Quantitative Determination of the Speciation of Surface Vanadium Oxides and Their Catalytic Activity

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A quantitative method based on UV−vis diffuse reflectance spectroscopy (DRS) was developed that allows determination of the fraction of monomeric and polymeric VOx species that are present in vanadate materials. This new quantitative method allows determination of the distribution of monomeric and polymeric surface VOx species present in dehydrated supported V2O5/SiO2, V2O5/Al2O3, and V2O5/ZrO2 catalysts below monolayer surface coverage when V2O5 nanoparticles are not present. Isolated surface VOx species are exclusively present at low surface vanadium coverage on all the dehydrated oxide supports. However, polymeric surface VOx species are also present on the dehydrated Al2O3 and ZrO2 supports at intermediate surface coverage and the polymeric chains are the dominant surface vanadia species at monolayer surface coverage. The propane oxidative dehydrogenation (ODH) turnover frequency (TOF) values are essentially indistinguishable for the isolated and polymeric surface VOx species on the same oxide support, and are also not affected by the Brønsted acidity or reducibility of the surface VOx species. The propane ODH TOF, however, varies by more than an order of magnitude with the specific oxide support (ZrO2 > Al2O3 > SiO2) for both the isolated and polymeric surface VOx species. These new findings reveal that the support cation is a potent ligand that directly influences the reactivity of the bridging V−O−support bond, the catalytic active site, by controlling its basic character with the support electronegativity. These new fundamental insights about polymerization extent of surface vanadia species on SiO2, Al2O3, and ZrO2 are also applicable to other supported vanadia catalysts (e.g., CeO2, TiO2, Nb2O5) as well as other supported metal oxide (e.g., Cr2O3, MoO3, WO3) catalyst systems.

1. Introduction

Supported vanadia catalysts constitute a very important class of catalytic materials because they have become the model catalytic systems for fundamental studies of supported metal oxides and are extensively employed as commercial catalysts (oxidation of o-xylene to phthalic anhydride, selective catalytic reduction (SCR) of NOx with NH3 to N2 and H2O, oxidative destruction of chlorinated hydrocarbons, and ammoxidation of alkyl aromatics to aromatic nitriles). In recent years, supported vanadia catalysts have also received much attention for selective oxidation and ammoxidation of C1−C4 hydrocarbons to olefins, oxygenates, and nitriles.

The molecular structures of the supported vanadia phase on oxide supports have been extensively characterized by different spectroscopic techniques (IR, Raman, XANES/EXAFS, UV−vis diffuse reflectance spectroscopy (DRS), solid-state 51V NMR, etc.). Under dehydrated conditions, four different types of vanadia species have been identified in supported vanadia catalysts: (1) isolated surface VOx species containing a terminal V=O bond and three bridging V−O−support bonds, (2) polymeric surface VOx species containing a terminal V=O bond and three bridging V−O−V−O−support bonds, (3) crystalline V2O5 nanoparticles (NPs), and (4) mixed oxide compounds or solid solutions with some oxide supports at elevated temperatures (e.g., Zr(V2O5)2, AlVOx, V2Ti3−xO2, NbVO5, Mg3(VO4)2, Mg2V2O7). Dehydrated surface VOx/VOx species, if present at all, must constitute a very small fraction of the dehydrated surface vanadia species since their presence in spectroscopically detectable amounts has not been established. Minor amounts of V2O5 NPs with distorted VOx coordination, however, can also be present in catalysts with incompletely dispersed vanadia below monolayer surface coverage and should not be confused with the surface VOx species. In such cases, the spontaneous dispersion of V2O5 NPs onto the exposed support sites as surface vanadia species can occur by heating to elevated temperatures. Below monolayer surface coverage (~8 V/nm2), isolated monomeric and polymeric surface VOx species are the dominant surface vanadia species and V2O5 NPs only become significant above monolayer surface coverage when the available support surface sites become saturated with the surface vanadia species.

Catalytic studies for many different oxidation reactions have demonstrated that the monomeric and polymeric surface VOx species are generally the catalytic active sites in supported vanadia catalysts since the crystalline phases possess very few exposed active surface sites or low turnover frequencies (TOFs; TOF is the number of molecules converted per catalytic active site per second and is a quantitative measure of the efficiency per exposed catalytic active site). The individual catalytic contributions of the isolated VOx and polymeric VOx species during these catalytic reactions, however, are still not completely resolved in the literature.

Determination of the individual catalytic contributions of isolated and polymeric surface vanadia species on oxide supports requires that these vanadia species be quantified under dehydrated conditions. Schoonheydt et al. have shown that the UV−
vis DRS signal can quantify both the $V^{5+}$ and $V^{4+}$ species below 1% $V$ on alumina and other catalyst support materials.\textsuperscript{24} The $V^{5+}$ UV−vis DRS signal was monitored with the ligand to metal charge transfer (LMCT) transition, and the $V^{4+}$ UV−vis DRS signal was monitored with the $d$−$d$ transition. Complementary quantitative ESR spectroscopy was also employed to confirm the $V^{4+}$ UV−vis DRS quantitative measurements of the catalysts, and both techniques were in excellent agreement. Argyle et al. quantified the extent of reduction of surface vanadia on alumina by monitoring the changes in the $V^{4+}$ $d$−$d$ transition and titrating the reduced $V^{4+}$ species with molecular $O_2$ to $V^{5+}$.\textsuperscript{27} Neither of these investigations, however, attempted to quantify the amount of isolated and polymeric surface $V^{4+}$ species on oxide supports below monolayer surface coverage. During typical propane oxidative dehydrogenation (ODH) reaction conditions, the surface vanadia species are almost completely present as surface $V^{5+}$ species because of the relatively weak reducing power of propane and the excess of molecular $O_2$ that is typically employed.\textsuperscript{5,20,22,27}

In the present investigation, UV−vis DRS is employed to quantify the concentration of monomeric and polymeric surface vanadia species because this spectroscopic method exhibits unique electronic transitions for different vanadia structures (isolated vs polymeric structures).\textsuperscript{24} The $V^{5+}$ LMCT transition shifts to lower energy values with extent of vanadia polymerization as a consequence of greater electron delocalization in polymerized structures.\textsuperscript{20−27} This has led some authors to employ the UV−vis edge energy ($E_g$) as a parameter to qualitatively monitor the extent of vanadia polymerization.\textsuperscript{19−22,27,30,31} This approach is related to the quantum confinement effect of small domains since the $E_g$ value monotonically decreases with the number of bridging $V−O−V$ bonds in the vanadia structure ($E_{g}\_V: V^9 > V^7 > V^5 > V^3 > V^4 > V^6$, where the superscript represents the number of bridging $V−O−V$ bonds in the VO$_3$ unit).\textsuperscript{21} The quantitative UV−vis DRS method is developed and applied to determine the relative surface concentrations of the monomeric and polymeric surface VO$_3$ species that are present in dehydrated supported vanadia catalysts ($V_2O_5/SiO_2$, $V_2O_5/Al_2O_3$, and $V_2O_5/ZrO_2$). This quantitative information is subsequently used to develop the molecular structure−activity relationship for propane oxidative dehydrogenation (ODH) to propylene over the supported vanadia catalysts.

2. Experimental Section

Catalyst Synthesis. The oxide supports used for this study were SiO$_2$ (Cabot, Cab-O-Sil EH-5, $S_{BET} = 330$ m$^2$/g), Al$_2$O$_3$ (Engelhard, $S_{BET} = 222$ m$^2$/g), and ZrO$_2$ (Degussa, $S_{BET} = 39$ m$^2$/g). The supported vanadia catalysts were prepared by the incipient wetness impregnation of 2-propanol solutions of vanadium isopropoxide (VO(O−Pr$_3$), Alfa-Aesar, 97% purity). Impregnation was performed inside a glovebox with continuously flowing N$_2$, and the samples were dried overnight at room temperature in the flowing N$_2$ environment. The samples were further dried in flowing N$_2$ at 120 °C for 1 h and 300 °C for another 1 h, and subsequently calcined in flowing air at 300 °C for 1 h and 450 °C for another 2 h to form the supported vanadia catalysts.

Raman Spectroscopy. The in situ Raman spectra in this study were collected with a combined UV/visible Raman spectrometer system (Horiba-Jobin Yvon LabRam-HR) equipped with a confocal microscope (Olympus BX-30), notch filter (532 nm), and single stage monochromator (Horina-Jobin Yvon LabRam-HR), and a 900 grooves/mm grating. The Raman spectra in this study were collected with visible laser excitation at 532 nm (20 mW, YAG laser) in the 300−1100 cm$^{-1}$ region. The laser power at the sample was kept below 0.5 mW to minimize any laser-induced alterations of the sample. The scattered photons passed through the notch filter and grating in the monochromator to remove the Rayleigh scattering, and were collected with a UV/visible sensitive LN$_2$-cooled CCD detector (Horiba-Jobin Yvon CCD-3000V). The spectral resolution of the Horiba-Jobin Yvon LabRam-HR is ~1 cm$^{-1}$ for the given parameters. The supported vanadia catalysts were loaded in powder form into an in situ cell (Linkam, TS1500) that allowed for sample treatments such as dehydration. The dehydrated Raman spectra were collected at room temperature in flowing 10% O$_2$/He (30 mL/min) after being dehydrated at 400 °C for 1 h in the flowing O$_2$/He to desorb the adsorbed moisture.

UV−Vis Diffuse Reflectance Spectroscopy. The in situ UV−vis DRS spectra were obtained with a Varian Cary 5E UV−vis spectrophotometer employing the integration sphere diffuse reflectance attachment. The finely ground powder samples of the bulk vanadate reference samples and the supported vanadia catalysts were loaded into an in situ cell (Harrick, HVC-DR2) and measured in the region of 200−800 nm at room temperature. A MgO reflectance standard was used as the baseline. The UV−vis DRS spectra of the bulk vanadate reference compounds were obtained under ambient conditions, and the spectra of the dehydrated supported vanadia catalysts were obtained after the samples were treated at 400 °C in flowing 10% O$_2$/He gas (30 mL/min) for 1 h to desorb the adsorbed ambient moisture. To minimize the effects of regular reflection and particle size, the samples were diluted with MgO. The amount of diluent used for a sample depended on the absorbance of the sample, which should result in the Kubelka−Munk function $F(R_a) < 1$ after dilution. The Kubelka−Munk function $F(R_a)$ was extracted from the UV−vis DRS absorbance and the edge energy ($E_g$) for allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of the plot of $[F(R_a)hv]^2$ against $hv$, where $hv$ is the incident photon energy.\textsuperscript{21}

Propane ODH over Supported Vanadia Catalysts. Propane oxidative dehydrogenation was carried out in an isothermal fixed-bed differential reactor (Pyrex tubing, 1/4 in. outside diameter and 1 ft long) using 20−100 mg of catalyst at atmospheric pressure. The reactant gas mixtures consisted of 18% C$_3$H$_8$/6% O$_2$/He (total 100 mL/min). The reactor effluent was analyzed by an on-line gas chromatograph (Hewlett-Packard 6890 Series) equipped with both a thermal conductivity detector (Carboxene-1000 packed column) and a flame ionization detector (Supelco capillary column (PQ1334-04)). The samples were pretreated in flowing O$_2$/He at 450 °C for 0.5 h before each run. The catalytic activity values, as measured by turnover frequency (the number of propane molecules converted per V atom per second), were obtained at the reaction temperature of 300 °C. The propane conversions were kept below 3% to avoid secondary reactions and to minimize heat and mass transfer limitations.

3. Results

Raman Spectroscopy. It is critical to confirm the absence of V$_2$O$_5$ NPs in the supported vanadia catalysts since their presence can affect the quantitative UV−vis DRS measurements of the surface vanadia species. The UV−vis DRS transitions are generally quite broad, and the presence of V$_2$O$_5$ NPs, which have a low $E_g$ value of 2.3 eV resulting from the five bridging $V−O−V$ bonds in the structure, will shift the broad band toward
the lower energy region and skew the quantitative results. Raman spectra, however, tend to give rise to sharp bands that allow discrimination between the different molecular structures. This is especially true for the detection of V₂O₅ NPs since their characteristic Raman bands, when excited in the visible range (514.5–532 nm), are typically about 10 times stronger than the two-dimensional surface vanadia species on oxide supports. ³⁴ Thus, the quantitative determination of the two-dimensional isolated and polymeric surface vanadia species by UV–vis DRS requires that three-dimensional vanadia structures, crystalline V₂O₅ NPs and mixed metal vanadate NPs containing multiple bridging V–O–V bonds, not be present in the current samples being employed for quantification. In addition, the Raman spectrum also contains complementary information about the dehydration extent of the catalysts and the nature of isolated and polymeric surface vanadia species since the bridging V–O–V bond vibrational modes are Raman active.

The Raman spectra of the dehydrated supported V₂O₅/SiO₂ catalysts are presented in Figure 1 as a function of vanadia loading (0.2–2.6 V/nm²). The SiO₂ support gives rise to Raman bands at 976, 802, 607, and 487 cm⁻¹ originating from Si–OH vibrations (976 cm⁻¹) and three to five Si-containing siloxane rings (802, 607, and 487 cm⁻¹). The addition of vanadia to SiO₂ results in the consumption of the surface Si–OH sites, as reflected in the decrease of the 976 cm⁻¹ band, and the preferential anchoring of the surface VO₄ units on the three-member siloxane rings, revealed by the selective decrease of the 607 cm⁻¹ band. The addition of vanadia to SiO₂ also produces several new Raman bands at 1070, 1035, 920, 465, and 337 cm⁻¹. The broad Raman bands at ~1070 and ~920 cm⁻¹ have previously been assigned to Si–O bonds created by the breaking of Si–O–Si siloxane bonds during the anchoring of surface vanadia onto the silica support. ¹⁹ The broad ~920 cm⁻¹ band is also observed on other supported vanadia catalysts and may possibly originate from the vibration of the bridging V–O–Si siloxane bond. ¹⁵ The sharp Raman band present at ~1035 cm⁻¹ is associated with the fully dehydrated terminal monoxo V=O bond of surface VO₄ species bonded to the SiO₂ surface (O=V(–O–Si)), and essentially remains at the same position and increases in intensity with increasing surface vanadia coverage. ⁴,³⁴,¹²,¹⁶,¹⁹,²⁰ The Raman bands at 337 and 465 cm⁻¹ originate from the ν₁ and ν₃g bending modes of the surface VO₄ species, respectively. Furthermore, the surface VO₄ species appear to be isolated since no Raman bands from bridging V–O–V bonds are detectable (see UV–vis section below for additional details). Above 12% V₂O₅/SiO₂, crystalline V₂O₅ NPs are also present on the silica support with a distinct and sharp Raman band at 994 cm⁻¹ (not shown for brevity). Thus, the maximum dispersion of vanadia on this SiO₂ support as a surface VO₄ species corresponds to ~12% V₂O₅/SiO₂ (~2.6 V/nm²) with the employed synthesis method. The low surface V₂O₅ density achievable on SiO₂ is well documented in the literature and is related to the low reactivity of the surface Si–OH groups relative to other oxide supports. ⁴,³⁴,¹²,¹⁴,¹⁶,¹⁸,²⁰,²²,³⁴

The Raman spectra of the dehydrated supported V₂O₅/Al₂O₃ catalysts shown in Figure 2 as a function of vanadia loading (0.3–8.1 V/nm²). This high surface area transitional alumina support does not give rise to any Raman active bands, and consequently all the observed Raman bands originate from the supported vanadia phase. Further increase in vanadia content results in strong Raman bands due to the presence of crystalline V₂O₅ NPs (not shown for brevity), which indicates that monolayer surface vanadia coverage on this Al₂O₃ support corresponds to ~20% V₂O₅/Al₂O₃ (8.1 V/nm²). As the surface vanadia coverage increases in the submonolayer region, the strong Raman band above 1000 cm⁻¹ broadens and shifts from 1018 to 1035 cm⁻¹ and new broad bands appear at ~930, ~750, ~550, ~450, and ~350 cm⁻¹. The Raman bands at 1018–1035 cm⁻¹ originate from the symmetric vibration of the fully dehydrated terminal monoxo V=O bond of the surface V₂O₅ species. ³⁴,¹⁴,¹⁷,²⁰,²⁷,³¹ The Raman bands at ~550 and ~750 cm⁻¹ have previously been assigned to the ν₁ and ν₃g vibrational modes, respectively, of the bridging V–O–V bonds of the polymeric surface VO₄ species. The Raman bands at ~350 and 450 cm⁻¹ originate from the ν₁ and ν₃g bending modes of the surface VO₄ unit, respectively. The broad band at ~930 cm⁻¹ has recently been assigned to the bridging V–O–alumina based on density functional theoretical (DFT) calculations. ¹⁶ The Raman spectra nicely reveal that crystalline V₂O₅ NPs are completely absent for these supported V₂O₅/Al₂O₃ catalysts below monolayer surface vanadia coverage and that the surface VO₄ species become polymerized with increasing surface vanadia coverage on the alumina support as demonstrated by the presence of bridging V–O–V vibrations.

The Raman spectra of the dehydrated supported V₂O₅/ZrO₂ catalysts are presented in Figure 3 as a function of vanadia loading (2.0–8.1 V/nm²). The ZrO₂ support gives rise to the strong Raman bands at 630, 610, 552, 528, 480, 375, and 330 cm⁻¹ that are associated with the ZrO₂ monoclinic phase. Unfortunately, these strong Raman bands from the ZrO₂ support prevent the collection of the vibrational modes of the surface vanadia species below 700 cm⁻¹. The addition of vanadia to the ZrO₂ support results in a new Raman band above 1000 cm⁻¹ that shifts from 1027 to 1036 cm⁻¹ with increasing surface...
vanadia density. This vibration is characteristic of the fully dehydrated terminal monoxo V=O bond of the surface VO₄ species.⁶,²⁰,²²,³⁰–³² Broad Raman bands are also observed at ~800 and 930 cm⁻¹ associated with the ν₂ vibration of bridging V−O−V bonds¹−³ and bridging V−O−zirconia bonds,¹⁶ respectively. Crystalline V₂O₅ NPs are not present in any of the submonolayer (<8.1 V/nm²) samples and only become significant above monolayer surface coverage (not shown for brevity). Thus, crystalline V₂O₅ NPs are not present in these catalysts and only surface monomeric and polymeric surface VO₄ species are present in the 1−4% V₂O₅/ZrO₂ supported catalysts, with the latter increasing in concentration with increasing surface vanadia coverage.

In summary, the Raman spectra revealed that for the supported vanadia catalysts and experimental conditions employed in the present investigation (1) crystalline V₂O₅ NPs are not present below monolayer surface coverage, (2) only two-dimensional surface vanadia species are present below monolayer surface coverage, (3) isolated surface vanadia species are present at low surface coverage on the different oxide supports, (4) polymeric surface vanadia species are present at high surface coverage on Al₂O₃ and ZrO₂ supports, and (5) fully dehydrated surface vanadia species are obtained with the current dehydration pretreatments.

UV−vis Diffuse Reflectance Spectroscopy. It has been previously demonstrated that a linear relationship exists between the UV−vis DRS edge energy, Eₐ (eV), and the number of bridging V−O−V bonds present in bulk vanadate structures.²¹ This general relationship has also been found to be independent of the local coordination for VO₄,²¹ MoO₄,³⁵ and WO₄³⁶ reference compounds and only dependent on the number of bridging M−O−M bonds present in the structures. The number of bridging V−O−V bonds for VO₄ coordinated vanadate materials varies from zero for isolated species to two for polymeric VO₄ chain species. The bulk orthovanadate Na₃VO₄ and metavandate NaVO₃ compounds contain isolated VO₄ units and polymeric VO₄ chains,²⁷,³⁸ respectively, that are analogous to the dehydrated surface VO₄ species present in supported vanadia catalysts. Thus it is possible to develop a quantitative relationship between the UV−vis edge energy and the number of bridging V−O−V bonds present in physical mixtures of bulk vanadates and to apply this relationship to the dehydrated surface VO₄ species. This assumption that the polymeric surface VO₄ species can be represented by polymeric VO₄ metavandate species. The UV−vis DRS spectra of bulk Na₃VO₄ (consisting of isolated VO₄ units) and bulk NaVO₃ (consisting of polymeric VO₄ chains) are shown in Figure 4. The Eₐ values for the bulk

\[ E_a = 3.02 + 0.53X_m \]  

where \( X_m \) refers to the fraction of monomer in the sample.

The UV−vis DRS Eₐ values of the dehydrated supported V₂O₅/SiO₂, V₂O₅/Al₂O₃, and V₂O₅/ZrO₂ catalysts are tabulated in Table 1. Note that the Eₐ values for the dehydrated supported vanadia catalysts exactly span the same edge energy range (3.01−3.63 eV) shown above for the bulk vanadate VO₄-containing compounds (3.02−3.55 eV). The coincidence of the bulk and dehydrated supported vanadia catalysts strongly supports the conclusion in the literature that dehydrated surface vanadia species possess VO₄ coordination. Polymeric VO₄/VO₄ structures can possess more than two bridging V−O−V bonds and give rise to much lower Eₐ values (2.3−2.8 eV).²¹ Hydration of the 20% V₂O₅/Al₂O₃ samples transforms the dehydrated surface VO₄ polymers to VO₆ coordinated V₁₀O₂₈·nH₂O clusters¹²,²¹ containing five bridging V−O−V bonds and decreases the Eₐ value to 2.65 eV. The hydration results further confirm...
the absence of any significant concentration of surface VO₆ coordinated species for the dehydrated supported vanadia catalysts. The fractions of dehydrated polymeric surface VO₄ species present on the SiO₂, Al₂O₃, and ZrO₂ supports as a function of surface vanadia coverage were determined from the reference relationship established for the bulk vanadate compounds in Figure 5 and are presented in Table 1 and also plotted in Figure 6. The small amount of polymeric surface VO₄ species estimated on SiO₂ at intermediate coverage is within the UV-vis DRS experimental error. The general trend is that dehydrated isolated surface VO₄ species predominate at low surface coverage and the fraction of dehydrated polymeric surface VO₄ species increases with increasing surface coverage up to monolayer with the extent of polymerization following the trend Al₂O₃ > ZrO₂ ≈ SiO₂ for the same surface vanadia density.

The analogous UV-vis DRS spectra for the dehydrated as well as hydrated supported vanadia catalysts have previously been reported. The only several representative UV-vis DRS spectra containing ~100% monomer (1% V₂O₅/SiO₂), about 50% polymer/50% monomer (10% V₂O₅/Al₂O₃), and ~100% polymer (20% V₂O₅/Al₂O₃) are presented in Figure 7 to show how the Kubelka-Munk function was utilized to determine the E₉ values. The UV-vis DRS measurements were limited to these three oxide supports because of their weak absorption in the UV-vis region (200–800 nm range). Oxide supports possessing strong UV-vis DRS absorption (e.g., TiO₂, Nb₂O₅, CeO₂), unfortunately, overshadow the UV-vis DRS spectra of the surface vanadia species and prevent accurate determination of the E₉ values for the surface vanadia species on these supports.

In summary, the UV-vis spectra of dehydrated supported vanadia catalysts revealed that (1) the surface vanadia species can be accounted for by assuming only the presence of monomeric and polymeric dehydrated surface VO₄ species (as long as crystalline V₂O₅ nanoparticles are not present to skew the measurement to lower E₉ values), (2) isolated surface VO₄ species predominate at low surface vanadia coverage, (3) both isolated and polymerized surface VO₄ species are present at intermediate surface coverage (with the exception of SiO₂ where isolated surface VO₄ species are almost exclusively present), and (4) polymeric surface VO₄ species predominate at high surface coverage (with the exception of SiO₂).

Propane ODH over Supported Vanadia Catalysts. The oxidative dehydrogenation of propane to propylene was also investigated over the supported vanadia catalysts to determine the relative contribution of isolated and polymeric surface VO₄ species for this catalytic reaction. The surface VO₄ species remain both dehydrated and almost fully oxidized under the chosen propane ODH reaction conditions due to the high reaction temperatures (350–450 °C) and the low reactivity of propane coupled with the relatively rapid reoxidation of the reduced sites. Consequently, essentially the same surface vanadia species are present under typical propane ODH reaction conditions as shown above for the dehydrated surface VO₄ species on the different supports. The influence of surface vanadia coverage on the TOF and selectivity values for propane ODH to propylene is given in Table 2 for the different supported vanadia catalysts. The propylene selectivity for supported V₂O₅/Al₂O₃ and V₂O₅/ZrO₂ catalysts systematically increases and the corresponding CO₂ selectivity slightly decreases with increasing surface vanadia coverage. These slight selectivity trends reflect the covering of the unselective exposed support sites by the surface vanadia species.

Figure 6. Fraction of surface V Coverage (%/nm²) for dehydrated supported vanadia catalysts as a function of surface vanadia coverage.

Figure 7. UV-vis DRS spectra and E₉ values of dehydrated 20% V₂O₅/Al₂O₃, 1% V₂O₅/SiO₂, and 10% V₂O₅/Al₂O₃ catalysts.

The number of surface VO₄ sites involved in the rate-determining step of propane ODH to propylene can also be determined from the simplified rate equation

\[
r (\text{mol/g-s}) = k' P_{C_3} V^n
\]

\[
k' = k_{RDS} K_{ADS}
\]

where \( V \) represents the number of vanadia atoms per gram of catalyst, \( k_{RDS} \) is the kinetic rate constant of the rate-determining step (rds), \( K_{ADS} \) is the propane equilibrium adsorption constant,
TABLE 2: TOF and Selectivity of Propane ODH to Propylene over Supported Vanadia Catalysts (350 °C, 18% C₃H₆/6% O₂/He, and Total Flow Rate of 100 mL/min)

<table>
<thead>
<tr>
<th>catalyst</th>
<th>surface coverage (V/nm²)</th>
<th>( A_\text{v} ) (mmol/g·h)</th>
<th>TOF ( (10^{-4} \text{ s}^{-1}) )</th>
<th>( \text{C}_3\text{H}_6 )</th>
<th>CO</th>
<th>( \text{CO}_2 )</th>
<th>oxygenates</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% ( \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 )</td>
<td>1.0</td>
<td>15.5</td>
<td>13</td>
<td>67.0</td>
<td>11.5</td>
<td>21.5</td>
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<tr>
<td>5% ( \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 )</td>
<td>1.7</td>
<td>23.7</td>
<td>12</td>
<td>69.3</td>
<td>10.2</td>
<td>20.5</td>
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</tr>
<tr>
<td>10% ( \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 )</td>
<td>3.6</td>
<td>51.4</td>
<td>13</td>
<td>75.6</td>
<td>8.8</td>
<td>15.6</td>
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</tr>
<tr>
<td>15% ( \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 )</td>
<td>5.8</td>
<td>59.3</td>
<td>10</td>
<td>80.8</td>
<td>10.9</td>
<td>7.2</td>
<td>1.1</td>
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<tr>
<td>20% ( \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 )</td>
<td>8.1</td>
<td>110.8</td>
<td>14</td>
<td>80.2</td>
<td>9.1</td>
<td>10.7</td>
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<tr>
<td>5% ( \text{V}_2\text{O}_5/\text{SiO}_2 )</td>
<td>1.5</td>
<td>8.7</td>
<td>2.8</td>
<td>67.4</td>
<td>22.1</td>
<td>10.5</td>
<td></td>
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<tr>
<td>10% ( \text{V}_2\text{O}_5/\text{SiO}_2 )</td>
<td>1.9</td>
<td>11.3</td>
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<td>64.0</td>
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<tr>
<td>12% ( \text{V}_2\text{O}_5/\text{SiO}_2 )</td>
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<td>13.3</td>
<td>2.8</td>
<td>62.2</td>
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<td>2.0</td>
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<tr>
<td>1% ( \text{V}_2\text{O}_5/\text{ZrO}_2 )</td>
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<td>98</td>
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<td>19.0</td>
<td>30.0</td>
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<tr>
<td>2% ( \text{V}_2\text{O}_5/\text{ZrO}_2 )</td>
<td>4.0</td>
<td>80.7</td>
<td>102</td>
<td>57.2</td>
<td>22.9</td>
<td>19.9</td>
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<tr>
<td>4% ( \text{V}_2\text{O}_5/\text{ZrO}_2 )</td>
<td>8.1</td>
<td>145</td>
<td>92</td>
<td>58.5</td>
<td>18.0</td>
<td>23.5</td>
<td></td>
</tr>
</tbody>
</table>

\( P_{C_3} \) is the partial pressure of propane (moles per liter), and \( n \) represents the number of surface \( \text{VO}_4 \) species or catalytic active sites involved in the propane ODH rate-determining step (breaking of the C–H bond of the middle carbon in the propane molecule). The zero-order dependence on the \( O_2 \) partial pressure and the first-order dependence on the propane partial pressure further reflect the almost fully oxidized state of the surface vanadia sites and the low surface coverage of reaction intermediates under the chosen reaction conditions, respectively. The value of \( n \) can be determined directly from the slope of the plot of \( \log r \) vs \( \log V \) as the surface vanadia coverage is varied in the submonolayer region, where the vanadia is 100% dispersed as surface vanadia species, at constant temperature and \( C_3 \) partial pressure. Such propane ODH kinetic plots are shown in Figure 9 for the different catalytic systems, which indicates that only one surface \( \text{VO}_4 \) site is involved in the rds for propane ODH to propylene.

4. Discussion

For dehydrated supported \( \text{V}_2\text{O}_5/\text{SiO}_2 \), the Raman band is constant at \( \sim 1035 \text{ cm}^{-1} \) at all surface vanadia coverage. For dehydrated supported \( \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 \) and \( \text{V}_2\text{O}_5/\text{ZrO}_2 \), the \( \text{V}═\text{O} \) vibration shifts with increasing surface vanadia coverage from 1018 to 1035 cm\(^{-1}\) and from 1027 to 1036 cm\(^{-1}\), respectively. The corresponding UV-vis DRS measurements reveal that this shift to higher wavenumbers in the terminal \( \text{V}═\text{O} \) vibration parallels the extent of surface polymerization of the surface \( \text{VO}_4 \) on the \( \text{Al}_2\text{O}_3 \) and \( \text{ZrO}_2 \) supports. It appears that the dehydrated surface \( \text{VO}_4 \) species become more distorted, reflected in shorter \( \text{V}═\text{O} \) bond lengths and higher wavenumber values, as the surface vanadia transforms from isolated to polymeric species. Recently it has been proposed that the Raman vibration for the terminal \( \text{V}═\text{O} \) bond of the surface \( \text{VO}_4 \) on \( \text{SiO}_2 \) is vibrationally coupled to the silica support phonons at this frequency. This may explain why the isolated surface \( \text{VO}_4 \) species vibrates at \( \sim 1035 \text{ cm}^{-1} \) when the same species on \( \text{Al}_2\text{O}_3 \) and \( \text{ZrO}_2 \) vibrate at \( 1018\text{–}1027 \text{ cm}^{-1} \); however, additional studies are required to fully understand such a vibrational coupling phenomenon.

The combined in situ Raman and UV-vis DRS studies on the same dehydrated supported vanadia catalysts also provide new insight into the nature of the \( \sim 900 \text{ cm}^{-1} \) Raman band typically observed for dehydrated supported metal oxide catalysts. For the supported \( \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 \) catalytic system at low surface vanadia coverage (see Figure 2 and Table 1), UV-vis DRS reveals that only isolated surface \( \text{VO}_4 \) species are present at 0.3 V nm\(^{-2}\) coverage and demonstrates that the corresponding broad Raman band in the \( \sim 900 \text{ cm}^{-1} \) region cannot originate from bridging \( \text{V}═\text{O}─\text{V} \) vibrations. For the supported \( \text{V}_2\text{O}_5/\text{SiO}_2 \) catalytic system (see Figure 1 and Table 1), Raman shows a band at \( \sim 920 \text{ cm}^{-1} \); however, UV-vis DRS only shows the presence of isolated surface \( \text{VO}_4 \) species, which supports the conclusion that this vibration does not originate from bridging \( \text{V}═\text{O}─\text{V} \) vibrations. The same conclusion cannot be extended for the current supported \( \text{V}_2\text{O}_5/\text{ZrO}_2 \) catalytic system (see Figure 3 and Table 1) since polymeric surface vanadia species are present at all surface vanadia coverages in the samples examined, but the 930 cm\(^{-1}\) band is also clearly present at high surface coverage. The current experimental observations are in agreement with the recent theoretical DFT calculations of Magg et al. that this vibration is not consistent with bridging \( \text{V}═\text{O}─\text{V} \) bonds, but originates from bridging \( \text{V}═\text{O} \) species on the silica support. The corresponding broad Raman band in the \( \sim 900 \text{ cm}^{-1} \) region is also clearly present at high surface coverage. The current experimental observations are in agreement with the recent theoretical DFT calculations of Magg et al. that this vibration is not consistent with bridging \( \text{V}═\text{O}─\text{V} \) bonds, but originates from bridging \( \text{V}═\text{O} \) species on the silica support.
Surface VO₄ Species and Their Catalytic Activity

from the bridging V=O—support bonds. Thus, Raman and IR bands typically observed at ~900 cm⁻¹ for dehydrated supported surface metal oxide species originate from the presence of bridging M=O—support bonds that anchor the surface metal oxide species to the underlying oxide support.

Although the Raman spectra of vanadia supported on other oxides are not reported here, the Raman spectra of all dehydrated supported vanadia catalysts exhibit a systematic increase in the wavenumber position of the terminal V=O bond of the surface VO₄ species with increasing surface vanadia coverage. These Raman vibrational shifts are apparently also related to the increasing extent of polymerization of the surface VO₄ species with increasing surface vanadia coverage on these oxide supports. The same Raman vibrational shifts with increasing surface metal oxide coverage are also observed for most supported metal oxide catalyst systems (e.g., MoO₃, WO₃, CrO₃, Nb₂O₅, Ta₂O₅), suggesting that such Raman shifts are also related to polymerization of the dehydrated surface MO₄ species with increasing surface metal oxide coverage.

The UV—vis DRS Eg values for the dehydrated V₂O₅/SiO₂ catalysts are almost independent of surface vanadia coverage and exhibit values of 3.52—3.55 eV, which indicates that these samples exclusively contain isolated surface VO₄ species, confirming what is already known from other characterization studies. For the dehydrated supported V₂O₅/Al₂O₃ catalysts, the Eg value continuously decreases with increasing surface vanadia coverage from 3.63 to 3.01 eV. The high Eg value at low surface vanadia coverage corresponds to 100% isolated surface VO₄ species and the lower Eg value at monolayer coverage corresponds to 100% polymeric surface VO₄ species, which is in agreement with the Eg values of the isolated VO₄ units present in bulk Na₃VO₄ (3.55 eV) and the polymeric VO₄ units present in bulk NaVO₃ (3.02 eV), respectively. The agreement in the Eg values between these bulk reference compounds and the dehydrated supported vanadia catalysts, as well as the absence of observed Eg values in the 2.3—2.8 eV range, further confirms that other surface vanadia species with greater than two bridging V=O—V bonds are either not present or are only present in a trace quantity. The continuous decrease in Eg values with increasing surface vanadia coverage on alumina reflects the increasing polymerization of the dehydrated surface VO₄ species as a function of surface coverage. The same trend is observed for supported V₂O₅/ZrO₂ catalysts where the Eg value decreases from 3.50 eV at low surface coverage to 3.12 eV at monolayer coverage. The Eg values for the dehydrated supported V₂O₅/ZrO₂ indicate that isolated surface VO₄ species are the major species present at low surface vanadia coverage (~90% monomer) and become a minor species at monolayer coverage where the polymeric surface VO₄ species predominate (~80% polymer). With the exception of the supported V₂O₅/SiO₂ catalyst system, the dehydrated surface VO₄ species on oxide supports are essentially isolated monomers at low surface coverage (<2 V/nm²) that progressively polymerize with increasing surface vanadia coverage and become extensively polymeric species at monolayer surface vanadia coverage (~8 V/nm²). In addition, the specific oxide support cations also influence the extent of polymerization at a given surface coverage since at intermediate surface vanadia density the fraction of polymers on the supports is Al₂O₃ > ZrO₂ > SiO₂.

The TOF values for propane ODH to propylene for each supported vanadia catalyst system were found to be almost invariant with surface vanadia coverage (extent of polymerization of the surface VO₄ species). This demonstrates that isolated surface VO₄ species and polymeric VO₄ species exhibit comparable catalytic activity for propane ODH to propylene and that the presence of bridging V=O—V bonds in the polymeric surface vanadia species does not affect the steady-state catalytic activity (see Figure 8). Simultaneously, the Raman vibration of the terminal V=O bond shifts for V₂O₅/Al₂O₃ (1018—1035 cm⁻¹) and V₂O₅/ZrO₂ (1027—1036 cm⁻¹) with increasing surface vanadia coverage arising from distortions caused by polymerization of the surface vanadia species. The invariance of the propane ODH reaction TOF value with these structural changes also suggests that the terminal V=O bond in the surface VO₄ species is not involved in the rate-determining step of the catalytic activation of the C—H bond of propane. This finding is consistent with the one VO₄ site requirement for the propane ODH reaction kinetics and suggests that an isolated surface VO₄ species catalytically functions similarly as an individual VO₄ unit that is part of a polymeric surface VO₄ chain structure. The propane ODH to propylene reaction is a two-electron process involving one O atom, reduction of V₅⁺ to V³⁺, which only requires one VO₄ unit. In summary, both isolated monomeric and polymeric surface VO₄ species catalytically function similarly during propane ODH and exhibit comparable TOF values on the same oxide support.

The constant propane ODH TOF values with surface vanadia coverage are somewhat surprising since many changes in the characteristics of the supported vanadia catalysts are simultaneously taking place with increasing surface coverage. As already discussed above, isolated surface vanadia species become progressively polymerized with increasing surface vanadia coverage. For the supported V₂O₅/Al₂O₃ catalyst system, both the surface Brønsted acidity and reducibility of the surface vanadia species are dependent on the surface vanadia coverage. Surface Brønsted acid sites begin to appear above ~2 V/nm², and their surface density rapidly increases with increasing surface coverage up to monolayer coverage. Similarly, the reduction temperature for the surface vanadia species dramatically decreases, reflecting ease of reduction, above ~2 V/nm² with increasing surface vanadia coverage. Although the polymerization of the surface VO₄ species significantly impacts both the surface Brønsted acidity and the reducibility of the surface vanadia species, it does not affect the propane ODH TOF value. Thus, the propane ODH reaction does not appear to be sensitive to either surface vanadia acidity or the surface vanadia redox properties.

The influence of the specific oxide support on the propane ODH TOF value of the surface VO₄ species is dramatic, as shown earlier in Table 2 and Figures 8 and 9. At low surface vanadia coverage, isolated surface VO₄ species are almost exclusively present for the supported 10% V₂O₅/SiO₂ (1.9 V/nm²), 3% V₂O₅/Al₂O₃ (1.0 V/nm²), and 1% V₂O₅/ZrO₂ (2.0 V/nm²) catalysts. However, the corresponding TOF values for these catalysts vary by more than an order of magnitude with the specific oxide support: ZrO₂ > Al₂O₃ > SiO₂. This trend demonstrates that the specific catalytic activity of the isolated VO₄ species on the different oxide supports does not originate from a structural effect, monomer vs polymer, but arises from a ligand effect of the different support cations. At monolayer surface coverage (~8 V/nm²), polymeric surface VO₄ units are the dominant surface vanadia species for V₂O₅/Al₂O₃ and V₂O₅/ZrO₂ and the propane TOF varies by a factor of ~5 for these two supported vanadia catalysts. The significant variation of the propane ODH TOF values for both isolated and polymerized surface VO₄ species with different supports demonstrates that the oxygen in the bridging V=O—support bond is the catalytic
active site involved in the kinetic rate determining step for propane activation over supported vanadia catalysts. Thus, the specific oxide support cation acts as a ligand that controls the catalytic activity of the bridging V=O–support bond for both isolated and polymerized surface VO₄ species.

The influence of the bridging V=O–support bond was also previously demonstrated by anchoring isolated surface VO₄ species on surface TiO₂, ZrO₂, and Al₂O₃ monolayers on a SiO₂ support to form bilayered supported vanadia catalysts, where the underlying support cation was found to influence the TOF for methanol oxidation to HCHO by more than a factor of ~10⁶⁻⁴⁴. This support effect was shown to be related to the electronegativity of the support cation in the bridging V=O–support bond. Decreasing the electronegativity of the support cation increases the basicity or electron density of the catalytic support bond. Decreasing the electronegativity of the support bond was also expected to take place on other oxide supports (e.g., TiO₂, Al₂O₃, Nb₂O₅, CeO₂).

For all supported metal oxide catalytic systems, the $E_g$ values decrease with increasing surface MO₂ coverage due to the increasing MO₂ domain size (e.g., isolated surface MO₂ species → polymeric surface MO₂ → crystalline MO₂ NPs) since the number of bridging M–O–M bonds generally increases with increasing domain size. The current propane ODH catalytic data show that, as the surface metal oxide domain size increases from isolated to polymeric species, the redox TOF values are essentially constant and independent of the decreasing $E_g$ values. Consequently, the simultaneous increase in redox TOF values with decreasing $E_g$ values sometimes reported for some catalytic systems may just be coincidental and related to other catalyst parameters being varied rather than related to the surface metal oxide domain size.

5. Conclusions

A quantitative method was developed to determine the surface concentrations of dehydrated monomeric and polymeric surface VO₄ species on SiO₂, Al₂O₃, and ZrO₂ supports. Supported V₂O₅/SiO₂ exclusively possesses isolated surface VO₄ species up to the maximum dispersion of the surface vanadia species (~2.6 V nm⁻²). For supported V₂O₅/Al₂O₃ and V₂O₅/ZrO₂ catalysts, isolated surface VO₄ species are only present at low surface vanadia coverage and the extent of polymerization significantly increases with surface vanadia density up to monolayer surface coverage (~8 V nm⁻²). This surface VO₄ polymerization trend as a function of surface vanadia coverage is also expected to take place on other oxide supports (e.g., TiO₂, Nb₂O₅, CeO₂).

The catalytic TOF for propane ODH to propylene, which only requires one surface VO₄ unit, is independent of the extent of polymerization of the surface VO₄ species, the $E_g$ value, the surface Bronsted acidity, and the reducibility of the surface vanadia species, and is only a function of the specific oxide support. The oxide support cation acts as a potent ligand for the reactivity of surface VO₄ species by affecting the electron density or basicity of the bridging V–O–support bond, the catalytic active site involved in the kinetic rate determining step. The reactivity of the bridging V–O–support bonds is related to the support cation electronegativity, with low electronegativity increasing the basicity or electron density of the bridging V–O–support bond.

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References and Notes

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