_2 units was estimated to be 329 µmol/g for 43CeAcM and 189 µmol/g for 33CeAcS. Assuming that reoxidation proceeds via the reaction

$$2 \operatorname{Ce}_2 \operatorname{O}_3 + \operatorname{O}_2 \rightarrow 4 \operatorname{CeO}_2$$

the uptake of one O_2 molecule corresponds to the formation of four molecules of CeO₂. Therefore, the predicted uptake for 43CeAcM and 33CeAcS are 82.2 µmol/g and 47.3 µmol/g, respectively, in good agreement with the experimentally observed uptakes of 77.4 and 75.6 µmol/g (first and second reduction at 723 K) for 43CeAcM and 39.7 and 41.4 µmol/g for 33CeAcS. This analysis suggests that only the surface of the ceria nanoparticles is reduced at 723 K. When reduction of CeO₂/MCM-41 is performed at 923 K, the uptake of oxygen increased to 101 µmol/g for 43CeAcM and 67.3 µmol/g for 33CeAcS. Therefore, after reduction nominal stoichiometries of CeO_{1.70} and CeO_{1.66} can be achieved for 43CeAcM and 33CeAcS, respectively. The extents of reduction at 923 K are slightly higher than those reported for unsupported ceria nanoparticles after reduction at 900 K, for which nominal stoichiometries of CeO_{1.82} to CeO_{1.79} have been reported [26,53].

5.3.9 X-ray absorption spectroscopy (XAS)

Further information about the transformations occurring during the reduction of dispersed ceria was obtained from in situ XANES data acquired while exposing the samples to 5% H₂/He at 723 K. The results are displayed in Figure 5.12. The oxidized state of the samples is shown in red, while the reduced state is shown in blue. The spectrum of the oxidized 43CeAcM in Fig. 5.12A is very similar to the spectrum of bulk CeO₂, which is comprised of four features, A, B, C, and D (see Figure 5.12). Features A,

B, and C were attributed to the hybridization of Ce 4f and O 2p in the initial state. Features B and C occur because of the effect of the ligand field splitting on the final state with one electron in the Ce 4f and one hole in the O 2p. Peak A occurs because of a final state that contains no electrons in the Ce 4f and no holes in the O 2p level. Finally, peak D corresponds to transitions to the bottom of the conduction band [56,106,107,108]. Upon reduction, the edge shifts to lower energies and an intense white line was observed. The spectrum obtained after reduction was very similar to that of CeAlO₃, which has been used as a reference for Ce³⁺ [56]. Upon raising the reduction temperature, changes in the XANES spectrum were observed above 500 K. The observation of three isosbestic points provides further evidence for the reduction of Ce⁴⁺ to Ce³⁺ with increasing temperature.

Figure 5.12B shows the corresponding spectra of 29CetBM. Remarkable differences can be observed between the XANES spectra of 29CetBM and 43CeAcM. The peaks D and A are similar, but peak B is significantly less intense for 29CetBM. The change in the intensity of peak B cannot be assigned unambiguously to changes in the structure of the ceria deposit. The absence of features for crystalline ceria in the XRD pattern of 29CetBM suggests that the particles of ceria in this sample are very small and possibly amorphous. A further indicator of small ceria particles is the low ratio of the intensities of peak B to peak A [107]. The position of the edge energy and height of peak A of 29CetBM indicate that cerium is predominantly in the 4+ state. The formation of an intense white line and a decrease in the edge energy upon heating the sample in H₂ above 500 K indicate that Ce⁴⁺ is reduced to Ce³⁺. The isosbestic points observed for this sample are identical to those observed for 43CeAcM, giving additional confirmation for the reduction of Ce⁴⁺.

Key differences between reduced 43CeAcM and 29CetBM spectra in Figure 5.12 are the less intense peak A in 29CetBM relative to 43CeAcM and the more intense white line. Since peak A arises from an empty Ce 4f orbital, and the white line is attributed to Ce^{3+} , these changes indicate that 29CetBM is more highly reduced than 43CeAcM. EXAFS spectra of the oxidized samples are compared to that of a simulated CeO₂ spectrum in Figure 5.13. The CeO₂ spectrum shows a peak centered at 1.8 Å associated with Ce-O backscattering and a second peak centered roughly around 3.5 Å indicative of Ce-Ce backscattering [106,107]. Comparison of the reference CeO₂ spectrum with the spectra of 29CetBM and 43CeAcM shows a peak corresponding to oxygen backscattering for both samples, with a slightly smaller distance for 29CetBM. Bulk CeO₂ shows Ce-Ce backscattering in the range 3-4 Å, but this peak is small for 43CeAcM and absent for 29CetBM. The absence of the peak at 3-4 Å indicates that the ceria in 29CetBM is well dispersed and is likely amorphous [106].

5.4 Conclusions

The structure of ceria dispersed on MCM-41 and SBA-15 is found to depend strongly on the composition of the cerium precursor used to deposit ceria. Cerium acetylacetonate leads to crystalline particles with diameters of ~ 3 nm, whereas cerium *t*butoxide leads to the formation of layer-like structures. Cerium isopropoxide, on the other hand, results in the formation of large amorphous agglomerates or partially crystalline structures. The pore size of the support influences the distribution of ceria. For MCM-41, any nanoparticles of ceria that are deposited are too large to fit inside the pores. By contrast on the larger-pore SBA-15, a gradient of nanoparticles is observed with a larger number of particles sitting on the outside of the silica particles or at the entrances to the pores.

The ceria nanoparticles are stable under reducing conditions and the reduction and reoxidation can be cycled multiple times without major changes to the samples. At 723 K only the surface of the nanoparticles is reduced, while partial bulk reduction occurs at 923 K. Similarly, at 723 K, the reducibility of the layer-like ceria structures is comparable to that of the nanoparticles. However, reduction of the layer-like ceria structures at 923 K is only partially reversible. This behavior is believed to be due to migration of a portion of the ceria into the silica structure, resulting possibly in the formation of cerium silicates.

Sample ID	precursor	support	Ce	Surface-area	Ce loading
			<i>content^a</i>	of support ^b	(expected ^c)
			[wt%]	$[m^2/g]$	[Ce atoms/nm ²]
09CeAcM	Ce(acac) ₃	MCM-41	2.21	1065	0.09 (0.10)
21CeAcM	Ce(acac) ₃	MCM-41	5.16	1090	0.21 (0.21)
43CeAcM	Ce(acac) ₃	MCM-41	9.55	1065	0.43 (0.52)
88CeAc2M	$Ce(acac)_3^d$	MCM-41	17.9	1065	0.88 (1.46)
21CeAcS	Ce(acac) ₃	SBA-15	3.29	693	0.21 (0.30)
33CeAcS	Ce(acac) ₃	SBA-15	5.49	750	0.33 (0.50)
17CetBM	Ce(O ^t Bu) ₄	MCM-41	3.99	1047	0.17 (0.23)
29CetBM	Ce(O ^t Bu) ₄	MCM-41	6.50	1047	0.29 (0.47)
35CetB2M	Ce(OtBu) ₄ ^d	MCM-41	9.00	1210	0.35 (0.93)
43CetBM	Ce(O ^t Bu) ₄	MCM-41	9.85	1090	0.43 (1.00)
14CetBS	Ce(O ^t Bu) ₄	SBA-15	2.64	818	0.14 (0.20)
34CetBS	Ce(O ^t Bu) ₄	SBA-15	6.07	817	0.34 (0.51)
55CetBS	Ce(O ^t Bu) ₄	SBA-15	8.65	735	0.55 (0.90)
29CeiPM	Ce(O ⁱ Pr) ₄	MCM-41	6.49	1047	0.29 (0.47)
51CeiPM	Ce(O ⁱ Pr) ₄ ^e	MCM-41	11.4	1090	0.51 (0.47)

Table 5.1: Summary of the properties of the catalysts used in this study.

^a From ICP-OES, Galbraith Laboratories, ^b single-point BET data is used, ^c For the case of complete grafting of precursor in solution, ^d Two grafting steps, ^e Sample refluxed during synthesis procedure

Sample ID BET surface area ^{a,b}		Average pore	Max. of pore diameter	
	(<i>Ce-free</i>) [<i>m</i> ² /g]	diameter ^b [nm]	distribution ^{b,c} [nm]	
88CeAc2M	984 (1065, MCM-41)	1.9 (1.8)	2.0 (2.2)	
43CeAcM	1086 (1065, MCM-41)	1.9 (1.8)	2.2 (2.2)	
21CeAcM	1111 (1090, MCM-41)	1.9 (2.0)	2.1 (2.3)	
09CeAcM	1162 (1065, MCM-41)	1.8 (1.8)	2.2 (2.2)	
33CeAcS	731 (750, SBA-15)	5.5 (5.5)	6.6 (6.6)	
21CeAcS	729 (693, SBA-15)	5.7 (5.8)	6.6 (6.6)	

Table 5.2: Single point BET surface areas of CeO₂/SiO₂ samples obtained from Ce(acac)₃

^a single-point BET data is used
^b corresponding data of the bare support given in brackets
^c diameter corresponding to maximum in the BJH desorption pore size distribution

Table 5.3: Single	point BET surface a	reas of CeO ₂ /SiO ₂ sam	ples obtained from Ce(O ^t Bu)	۱.
				e

Sample ID	BET surface area ^{a,b}	Average pore	Max. of pore diameter	
	$(Ce-free) [m^2/g]$	diameter ^b [nm]	distribution ^{b,c} [nm]	
43CetBM	631 (1090, MCM-41)	2.4 (2.0)	1.7 (2.3)	
29CetBM	825 (1047, MCM-41)	2.0 (1.8)	2.1 (2.2)	
55CetBS	436 (735, SBA-15)	5.0 (4.7)	4.9 (5.6)	
34CetBS	516 (817, SBA-15)	4.6 (4.3)	4.9 (5.6)	
14CetBS	589 (687, SBA-15)	4.8 (4.7)	5.7 (6.1)	

^a single-point BET data is used
^b corresponding data of the bare support given in brackets
^c diameter corresponding to maximum in the BJH desorption pore size distribution



Figure 5.1: XRD patterns of selected CeO₂/MCM-41 samples; (a) 0.88 Ce/nm^2 obtained by two graftings of Ce(acac)₃, (b) 0.43 Ce/nm^2 obtained using Ce(acac)₃, (c) 0.21 Ce/nm^2 obtained using Ce(acac)₃, (d) 0.51 Ce/nm^2 obtained using Ce(OⁱPr)₄, (e) 0.29 Ce/nm^2 obtained using Ce(OⁱBu)₄. XRD patterns have been smoothed by adjacent averaging over 10 points.



Figure 5.2: XRD patterns of selected CeO₂/SBA-15; (a) 0.33 Ce/nm² obtained using Ce(acac)₃, (b) 0.34 Ce/nm² obtained using Ce(O^tBu)₄, (c) 0.55 Ce/nm² obtained using Ce(O^tBu)₄. XRD patterns have been smoothed by adjacent averaging over 10 points.



Figure 5.3: TEM pictures of different CeO_2/MCM -41 samples; (A) pure MCM-41 support, (B) 0.43 Ce/nm² obtained using $Ce(O^tBu)_4$, (C) 0.29 Ce/nm² obtained using $Ce(O^iPr)_4$, (D) 0.43 Ce/nm² obtained using $Ce(acac)_3$.



Figure 5.4: Particle size distribution of 0.43 Ce/nm² sample obtained from Ce(acac)₃.



Figure 5.5: TEM pictures of different CeO₂/SBA-15 samples; (A) pure SBA-15 support, (B) 0.55 Ce/nm² from Ce(O^tBu)₄ (sample 55CetBS), (C) and (D) 0.33 Ce/nm² from Ce(acac)₃ (sample 33CeAcS).



Figure 5.6: Raman spectra of selected CeO₂/MCM-41 samples; (a) physical mixture of CeO₂ in MCM-41 with 10wt% Ce, (b) 0.43 Ce/nm² from Ce(acac)₃, (c) 0.43 Ce/nm² from Ce(O^tBu)₄, (d) MCM-41; all samples were measured in quartz tubes.



Figure 5.7: Raman spectra of selected $CeO_2/SBA-15$ samples; (a) physical mixture of CeO_2 in MCM-41 with 10wt% Ce; (b) 0.55 Ce/nm² from Ce(O^tBu)₄, (c) 0.34 Ce/nm² from Ce(O^tBu)₄, (d) 0.14 Ce/nm² from Ce(O^tBu)₄; all samples were measured in quartz tubes.



Figure 5.8: UV-Vis diffuse reflectance spectra of selected CeO_2/SiO_2 samples in comparison with bulk CeO_2 (gray); (A) Samples from $Ce(O^iPr)_4$ and $Ce(acac)_3$, (a) 0.29 Ce/nm^2 obtained using $Ce(O^iPr)_4$ on MCM-41 (orange), (b) 0.43 Ce/nm^2 obtained using $Ce(acac)_3$ on MCM-41 (brown), (c) 0.33 Ce/nm^2 obtained using $Ce(acac)_3$ on SBA-15 (purple), (d) 0.51 Ce/nm^2 obtained using $Ce(O^iPr)_4$ on MCM-41 (red); (B) (e) 0.34 Ce/nm^2 obtained from $Ce(O^iBu)_4$ on SBA-15 (green), (f) 0.29 Ce/nm^2 obtained from $Ce(O^iBu)_4$ on MCM-41 (blue), (g) 0.17 Ce/nm^2 obtained from $Ce(O^iBu)_4$ on MCM-41 (pink).



Figure 5.9: Direct (A) and indirect (B) UV-Vis absorption edge energies as a function of cerium surface coverage; samples from $Ce(O^tBu)_4$ on MCM-41 (red solid squares), samples from $Ce(O^tBu)_4$ on SBA-15 (orange open squares), samples from $Ce(acac)_3$ on MCM-41 (light blue solid circles), samples from $Ce(acac)_3$ on SBA-15 (dark blue open circles), samples from $Ce(O^tPr)_4$ on MCM-41 (green solid triangles).



Figure 5.10: Oxygen uptake of 0.43 Ce/nm² obtained using Ce(acac)₃ on MCM-41 (black squares) and 0.43 Ce/nm² obtained using Ce(O^tBu)₄ on MCM-41 (blue circles) as a function of reoxidation temperature. All samples have been reduced in 10% H₂/He at 923 K.



Figure 5.11: Oxygen uptake of 0.34 Ce/nm² obtained from Ce(O^tBu)₄ on SBA-15 (blue), 0.43 Ce/nm² obtained using Ce(O^tBu)₄ on MCM-41 (cyan), 0.33 Ce/nm² obtained using Ce(acac)₃ on SBA-15 (red) and 0.43 Ce/nm² obtained using Ce(acac)₃ on MCM-41 (orange) in consecutive reduction and reoxidation cycles. Fresh sample was used for 0.43 Ce/nm² obtained using Ce(acac)₃ at 923 K. The second reduction cycle at 723 K was skipped for 0.43 Ce/nm² obtained using Ce(O^tBu)₄.



Figure 5.12: XANES of selected CeO₂/MCM-41 samples during reduction: (A) 0.43 Ce/nm² obtained using Ce(acac)₃ on MCM-41, oxidized (red), reduced (blue) and spectra taken during heating ramp (black); (B) 0.29 Ce/nm² obtained from Ce(O^tBu)₄ on MCM-41, oxidized (red), reduced (blue) and spectra taken during heating ramp (black). Lettered lines correspond to transitions in bulk CeO₂ for reference.



Figure 5.13: Normalized magnitude of k^3 weighted Ce L_{III}-edge EXAFS data (a) 0.29 Ce/nm² obtained from Ce(O^tBu)₄ on MCM-41, oxidized, (b) 0.43 Ce/nm² obtained using Ce(acac)₃ on MCM-41, oxidized, (c) simulated CeO₂.

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Chapter 6

Investigation of the structure and activity of VO_x/CeO₂/SiO₂ catalysts for methanol oxidation to formaldehyde

Abstract

The effect of ceria on the partial oxidation of methanol to formaldehyde over $VO_x/CeO_2/SiO_2$ catalysts was investigated. A two-dimensional layer of ceria on silica was prepared by grafting cerium (IV) *t*-butoxide (Ce(OC₄H₉)₄) onto high surface area, mesoporous silica, SBA-15, and then calcining the resulting product in air at 773 K. Ce surface concentrations obtained this way ranged from 0.2 to 0.9 Ce nm⁻². Next, V was introduced by grafting VO(OⁱPr)₃ onto CeO₂/SiO₂ in order to achieve a surface concentration of at 0.6 V nm⁻². XANES spectra indicate that all of the V is in the 5+ oxidation state and Raman spectra show that vanadia exist as pseudo-tetrahedra bonded to either silica or ceria. Data from Raman spectroscopy and temperature-programmed desorption of adsorbed methanol indicate that with increasing Ce surface density, most of the V becomes associated with the deposited ceria. The turnover frequency for methanol oxidation is nearly two orders of magnitude higher for VO_x/CeO₂/SiO₂ than for VO_x/SiO₂, whereas the apparent activation energy and apparent first-order pre-exponential factor are 17 kcal/mol and 1.4×10^6 mol CH₂O (mol V•atm•s)⁻¹, respectively, for VO_x/SiO₂.

6.1 Introduction

The catalytic activity of supported vanadia shows significant differences as a function of support composition [1,2,3,4,5,6]. These differences are well documented for the case of oxidation of methanol to formaldehyde, where the rate of CH₂O formation has been shown to proceed more rapidly by over an order of magnitude when vanadia is supported on titania, zirconia, or ceria than on silica [1,6,7,8]. A similar increase in activity for the oxidation of methanol to formaldehyde is seen for bilayered catalysts in which TiO_x or ZrO_x is grafted in submonolayer quantities onto silica [4,5,9,10]. Despite many attempts to understand the origin of this support effect, a consensus regarding the cause(s) has not emerged [1,2,3,4,5,9,10,11,12,13,14,15]. In order to elucidate the mechanism by which the support composition affects the activity of the supported vanadate species, the underlying support surface must be thoroughly characterized. Careful characterization of the supported vanadia layer is also important to understand how the different vanadia structures impact the reaction rate.

A number of investigators have found it advantageous to use silica as the support material and to graft the modifying oxide (e.g., TiO_x , ZrO_x) layer onto the silica. If the modifying layer is deposited using an organometallic precursor, it can react with surface silanol groups to form an amorphous, two-dimensional oxide layer. Either isolated monovanadate or polyvanadate species can then be grafted onto such a modified support, with most of the vanadate species becoming attached to the modifying layer [4,5,9,10].

Until recently, attempts to carry out similar studies with $VO_x/CeO_2/SiO_2$ have been hampered by the difficulty of dispersing ceria as a two-dimensional layer; therefore, most of what is known about the effects of ceria on the activity of vanadia for the oxidation of methanol has come from studies of $VO_x/CeO_2/SiO_2$ in which the ceria is present as nanoparticles of CeO_2 and from studies of vanadia supported on bulk ceria.

Previous studies of $VO_x/CeO_2/SiO_2$ bilayered catalysts have focused on characterization of oxide phases by Raman spectroscopy but have not identified how ceria promotes the activity of vanadia [16,17,18,19]. Studies by Vohs and co-workers of methanol oxidation on vanadia supported on polycrystalline CeO₂ [20,21] and on the (111) surface of monocrystalline CeO₂ [21,22,23] have shown that the rate-limiting step in the formation of formaldehyde involves the transfer of a H atom from the methyl group of adsorbed methoxy species bonded to ceria-supported vanadate species. Abbott et al. have also investigated methanol oxidation over vanadia supported on CeO₂(111) thin films [24]. The authors propose that Ce³⁺ adjacent to isolated vanadate structures are responsible for the increased reactivity for methanol oxidation but do not fully explain how these centers contribute to the reaction. Insight into the structure of ceria supported vanadia has been provided by DFT carried out by Metiu and coworkers and Sauer and coworkers [25,26]. Both sets of authors find that isolated vanadate species on CeO₂(111) can exist in at least two types of distorted tetrahedral environments.

In the present study we extend our earlier work on methanol oxidation catalyzed by vanadate species supported on silica and on two-dimensional layers of titania and zirconia supported on silica [3,4,5]. This effort was enabled by our recent studies showing amorphous, two-dimensional layers of ceria can be deposited onto silica using cerium (IV) *t*-butoxide as the precursor [27]. In all cases, the surface density of vanadia was maintained low enough so that the only isolated monovanadates were observed. The catalysts were characterized by Raman and UV-visible spectroscopy, and X-ray Absorption Near Edge Spectroscopy (XANES). The catalytic properties of $VO_x/CeO_2/SiO_2$ catalysts were studied using methanol as a probe molecule. Our results indicate that the ceria domain participates in the reaction by providing an alternative mechanism for H-abstraction from adsorbed methoxy species in the rate-determining step leading to formaldehyde. The results obtained with $VO_x/CeO_2/SiO_2$ are compared with those reported in our earlier work on $VO_x/TiO_2/SiO_2$ and $VO_x/ZrO_2/SiO_2$. It is noted that the catalytic activity and the apparent rate parameters for $VO_x/TiO_2/SiO_2$, $VO_x/ZrO_2/SiO_2$, and $VO_x/CeO_2/SiO_2$ are very similar, but differ significantly from those for VO_x/SiO_2 .

6.2 Experimental Methods

SBA-15, a high surface area mesoporous silica, was synthesized according to the method described in refs. [27,28]. Briefly, Pluronic P123 (<MW> = 5800) was suspended in water and stirred for 1.5 h, then 120 cm³ of 2 M HCl was added and the resulting mixture stirred for an additional 2 h. Next tetraethyl orthosilicate (TEOS) was added dropwise while the mixture was held at 308 K and stirred for 24 h. Stirring was stopped, and the mixture was heated at 373 K for 24 h. The precipitate was filtered and washed six times with deionized water and once with 50 cm³ of acetone. After drying overnight in air, the filtrate was heated to 773 K at 2 K min⁻¹ and held for 4 h.

Cerium was grafted onto SBA-15 using cerium (IV) *t*-butoxide (Ce(OC₄H₉)₄, Gelest), as described in ref. [27]. The Ce(O^tBu)₄ was dissolved in 70 cm³ of anhydrous toluene at ambient temperature in an inert atmosphere before mixing with the SBA-15 support. The liquid was removed and the resulting sample rinsed three times with anhydrous toluene before drying at ambient temperature under vacuum. The samples were then heated to 573 K in He, after which the gas was switched to synthetic air, and the sample heated to 773 K for 4 h.

Vanadium was grafted onto CeO_x/SiO_2 , in a single grafting step, using $VO(O^1Pr)_3$ (Alpha, 96% pure) as the vanadium precursor. The desired quantity of vanadium is mixed with ~60 cm³ of anhydrous toluene in a dry N₂ atmosphere before mixing with the support after drying under vacuum at 393 K for 4 h [4,5]. After stirring at ambient temperature for 4 h, the sample was rinsed 3 times with anhydrous toluene before treating in synthetic air at 823 K for 6 h. The resulting catalysts were stored in a glove box without exposure to the atmosphere.

CeVO₄ was synthesized by mixing Ce(NO₃)₃•6H₂O and vanadyl acetylacetonate together with a mortar and pestle in a 1:1 molar ratio before treating in synthetic air to 1023 K for 8 h. The resulting product was dark purple.

The surface area of SBA-15 before and after cerium grafting were determined by nitrogen physisorption at 77 K using an Autosorb-1 instrument (Quantachrome) using the single point BET method. The weight percentage of cerium and vanadium was determined using inductively coupled plasma (ICP) analysis by Galbraith Laboratories. The apparent surface densities of Ce and V were calculated based on the surface area after Ce grafting.

Raman spectra were acquired using a Jobin Yvon-Horiba spectrometer equipped with a confocal microscope and a 532 nm Nb/YAG laser. Prior to the acquisition of Raman spectra, samples were sealed in a sample holder in the glove box. Eight scans of 4 s each were acquired at room temperature using 15 mW of laser power at the sample.

V K-edge and Ce L_{III} -edge XAS measurements were performed at the Advanced Photon Source (APS) on beamline 10-BM using a Si(111) monochromator crystal. The beam was detuned by 50% at the V K-edge. All scans were taken in transmission mode using 20 cm ionization chambers filled with 85% N₂/15% He in I₀ (before the sample) and 60% N₂/40% Ar in I_t (after the sample). A reference V foil was placed after the sample for energy calibration. Scans were collected with a hold time of 1 s and a step size of 0.5 eV from 5455 to 5505 eV, 10 eV to 5705 eV , and 0.5 eV to 5750 eV. The sample mass was adjusted to obtain an absorbance of 2.5 and boron nitride was added, as needed, to form a self-supporting pellet. The sample cell is a continuous-flow glass tube reactor (length 18 in., diameter 0.75 in.) isolated from the atmosphere with polyimide windows and stainless steel valves fitted at both ends.

The XAS data were analyzed with the IFEFFIT software and its complementary GUI Athena [29,30]. The edge energy was defined as the first inflection point after any pre-edge feature. The V K-edge XANES data were normalized by subtracting a pre-edge line fit to the data from -26.5 to -18 eV relative to the edge energy and a quadratic polynomial (k weight = 2) fit to the data from 41 to 224.5 eV relative to the edge energy.

An *in-situ* XANES experiment was performed in order to identify the effects of temperature and gas composition on the oxidation states of V and Ce. This experiment was initiated by heating the catalyst pellet to 600 K in 60 cm³ min⁻¹ He. While held at

600 K, the gas flow was switched to 60 cm³ min⁻¹ 5000 ppm MeOH/He until no changes were observed in the V K-edge or Ce L_{III} -edge XANES. The catalysts were then heated at 773 K in the same MeOH/He flow and scans acquired until no changes were observed in the resulting spectra. Finally, 60 cm³ min⁻¹ of 10% H₂/He was passed over the catalyst until the XANES spectra exhibited no changes at 773 K. The extent of reduction of V was determined by carrying out V K-edge linear combination analysis (LCA) using the scan at 300 K in He and the scan after 773 K in 5000 ppm methanol as reference spectra to represent the fully oxidized (V⁵⁺) and reduced catalyst, respectively. The data were fit from -20 to 30 eV relative to the edge energy using Athena. For ceria, the extent of reduction from Ce⁴⁺ to Ce³⁺ was performed using the peak intensity at 5727 eV for the Ce L_{III}-edge. This peak height was normalized by the values obtained from the reference spectra at 300 K in He and after treatment in 5000 ppm methanol at 773 K to represent Ce⁴⁺ and Ce³⁺, respectively.

Diffuse reflectance UV-Visible spectra were recorded using a Harrick Scientific diffuse reflectance attachment (DRP) with a reaction chamber (HVC-DRP) and a Thermo Scientific Evolution 300 spectrophotometer. The spectra were acquired after loading the samples in the glove box at ambient temperature without exposing the sample to the atmosphere. The edge energy was calculated using Tauc's law for indirect transitions in amorphous and crystalline semiconductors [31]. In this expression, a straight line is fit through a plot of $[A \cdot hv]^{1/2}$ versus hv, where A is the absorbance and hv is the incident photon energy. The x-intercept of this linear fit is the reported edge-energy.

Temperature programmed reaction (TPR_x) experiments were performed using a mixture of approximately 25 mg of catalyst and 25 mg of bare SBA-15. The mixture was placed in a quartz reactor and supported with quartz wool. The sample was heated at 4 K min⁻¹ to 773 K in a flow of high purity O_2 in He (20% O_2 /He) flowing at 60 cm³ min⁻¹ and then held at 773 K for 1 h. Next, the sample was cooled in this gas mixture to 363 K, after which a mixture of 4% MeOH/7.5% O_2 /He was flowed over the catalyst for 10 min at 363 K before the reactor temperature was increased at 2 K min⁻¹ to 823 K. The reactor effluent was analyzed with a MKS Cirrus mass spectrometer. The concentrations of species formed were analyzed using a matrix-deconvolution method with calibrated response factors.

Temperature Programmed Desorption (TPD) profiles were acquired using a pretreatment procedure similar to that used for TPRx, except upon cooling to 363 K, the reactor was purged with He until no O_2 was observed. Next, 30 cm³ min⁻¹ of 4% MeOH/He was passed over the catalyst for 3 min, and the reactor purged in 30 cm³ min⁻¹ He for 45 min. After the purge, the reactor was heated at 4 K min⁻¹ to 773 K and the effluent analyzed by a MKS Cirrus mass spectrometer as for the TPR_x data.

6.3 Results and Discussion

6.3.1 Catalyst Characterization

The names and BET surface areas of all samples are reported in Table 6.1. The number after V and before Ce gives the Ce surface coverage, the letters, tB, after Ce correspond to the $Ce(O^{t}Bu)_{4}$ precursor, and the final letter, S, refers to the support, SBA-15. After ceria grafting, the surface area per gram of silica decreased for all samples decreased the diameter of the mesopores and partially blocked the micropores of SBA-15
[27]. The vanadium surface density was held constant at ~ 0.6 V nm⁻², while the ceria layer density was increased from 0.2 to 0.9 Ce nm⁻². Assuming a monolayer coverage of 7 M nm⁻² (M = V, Ce), both the V and Ce surface coverages are ≤ 0.1 of a monolayer.

6.3.1.1 Raman

The Raman spectra for the catalysts are shown in Figure 6.1. The spectrum for SBA-15 shows a strong band near 470-500 cm⁻¹, weak bands at 670 cm⁻¹ and 800 cm⁻¹, and more intense bands at 900 and 970 cm⁻¹. The two peaks at 470 and 670 are due to the breathing modes of the silica [32], while the higher frequency peaks are due to Si-OH vibrational modes [33].

Sample 85CetBS in Figure 6.1 is illustrative of the Raman spectrum taken after Ce grafting. No evidence of crystalline CeO₂ is observed, except for a weak band at 455 cm⁻¹ for the highest surface density [27]. However, a new band is observed centered at 950 cm⁻¹ which grows with Ce surface coverage. This peak is, therefore, attributed to Ce-O-Si vibrations. The position of this feature is similar to that observed at 963 cm⁻¹ in the infrared spectra of cerium oxides incorporated into mesoporous silica [34]. A broad peak is also observed in the region of 300-450 cm⁻¹, which could be a result of breathing modes of ceria present on the surface silica, since this region corresponds to similar vibrations in SiO₂ [32].

Upon grafting of V, peaks appear at 1040 and 850 cm⁻¹. The feature at 1040 cm⁻¹ is due to the V=O stretch for pseudo-tetrahedral vanadate species but definitive assignment of this feature is difficult for the following reasons. Isolated vanadate species grafted on silica have been observed to exhibit a V=O vibration in the region of 1035 to 1043 cm⁻¹ [3,19,35,36]. However, a similar band for V=O vibrations has been observed in the region from 1022 to 1039 cm⁻¹ for isolated vanadate species supported on bulk ceria [1,37]. Likewise, theoretical calculations of the vibrational spectrum for isolated pseudo-tetrahedral vanadates present on CeO₂(111), Structure A in Figure 6.15, show the V=O band for such species should be in the range of 1040 to 1046 cm⁻¹ [25,38]. For these reasons, the position of the band at 1040 cm⁻¹ cannot be used to differentiate between pseudo-tetrahedral vanadia bound to silica or ceria. Interestingly, the intensity of this peak decreases in intensity with increasing Ce surface density. Therefore, we believe that the peak at 1040 cm⁻¹ is most likely due to the presence of pseudo-tetrahedral vanadate species on silica. This assignment is supported by information derived from methanol temperature programmed desorption (TPD) data, which are discussed below.

The band at 850 cm⁻¹ may be attributable to V=O vibrations for a vanadate group in which V is connected to the ceria domain through three bridging oxygen atoms, as illustrated for Structure B in Figure 6.2. DFT calculations of the spectrum for this structure formed on the (111) surface of CeO₂ exhibit a band at 876 cm⁻¹ [25]. The proposed assignment of the band at 850 cm⁻¹ is further supported by work on bilayered VO_x/CeO₂/SiO₂ catalysts, in which a broad peak at 850 cm⁻¹ was observed upon heating the sample to 773 K. Raising the temperature to 1073 K caused this feature to narrow into an intense peak at 853 cm⁻¹ characteristic of CeVO₄ formation [16,17]. Thus, the band at 850 cm⁻¹ observed in the present study could be a precursor to CeVO₄; however, no evidence was observed for CeVO₄ in the spectra of VCetBS as indicated by the absence of peaks at 853, 780 and 790 cm⁻¹ characteristic of CeVO₄. The spectra presented in Figure 6.1 also show no evidence for V_2O_5 , which has bands at 998, 702, 529, or 287 cm⁻¹[8].

6.3.1.2 UV-Visible Spectroscopy

The UV-visible edge energies for catalysts with and without V grafted are shown in Figure 6.3. The edge energy for the CeO₂/SBA-15 samples is ~3.4 eV, independent of the CeO_x surface density. After V grafting, the edge energy decreased by 0.7 - 1.0 eV to ~2.6 eV. This edge energy is also lower than that for tetrahedral vanadates on silica, 3.17 eV [5]. The observation of an edge energy for the bilayered catalysts lower than that for either VO_x/SiO₂ or CeO_x/SiO₂ is presumed to be due to the presence of V-O-Ce bonds.

6.3.1.3 XANES

The V K-edge XANES spectra acquired at ambient temperature are shown in Figure 6.4A. The large pre-edge feature for all samples occurs because of hybridization between the O 2p and V 3d orbitals in a non-centrosymmetric environment [39] and indicates predominantly tetrahedral or pseudotetrahedral V species on the surface. This conclusion is supported by examination of the XANES spectra for V⁵⁺ standards presented in Figure 6.4B, which show that as the vanadia environment changes from square pyramidal, V₂O₅, to distorted tetrahedral, NH₄VO₃, to tetrahedral, CeVO₄ [40], the pre-edge feature increases as a result of increasing p-d orbital hybridization. Agreement of the edge energy for the VCetBS samples (Figure 6.17A) with that for V⁵⁺ standards (Figure 6.17B) further supports the conclusion that all of the V in these samples is in the 5+ oxidation state. Electron paramagnetic resonance (EPR) spectra of VCetBS samples were also acquired and these showed no evidence for a signal attributable to V⁴⁺ (data not shown) [41].

6.3.1.4 MeOH Temperature Programmed Desorption (TPD)

The catalysts were further characterized by taking TPD spectra of adsorbed MeOH. Figure 6.5 illustrates the MeOH, CH_2O , and CH_4 profiles observed for samples of V19CetBS, V51CetBS, V85CetBS, and 85CetBS. In addition to these products, the formation of H_2O , CO, and CO_2 were observed. The spectra for these products are shown in the Supporting Information. Infrared absorption data for these catalysts indicate that methanol initially adsorbs dissociatively producing methoxy and hydroxyl groups bound to Si, Ce, and V (data not shown), as observed previously for silica and ceria supported vanadia [3,19,42].

For all catalysts, MeOH desorbs at 363 K, a temperature well below that for the appearance of any other products. A broad desorption peak for CH₂O begins around 415 K for catalysts containing V. It is noted that in the absence of V, the appearance of formaldehyde occurs at a temperature of ~50 K higher than for the corresponding VCetBS samples (compare spectra for 85CetBS and V85CetBS). As the Ce surface density increases, the intensity of the formaldehyde profile at 625 K decreases with a concomitant decrease in the production of methane. No methane is observed for CetBS samples. The formation of methane can be attributed to the decomposition of silicabonded methoxy species that are adjacent to silica-supported mono-vanadate species [3]. While the methane peak temperature for VCetBS catalysts occurs at a slightly higher temperature, ~650 K, than that for VO_x/SiO₂, 625 K [3], the decrease in the quantity of

methane formed with increasing ceria surface density and its absence in 85CetBS suggests that methane is produced as a result of isolated VO_x/SiO_2 structures not bound to ceria.

The formaldehyde profiles for VCetBS catalysts are broad, but in every case, the onset of formaldehyde production begins at significantly lower temperatures (~415 K) than that for isolated vanadate species supported on silica (~500 K) [3,43]. A lower formaldehyde production temperature for VO_x/CeO₂ than VO_x/SiO₂ has previously been observed by the group of Vohs and coworkers [20,43]. In these studies, surface coverages of 0.3 and 3.5 V nm⁻² for VO_x/SiO₂ and 3.4 V nm⁻² for VO_x/CeO₂ were used, and the peak temperature of formaldehyde desorption decreased from ~675 K for VO_x/SiO₂ [43] to ~600 K or lower for VO_x/CeO₂ [20] (for TPD profiles acquired with a heating rate of 15 K min⁻¹).

6.3.2 Studies of Methanol Oxidation

The rates of methanol oxidation on CetBS and VCetBS are shown in Figure 6.6 as a function of the ceria surface density. For both sets of samples, the rates are expressed per unit surface area. At 543 K, the ceria layer is active for methanol oxidation, and the rate of formaldehyde production increases linearly with increasing Ce surface density. Under the reaction conditions used, silica shows no activity for methanol oxidation.

After grafting V, the rate of CH₂O formation per unit surface area increases relative to that for CetBS, by about a factor of two. For reference, the rate of formaldehyde formation on VO_x/SiO₂ under equivalent reaction conditions and vanadium loadings is 3.5×10^{-10} mol CH₂O•(s•m²)⁻¹. Therefore, the high activity of VCetBS is due to the portion of the vanadium interacting with the ceria layer deposited on the SBA-15.

The apparent rate constant for formaldehyde production attributable to vanadia was determined by subtracting the contribution to the CH₂O formation rate due to the ceria layer and dividing the resulting rate per surface area by the methanol vapor pressure and the surface density of vanadia as determined by ICP. As shown in Figure 6.7, the VCetBS samples show a constant rate with increasing Ce surface density that is an order of magnitude larger than for $0.3VO_x/SiO_2$ [3]. This increase with Ce surface density is similar in magnitude to that observed in our previous work for VO_x/TiO₂/SiO₂ and VO_x/ZrO₂/SiO₂ catalysts (~ 0.6 V nm⁻²) [4,5], which are also shown in Figure 6.7. Taking into account the uncertainty in the data, it can be concluded that the values of k_{app} are very similar to those for VO_x/TiO₂/SiO₂, VO_x/ZrO₂/SiO₂, and for VO_x/CeO₂/SiO₂ once the data are corrected for the activity of the ceria deposit.

The apparent activation energy and pre-exponential factor for methanol oxidation on VCetBS catalysts are presented in Table 6.2. The apparent activation energy is approximately 17 kcal mol⁻¹ for all samples. This value is comparable to the activation energy of 18 kcal mol⁻¹ for our bulk CeVO₄ sample and similar to that reported by Feng et al. for vanadia supported on bulk CeO₂, 16 kcal mol⁻¹ [20]. Table 6.2 also shows that the apparent pre-exponential factor is essentially the same for all samples (~ 1x10⁶ mol CH₂O (mol V•atm•s)⁻¹).

The apparent pre-exponential factors and activation energies obtained in this study are compared with those reported in our work with isolated vanadate species supported on two-dimensional layers of titania and zirconia deposited on silica and with isolated vanadate species supported on silica. As seen in Table 6.3, activation energies and pre-exponential factors for VO_x/TiO₂/SiO₂, VO_x/ZrO₂/SiO₂, and VO_x/CeO₂/SiO₂ are all very similar and significantly smaller than those for VO_x/SiO₂. A further observation is that both the pre-exponential factor and the activation energy for methanol oxidation occurring on VO_x/SiO₂ are larger than those for the other three catalysts, even though active form of vanadia is the same. This suggests that the there may be significant differences in the mechanism by which formaldehyde is formed on VO_x/TiO₂/SiO₂, VO_x/ZrO₂/SiO₂, and VO_x/CeO₂/SiO₂ versus VO_x/SiO₂. This point is discussed in more detail below.

To understand the reason for the increased rate of methanol oxidation on $VO_x/CeO_2/SiO_2$ relative to VO_x/SiO_2 , it is useful to first review the mechanism of methanol oxidation proposed for the latter catalyst. Both experimental and theoretical studies suggest that CH₂O is formed via the following sequence of steps [1, 3,12,44]. Reaction is initiated by the dissociative adsorption of methanol across a V-O-Si bond to produce V-OCH₃ and Si–OH species. Next, a hydrogen atom from V-OCH₃ is abstracted by the V=O bond of the vanadate species, resulting in the release of CH₂O and the formation of a V-OH species. This step is taken to be the rate determining. Water is then formed by condensation of the V-OH and SiOH groups. Finally, the active site is reoxidized with gas-phase oxygen to return to the fully oxidized initial state [3,12]. Calculations of the enthalpy of methanol adsorption, the apparent activation energy, and the apparent first-order rate coefficient for methanol oxidation were all found to be in close agreement with experiment based on this mechanism [12].

When ceria is present on the surface, the Raman spectra presented here and theoretical studies of the interactions of isolated vanadate species bonded to bulk ceria [25] indicate that the vanadate species are present in the form of VO₃ species (see Figure 6.2 and Structure A in Figure 6.8). Methanol can then adsorb dissociatively by cleavage of a V-O-Ce bond (Reaction 1 Figure 6.8). It is not possible to determine whether the methoxy group is bound to V or Ce because of a single peak in the IR for adsorbed methoxy species and the broad silica absorption band, which obscures the observation of C-O stretches [42]. However, in previous work by Jehng a Raman peak was observed at ~1068 cm⁻¹ upon methanol adsorption on VO_x/CeO₂/SiO₂ catalysts. This feature was attributed to vibrations of V=O bonds in Structure B in Figure 6.21 [19,45,46]. Therefore, we assume that methanol adsorption results in the formation of V-OCH₃ and Ce-OH species and that Reaction 1 is quasi-equilibrated. This second assumption is supported by the observation that desorption of methanol via the reverse of Reaction 1, seen in the TPD spectra presented in Figure 6.5, occurs at a significantly lower temperature than the conversion of methoxy groups to formaldehyde.

The elementary processes by which V-OCH₃ species react to form CH₂O and H₂O on VO_x/CeO₂/SiO₂ cannot be determined directly from the available data. If they were identical to those occurring on VO_x/SiO₂, then one would expect that the oxidation state for V to decrease from 5+ to 3+ and the oxidation state of Ce to remain constant at 4+. If, on the other hand, the transfer of the H atom from V-OCH₃ were to occur via reaction with a Ce-OH group to form CH₂O and H₂O concurrently, then one would expect the oxidation state of V to decrease from 5+ to 4+ and the oxidation state of Ce to decrease from 4+ to 3+.

To gain insight into what species are reduced at temperatures where methanol oxidation occurs, an *in situ* XANES experiment was conducted with V85CetBS. As

shown in Figure 6.9, the sample was first characterized in He at 300 K. Under this condition both V and Ce were found to be in their fully oxidized states: V^{5+} and Ce^{4+} [47]. Next, the sample was heated to 600 K in He. Raising the temperature to this level had no effect on the oxidation state of V but resulted in a small amount of Ce undergoing reduction from Ce^{4+} to Ce^{3+} due presumably to the loss of O₂. Exposure of the sample at 600 K to 0.5% methanol in He resulted in a progressive reduction of V⁵⁺ and Ce⁴⁺, with the reduction of ceria occurring more rapidly than the reduction of vanadia. Since CH₂O and H₂O are the only products formed at 600 K, the results of this experiment suggest that the ceria layer to which the vanadate species are bound participates in the formation of the products. We propose that this process may occur via Reaction 2 in Figure 6.8. H-abstraction to the ceria domain would initially result in formation of Ce³⁺ and V⁴⁺ species. Transfer of an electron from the V⁴⁺ to the ceria layer could then result in the formation of two Ce³⁺ centers (structure D in Figure 6.8). A similar mechanism for H-abstraction has been proposed based on DFT calculations of the energetics of methanol oxidation occurring on isolated vanadate species supported on TiO₂(111) [14].

The reaction mechanism presented in Figure 6.8 leads to the conclusion that the apparent first order rate coefficient for methanol oxidation, k_{app} , is given by

$$k_{app} = k_2 K_1, \tag{6.1}$$

where K_1 is the equilibrium constant for Reaction 1 and k_2 is the rate constant for reaction 2. Consistent with this definition, the apparent activation energy, E_{app} , and preexponential factor, k_{app}^0 , are given by

$$E_{app} = E_2 + \Delta H_1 \tag{6.2}$$

and

$$k_{app}^0 = k_2^0 K_1^0, (6.3)$$

where ΔH_1 and K_1^0 are the enthalpy change and the pre-exponential factor for the equilibrium constant for Reaction 1, respectively, and E_2 and k_2^0 are the activation energy and pre-exponential factor, respectively, for Reaction 2.

The data presented in Table 6.6 indicate that the values of k_{app}^0 and E_{app} are similar for VO_x/TiO₂/SiO₂, VO_x/ZrO₂/SiO₂, and VO_x/CeO₂/SiO₂, and differ significantly from the corresponding values for VO_x/SiO₂. This then raises the question of whether observed differences in the apparent rate parameters are due solely to difference in the rate parameters for the rate-limiting step, Reaction 2 in Figure 6.8 for VO_x/TiO₂/SiO₂, VO_x/ZrO₂/SiO₂, and VO_x/CeO₂/SiO₂ or its equivalent for VO_x/SiO₂, or to a mixture of differences in the equilibrium constants for Reaction 1 and the rate constant for Reaction 2. Some insights into this question can be obtained by examining reported values of the heat of methanol adsorption on isolated vanadate species supported on different metal oxide supports. For bare silica, the initial heat of methanol adsorption has been reported to range from -16 to -19 kcal mol⁻¹ [48], which is comparable to that measured on ceriasupported vanadate species, -19 kcal mol⁻¹ [20]. While experimental values of the heat of adsorption for isolated vanadate species supported on silica, titania, and zirconia have not been reported, theoretical calculations of the energy for the addition of methanol across a V-O-M (M = Si, Ti, Zr) bond are virtually the same, ~ 21 kcal/mol [49]. We also observe that the equilibrium constant for methanol adsorption on a monolayer of vanadia supported on SiO₂, Al₂O₃, TiO₂, and CeO₂ does not vary significantly [42]. Taken together these observations suggest that the observed difference in the activity of $VO_x/TiO_2/SiO_2$, $VO_x/ZrO_2/SiO_2$, and $VO_x/CeO_2/SiO_2$ with respect to VO_x/SiO_2 are less likely due to differences in the equilibrium constant for methanol adsorption than to the differences in rate coefficient for the rate-limiting step. We also note that as the apparent activation decreases so does the magnitude of the pre-exponential factor (see Table 3), suggesting that there is a compensation effect.

6.4 Conclusions

Bilayered $VO_x/CeO_2/SiO_2$ catalysts were prepared in which isolated monovanadate species were dispersed on an amorphous, two-dimensional layer of ceria bonded to SBA-15. The vanadia exists as pseudo-tetrahedral vanadate species bonded to both silica and ceria, with the fraction bound to ceria increasing with ceria surface density. The turnover frequency for methanol oxidation to formaldehyde is about twenty-fold higher for $VO_x/CeO_2/SiO_2$ catalysts than for VO_x/SiO_2 . The increase in activity is due to the lower activation energy for the rate-determining H-abstraction step from a surface methoxy bound to a V-O-Ce site. This lower activation energy is possible because oxygen bound to ceria adjacent to vanadia abstracts the proton instead of the vanadyl oxygen.

			CeO _x /SBA-15		
			surface areas	V	
			(Ce-free),	coverage,	Ce coverage,
Sample Name	V, wt%	Ce, wt%	$m^2 g^{-1}$	V nm ⁻²	Ce nm ⁻²
V19CetBS	2.9	2.6	589 (687)	0.6	0.2
V51CetBS	2.6	6.1	516 (817)	0.6	0.5
V85CetBS	2.7	8.7	436 (735)	0.7	0.9

Table 6.1. Surface areas of CeO_x/SBA-15 with V and Ce weight percentages and surface coverages.

Table 6.2. Apparent pre-exponential factors and activa	ation energies for catalyst samples.
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	Apparent pre-exponential factor at 543 K, k ⁰	Apparent activation energy,
Sample Name	$(mol CH_2O\bullet(mol V\bullet atm\bullet s)^{-1})$	E_{app} (kcal mol ⁻¹)
$0.3 \text{VO}_{\text{x}}/\text{SiO}_{2}^{\text{a}}$	2.3×10^7	23
V19CetBS	$1.0 \ge 10^6$	17
V51CetBS	$1.0 \ge 10^6$	17
V85CetBS	$2.2 \text{ x } 10^6$	18

^aData from ref. [3].

	Apparent pre-exponential	
	factor, k ⁰	Apparent activation energy,
Sample Name	$(mol CH_2O\bullet(mol V\bullet atm\bullet s)^{-1})$	E_{app} (kcal mol ⁻¹)
VO _x /SiO ₂ ^a	2.3×10^7	23
VO _x /TiO ₂ /SiO ₂ ^b	$1.8 \ge 10^6$	18
$VO_x/ZrO_2/SiO_2^c$	$4.0 \ge 10^6$	16
VO _x /CeO ₂ /SiO ₂ ^d	2.2×10^{6}	18

Table 6.3. Apparent pre-exponential factors and activation energies for catalyst samples. In the case of $VO_x/MO_2/SiO_2$ (M = Ti, Zr, Ce), the pre-exponential factor is based on V atoms fully associated with MO₂.

^aData from ref. [3]. ^bData from ref. [4]. ^cData from ref. [5]. ^dData for V85CetBS



Figure 6.1. Raman spectra of VCetBS catalysts after treating in syn. air to 773 K for 4 h. Spectra of the bare SBA-15 support, $CeVO_4$, and 85CetBS are also included.



Figure 6.2. VO_x structures on CeO_2 (111) surface as determined by density functional theory calculations: VO_2 (A) and VO_3 (B). Figure adapted from ref. [25]. The nomenclature, VO_x , is used such that x is the number of oxygens from the gas phase that are not part of the CeO_2 (111) surface.



Figure 6.3. UV-visible absorption edge energies for $VO_x/CeO_2/SiO_2$ catalysts. Data were acquired at ambient temperature without exposing samples to moisture.



Figure 6.4. V K-edge XANES acquired at ambient temperature under He for VCetBS catalysts (A) and V standards (B). The energy is referenced to the initial peak of the V foil derivative spectrum (0 eV).



Figure 6.5. Temperature Programmed Desorption (TPD) profiles for selected catalysts for the following species: MeOH (burgundy diamonds), formaldehyde (blue down triangles), and CH_4 (pink left triangles). Data are normalized to sample mass.



Figure 6.6. CH₂O formation rates per surface area of catalyst at 543 K for samples with V (open symbols) and without V (closed symbols).



Figure 6.7. Apparent rate constants for VCetBS, $VO_x/TiO_2/SiO_2$, and $VO_x/ZrO_2/SiO_2$ catalysts as a function of M surface density (M = Ce, Ti, Zr) at 543 K. Apparent rate constants for $VO_x/TiO_2/SiO_2$ and $VO_x/ZrO_2/SiO_2$ catalysts are from refs. 4 and 5, respectively. Curve is to guide the eye.



Figure 6.8. Proposed mechanism for methanol oxidation on $VO_x/CeO_2/SiO_2$ catalysts derived from the $Ce(O^{1}Bu)_4$ precursor.



Figure 6.9. Extent of oxidation for V K-edge and Ce L_{III} -edge on V85CetBS in He and 0.5%MeOH/He flow. The V K-edge was analyzed by a linear combination fit of the V K-edge under He at 300 K (value of 1.0) and under 5000 ppm methanol flow at 773 K (value of 0.0). The Ce L_{III} -edge was analyzed by the height of the feature at 261.5 eV normalized between the height at 300 K in He (1.0) and the height under methanol flow at 773 K (0.0).

6.5 Supporting Information



Figure S6.1. Temperature Programmed Desorption (TPD) profiles for selected catalysts for the following species: H_2O (green up triangles), CO (red circles) and CO₂ (black squares). Data are normalized to sample mass.

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Appendix A

Matrix deconvolution of mass spectra

A.1 Introduction

Mass spectrometers (ms) are useful tools for analyzing gas phase products in reactions rapidly. Spectra may be acquired several times per second, and many m/z (mass divided by charge) values can be monitored simultaneously to determine the quantity and types of compounds in a reactor's effluent. The challenge arises when converting the m/z values to mole fractions of reaction products because each chemical will contribute signal to multiple m/z values, and these will often overlap with other products for a given reaction. This appendix will describe one method for converting raw m/z data into mole fractions using a matrix deconvolution method.

A.2 Experimental setup

Before beginning an experiment, the expected compounds leaving a reactor should be identified and their cracking patterns obtained from a reference source, such as the NIST chemistry webbook [1]. Each chemical will crack on multiple m/z values, so selection of appropriate m/z values to monitor is important for proper data analysis. McLafferty and Turecek provide a guide for selecting the appropriate m/z values to use [2]. When selecting the m/z values, determine an m/z value for which one compound has a high cracking fraction with little to no contribution from other compounds. Typically, high m/z values satisfy this requirement for most chemicals. Unfortunately, not all systems provide such a situation for all products. In this case, attempts should be made to come as close to the above criteria as possible because significant overlap between m/z values for different products may significantly alter your accuracy, see below.

Once an appropriate m/z value has been selected for each chemical you expect to detect, the deconvolution matrix may begin to be constructed. First, the response factor matrix must be determined. This matrix consists of an NxN matrix, where N is the number of compounds, with the rows consisting of the m/z values selected above and the columns consisting of each compound. An example of this is shown below in Table A.1. In this example there are 4 compounds and 4 m/z values, each corresponding to the highest intensity value with the lowest contribution from the other compounds as possible. The numbers in the matrix are obtained by calibrating the ms (see below).

m/z	He	H ₂ O	CH ₃ OH	O ₂
4	100	0	0	0
18	0	100	7	0
31	0	0	100	0
32	0	0	74.4	100

Table A.1. Sample response factor matrix from mass spectrometer deconvolution.

In order to determine how to use this matrix, we must first return to our goal of converting m/z intensities to mole fractions of compounds. We will illustrate this for a simple system with the gases in Table A.1. Generally, we may represent the raw ionization intensities as a summation of the intensity at the m/z for a given compound, if we assume linear behavior, as shown in Equation (A.1).

$$I_i = \sum_{j}^{N} I_{i,j} \tag{A.1}$$

Where, I_i is the overall ionization signal for mass *i*, and $I_{j,I}$ is the ionization signal for component, *j*, and mass, *i*. For the current example, this equation will become for m/z = 4:

$$I_4 = I_{4,He} + I_{4,H20} + I_{4,CH30H} + I_{4,02}$$
(A.2)

Where, I_4 is the total intensity of m/z = 4, $I_{4,He}$ is the intensity of m/z = 4 from He, $I_{4,H2O}$ is the intensity of m/z = 4 from H₂O, $I_{4,CH3OH}$ is the intensity of m/z = 4 from CH₃OH, and $I_{4,O2}$ is the intensity of m/z = 4 from O₂.

Each individual contribution to the overall signal can be represented, generally, by

$$I_{i,j} = RF_{i,j} \cdot x_j \tag{A.3}$$

where, $RF_{i,j}$ is the response factor for component, *j*, on mass, *i*, and x_j is the mole fraction of component, *j*. When combining eqns. (A.1) and (A.3) for all m/z values, we obtain the matrix equation

$$[I_i] = [RF_{i,j}] \cdot [x_j] \tag{A.4}$$

where $[I_i]$ is the overall ionization vector, $[RF_{i,j}]$ is the response factor matrix, and $[x_j]$ is the mole fraction matrix. For the current example, equation (A.4) will become

$$\begin{bmatrix} I_4\\I_{18}\\I_{31}\\I_{32}\end{bmatrix} = \begin{bmatrix} RF_{4,He} & RF_{4,H20} & RF_{4,CH30H} & RF_{4,CH20}\\RF_{18,He} & RF_{18,H20} & RF_{18,CH30H} & RF_{18,CH20}\\RF_{31,He} & RF_{31,H20} & RF_{31,CH30H} & RF_{31,CH20}\\RF_{32,He} & RF_{32,H20} & RF_{32,CH30H} & RF_{32,CH20} \end{bmatrix} \cdot \begin{bmatrix} x_{He} \\ x_{H20} \\ x_{CH30H} \\ x_{CH20} \end{bmatrix}$$
(A.5)

The task, therefore, is to invert the matrix shown in equation (A.4) to solve for the unknown mole fractions using the measured ionization intensities for the measured m/z values and the response factors obtained from ms calibration. Rearrangement of equation 11 to solve for the mole fractions is done by multiplying by the inverse of the response factor matrix.

$$[RF]^{-1} \cdot [I] = [x] \tag{A.6}$$

In this manner, mole fractions of compounds may be obtained from measured m/z values and calibrated response factors.

A.3 Mass spectrometer calibration

The measured ionization current for a given m/z depends not only on the mole fractions of the gas phase species, but also on the state of the filament in the ms. For example, under oxidizing conditions, the overall signal intensity of the ms may decrease over time as the filament gradually oxidizes and loses ionization efficiency. The converse may also be true of reducing conditions. Because of these changes, the raw ionization intensity is not sufficient to accurately determine the mole fraction. Typically, an internal standard, usually an inert gas, of known concentration is used to normalize. Another criteria for a sufficient internal standard is that the m/z value have no contribution from other compounds. This internal standard must be present during the calibration and the experiment.

To account for these changes in ionization intensity with time, we may define the response factor as

$$RF_{i,j} = \frac{I_{i,j} x_{ref}}{I_{i_{ref}, ref} x_j}$$
(A.7)

Where x_{ref} is the mole fraction of the internal standard, $I_{i_{ref},ref}$ is the ionization intensity of the internal standard on the m/z for the internal standard, i_{ref} . The response factors may be obtained by flowing known concentrations of a compound, *j*, to the ms and plotting $I_{i,j}x_{ref}/I_{i_{ref},ref}$ vs x_j . The resulting linear slope through 0 will be the response factor.

Having defined the response factors in equation (A.7), we may now rewrite equation (A.4) to account for the normalized ionization intensities and equation (A.8).

$$\left[\frac{I_i x_{ref}}{I_{i_{ref}, ref}}\right] = \left[RF_{i,j}\right] \cdot \left[x_j\right]$$
(A.8)

Inverting equation (A.8) in the same way as before will allow for the mole fractions to be obtained from measured m/z values and calibrated response factors as described above. An offset in the response factor calibration may be handled by modifying equation (A.8) as follows.

$$\left[\frac{I_i x_{ref}}{I_{i_{ref}, ref}}\right] - [B_i] = \left[RF_{i,j}\right] \cdot \left[x_j\right]$$
(A.9)

where B_i is the offset for a given mass, *i*. The method described above will not work rigorously if a given m/z value has contributions from multiple components, each with its own unique offset.

A.4 Feasibility test

A good way to check the feasibility of a given experiment is to calculate the condition number of the resulting matrix. The condition number here represents the maximum ratio of the relative error in x divided by the relative error in I. For example, a condition number of 10 means that the resulting mass calculations could have a relative error 10 times the relative error in the initial ionization current. The condition number of a given matrix may be calculated according to

$$\kappa(A) = \|A\| \cdot \|A^{-1}\| \tag{A.10}$$

Where $\kappa(A)$ is the condition number for matrix *A* and ||A|| and $||A^{-1}||$ are the operator norms of matrix *A* and the inverse of matrix *A* [3]. The condition number of the matrix shown in Table A.7 can be shown to be 3.3.

References

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