

From Surface-Inspired Oxovanadium Silsesquioxane Models to Active Catalysts for the Oxidation of Alcohols with O₂—The Cinnamic Acid/Metavanadate System

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Abstract: Silsesquioxane dioxovanadate(V) complexes were investigated with respect to their potential as a catalyst for the oxidative dehydrogenation of alcohols with O₂ as an oxidant. The turnover frequencies determined were comparatively low, but during the oxidation of cinnamic alcohol an increase in activity was observed in the course of the process, which was inspected more closely. It turned out that during the oxidation of cinnamic alcohol, not only was the aldehyde formed but also cinnamic acid, which in turn reacts with the silsesquioxane complex em-

ployed to give NBu₄[O₂V(O₂CC₂H₂Ph)₂], which can also be obtained from NBu₄VO₃ and cinnamic acid and represents a far more active catalyst, not only for cinnamic alcohol but also for other activated alcohols and hydrocarbons. The rate-determining step of the conversion corresponds to an hydrogen-atom abstraction from the C–H units, as shown by the deter-

mination of the kinetic isotope effect in case of 9-hydroxyfluorene, and the reoxidation of the reduced catalyst proceeds via a peroxy intermediate, which is also capable of oxidizing one alcohol equivalent. Furthermore the influence of the organic residues at the carboxylate ligands on the catalyst performance was investigated, which showed that the activity increases with decreasing p*K*_s value. Moreover, it was found that during the oxidation the catalyst slowly decomposes, but can be regenerated by addition of excessive carboxylic acid.

Keywords: alcohols • homogeneous catalysis • oxidation • silsesquioxane • vanadium

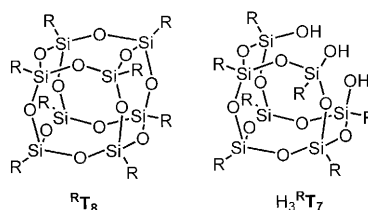
Introduction

The oxidative dehydrogenation (ODH) of light alkanes and methanol is currently a matter of intense research, especially as the resulting products—alkenes and formaldehyde—are important bulk chemicals in industry, and supported vanadium oxides have proved to be among the best catalysts for these processes.^[1] The nature of the active sites and units on the surfaces of these catalysts are still discussed controversially,^[2] though, and many different approaches have been pursued to reveal new insights. Naturally, the results of corresponding studies can also provide a stimulus for the synthesis of molecular model compounds.^[3,4] These can then be investigated in the homogeneous phase and may serve to support or disprove proposals made concerning the struc-

ture, function, or the spectroscopic signatures of corresponding surface species. The construction of molecular models for metal–oxo surface sites requires ligands that are capable of mimicking the environments that metaloxo moieties experience on oxidic support or bulk materials, and for the modeling of silica supports in particular silsesquioxane-based ligands have established themselves.^[5,6] Silsesquioxanes in general exhibit one-dimensionally extended or cage structures that are saturated by organic residues. Some of these, for example, the structure of the octamer ^RT₈, resembles skeletal frameworks found in crystalline forms of silica, and silsesquioxanes in general are therefore discussed as molecular sections of silica. If formally one of the R–Si³⁺ corners is removed from the ^RT₈ cage, protonation of the re-

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201000171>.

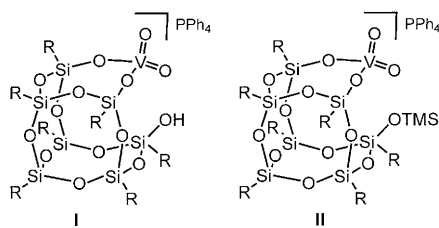


sulting siloxide units yields in compound $H_3^R T_7$, which possesses both structural and electronic similarities to hydroxylated silica surface sites.^[7]

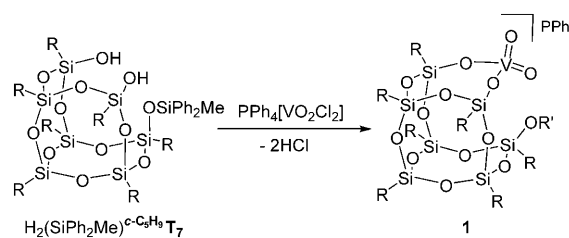
Correspondingly, with such compounds, for instance, processes occurring during the grafting of molecular precursors on silica surfaces can be investigated on the molecular level.^[7e,8,9] If on the other hand the protons of $H_3^R T_7$ are replaced by transition-metal cations, the resulting complexes simulate situations in which such cations are bound to silica supports, but have the advantage of being treatable with the methods of molecular chemistry.^[5-7] A second ligand system that is often employed for the more general modeling of an oxidic coordination platform are calixarenes,^[10] and in the context of the above-mentioned supported oxovanadium catalysts employed for ODH processes, we have recently reported the results of structure–function analyses performed for calixarene-based model compounds with respect to the ODH of alcohols.^[3,11] Furthermore we have utilized oxovanadium silsesquioxane complexes as spectroscopic models.^[9] In the next step those were to be tested as functional models, especially, since—due to the more exact mimicking of surface sites in comparison to the calixarene complexes—a higher reactivity was expected. Here we report the findings made in the course of corresponding ODH studies: Serendipitously they led to a more simple system, which proved to represent an efficient catalyst for the ODH of activated alcohols.

Results and Discussion

The investigation was started by testing the complexes **I** and **II**^[9] as potential catalysts for the ODH of alcohols. Moreover, we were interested to complement these complexes by



a derivative containing a larger siloxide dangling group in order to study the influence of its size on the reactivity of the metal site. Synthesis of the $OSiMePh_2$ analogue **1** (see Scheme 1) was achieved according to the route established for the synthesis of **I**, but reacting the corresponding ligand $H_2(Ph_2MeSi)^{c-C_6H_5} T_7$ with $[PPh_4][VO_2Cl_2]$. This led to the expected replacement of the two protons by the VO_2^+ group. Its two $V=O$ bond lengths and $O-V-O$ angles within **1** are almost identical to those observed for the other two compounds, as revealed by a single-crystal X-ray analysis (see Figure 1).



Scheme 1. Formation of **1** ($R = c-C_6H_5$, $R' = SiMePh_2$).

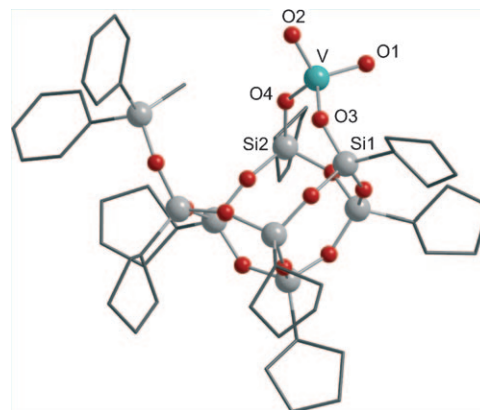


Figure 1. Molecular structure of the anion of **1**. Selected bond lengths [Å] and angles [°]: $V-O1$ 1.626(6), $V-O2$ 1.609(5), $V-O3$ 1.819(5), $V-O4$ 1.838(5), $Si1-O3$ 1.600(6), $Si2-O4$ 1.594(5); $O1-V-O2$ 108.0(3), $O1-V-O3$ 109.7(3), $O2-V-O4$ 110.3(3), $O3-V-O4$ 109.0(2).

As substrates we chose aliphatic alcohols, activated alcohols and activated hydrocarbons, which were dissolved in CH_3CN (2 mL) and heated to $80^\circ C$ in the presence of molecular sieves and catalytic amounts (1 mol %) of the complexes **I**, **II**, or **1**, respectively, in an O_2/Ar atmosphere. After 3 h the reaction mixtures were analyzed by 1H NMR spectroscopy, and the yields were determined by integration and comparison of specific signals originating from substrates and oxidation products. In case of a similar study performed for the above-mentioned calixarene models the highest activities had been observed for 9-hydroxyfluorene, cinnamic alcohol, and benzylic alcohol (in this order),^[3,11b] and for a given catalyst a correlation between the TOFs and the strengths of the alcoholic C–H bonds had become evident; hence, hydrogen-atom abstraction has been proposed as a rate-determining step, and this hypothesis has gained support from the isolation of a catalysis intermediate. In contrast, employing the silsesquioxane models **I**, **II**, and **1**, the highest activity was observed for cinnamic alcohol in case of all three complexes (see Figure 2), which seemed to point to a different type of mechanism.

However, the results proved difficult to reproduce (a further difference to the calixarene chemistry), so that the course of the product formation was inspected more closely for the case of cinnamic alcohol. This showed that the catalytic process required an induction period to develop its full activity: If a solution of cinnamic alcohol in acetonitrile is warmed to $80^\circ C$ in the presence of molecular sieves and

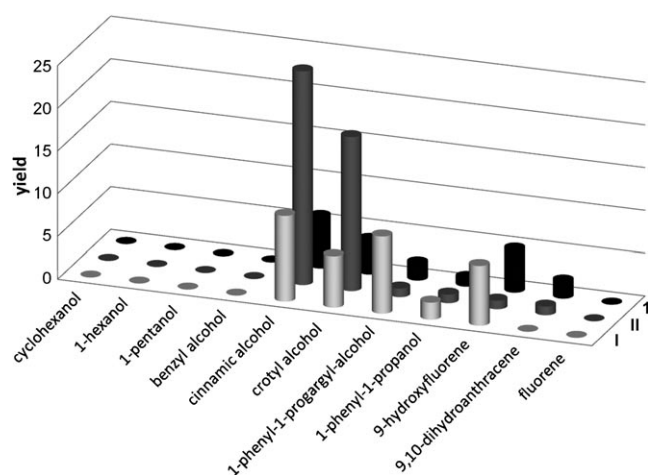


Figure 2. TOF data for the oxidation of alcohols with **I**, **II** and **I** as catalysts: Alcohol (1 mmol), catalyst (0.01 mmol) and molecular sieves (0.5 g, 3 Å) in CH₃CN (2 mL) were heated to 80 °C in an O₂/Ar atmosphere. After 3 h the reaction mixtures were analyzed by ¹H NMR spectroscopy.

1 mol% of **II** in an O₂/Ar atmosphere, the reaction proceeds sluggishly within the first 1.3 h. Only after the formation of about 10% of cinnamic aldehyde was a steeper increase of the product yield observed (see Figure 3).

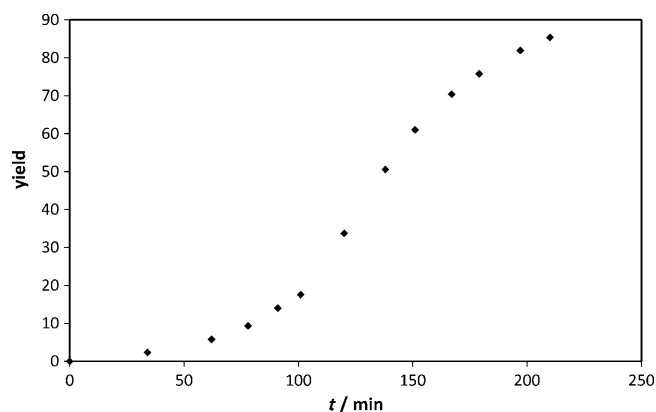


Figure 3. Yield versus time plot for the following reaction conditions: cinnamic alcohol (2 mmol), **II** (0.02 mmol) and molecular sieves (1 g, 3 Å) in CH₃CN (4 mL) were heated to 80 °C in an O₂/Ar atmosphere.

This indicated that **II** as such is only slightly active, but undergoes a transformation (which needs the aldehyde product) to a more efficient catalyst. When **I** or **I** were employed as catalysts the yield/time plots looked nearly identical, but **II** was more active, so that all further investigations were performed with **II**.

The active catalyst: When **II** was treated with cinnamic alcohol for 6 h under the conditions described above, but in the absence of O₂, no reaction took place, which showed that the alcohol itself does not play a role in the conversion of

II. However, the above-mentioned acceleration of catalysis after an approximate 10% oxidation of the alcohol to the aldehyde proved reproducible, and thus required an explanation. Cinnamic aldehyde is known to undergo autoxidation in air,^[12] which raised the idea that beyond a certain critical concentration of cinnamic aldehyde, such a process could be triggered leading to a fast conversion of the alcohol via radical chains. To test whether such autoxidation occurs under the conditions chosen here, experiments were performed in the presence of radical starters, which did not lead to any alterations. Furthermore it turned out that the presence of adequate amounts of the aldehyde right from the start (10 mol%) neither made the vanadium component redundant nor eliminated the induction period. We noted that part of the cinnamic aldehyde formed in the course of the oxidation of cinnamic alcohol was further oxidized to give cinnamic acid; hence the influence of this product on the catalytic performance was tested in the next step. Indeed, after the addition of 5 mol% cinnamic acid to the system with only 0.25 mol% **II** as catalyst no induction period was required anymore for an efficient catalysis (TOF = 250 h⁻¹, see Figure 4).

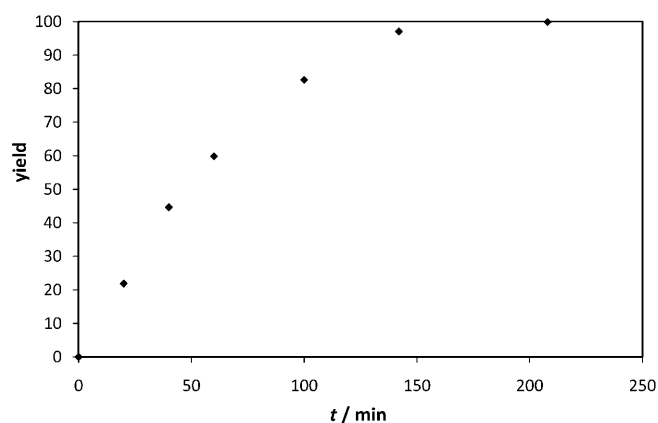
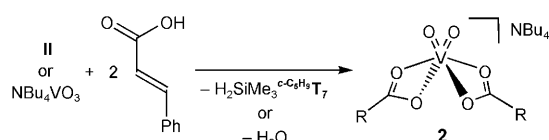


Figure 4. Yield versus time plot for the oxidation of cinnamic alcohol in the presence of cinnamic acid (5 mol%) and **II** (0.25 mol%) as the catalyst.

Hence, now the reaction of **II** with cinnamic acid was investigated. On treatment of a solution of **II** in [D₃]acetonitrile with ten equivalents of cinnamic acid, the signal initially observed for **II** at -587 ppm disappears in favor of a new signal at -513 ppm, which can also be observed if NBu₄VO₃ is reacted with cinnamic acid. Accordingly, the presence of cinnamic acid leads to the detachment of the silsesquioxane ligand from the VO₂⁺ unit (i.e., to leaching), and—bearing in mind that there are some examples of compounds containing VO₂⁺ units bound to two carboxylate functions as part of a chelating ligand known in the literature^[13]—the formation of NBu₄[O₂V(O₂CR)₂] (R = C₂H₅Ph) (**2**) seemed likely (Scheme 2), which would then correspond to the active catalyst.^[14]

This hypothesis was confirmed by isolation and characterization of this product from a corresponding conversion on

Scheme 2. Formation of **2** ($R = C_2H_5Ph$).

the synthetic scale. The result of a single-crystal X-ray analysis is shown in Figure 5.

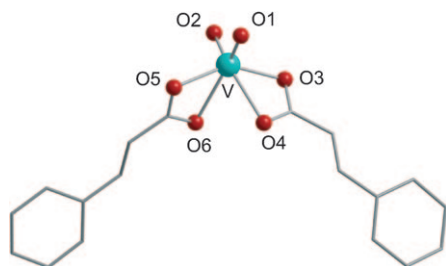


Figure 5. Molecular structure of the anion of **2**. Selected bond lengths [Å] and angles [°]: V–O1 1.618(4), V–O2 1.614(5), V–O3 1.985(5), V–O4 2.380(5), V–O5 1.998(4), V–O6 2.314(4); O1–V–O2 105.7(3), O1–V–O6 153.2(2), O2–V–O4 156.0(2), O1–V–O5 97.3(2), O2–V–O3 99.7(3).

The oxygen atoms, which coordinate the vanadium atom altogether form a distorted octahedron. The V=O bond lengths are almost identical to those observed for **1**. The carboxylate ligands bind in a bidentate fashion, but the V–O4 (2.380(5) Å) and the V–O6 bonds (2.314(4) Å) are significantly longer than the distances of V to O3 and O5.

Indeed **2** turned out to be a much more effective ODH catalyst in comparison to **II**, not only in case of cinnamic alcohol, but also for 9-hydroxyfluorene, benzyl alcohol, cinnamic alcohol, crotyl alcohol, 1-phenyl-1-propargyl-alcohol, 1-phenyl-1-propanol and 9,10-dihydroanthracene (TOFs = 336, 35, 220, 12, 164, 25, and 64 h^{-1} , respectively; 9,10-dihydroanthracene was mainly oxidized to anthraquinone, 9,10-dihydroanthracene-9,10-diol, and anthracene), and it is worth noting that **2** can also be prepared in-situ by addition of NBu_4VO_3 and cinnamic acid in a ratio of 1:2 to the reactions. The TOFs reached for the above-mentioned series of alcohols are even higher than those observed in case of the most effective oxovanadium calixarene complexes, which in turn had been superior to the reference system $OV(acac)_2$, reported to represent an efficient catalyst for the aerobic oxidation of 1-phenyl propargylic alcohol (see Figure 6).^[15]

Unfortunately, **2** is not indefinitely robust under the chosen conditions and loses nearly all activity, for instance within 40 min of catalytic oxidation of 9-hydroxyfluorene, possibly due to CO_2 elimination or C=C bond cleavage at the carboxylate ligand. It can be regenerated, though, through the addition of further equivalents of cinnamic acid, as shown in Figure 7.

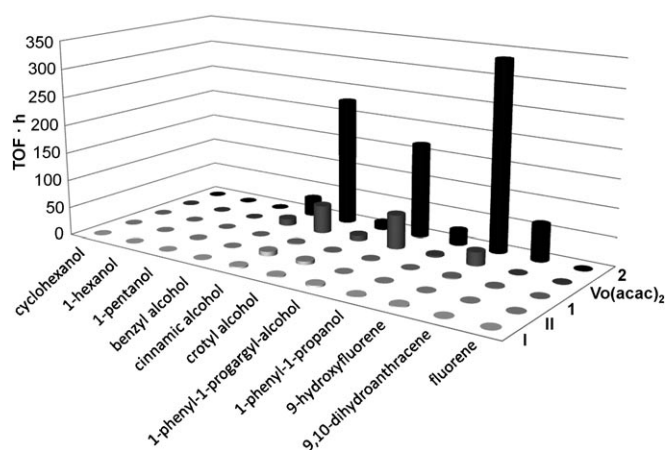


Figure 6. TOF data for the oxidation of alcohols with several catalysts: Alcohol (2 mmol), catalyst (x mmol; $x=0.02$ for **I**, **II**, **1** and $VO_2(acac)_2$; $x=0.005$ for **2**) and molecular sieves (1 g, 3 Å) in CH_3CN (4 mL) were heated to 80 °C in an O_2/Ar atmosphere.

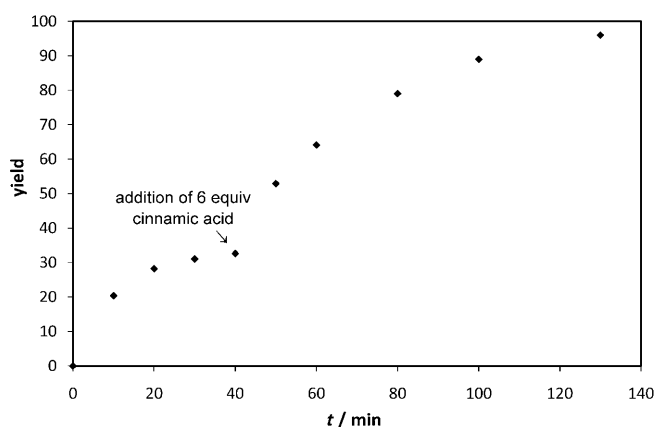


Figure 7. Yield versus time plot for the following reaction conditions: 9-hydroxyfluorene (2 mmol), **2** (5 μ mol) and molecular sieves (1 g, 3 Å) in CH_3CN (4 mL) were heated to 80 °C in an O_2/Ar atmosphere; after 40 min six equivalents of cinnamic acid were added.

Consequently, if sufficient amounts of cinnamic acid are added straight away, this guarantees continuous self-healing, so that, for instance, 2 mmol 9-hydroxyfluorene can be quantitatively oxidized to fluorenone in the presence of 0.25 mol% of NBu_4VO_3 and 5 mol% of cinnamic acid within 2 h (it might be worth pointing out that fluorenone is an important compound that is utilized as an element in organic solar cells and display devices, and also belongs to an interesting class of compounds for biomedical applications).^[16] Naturally the question arose whether cinnamic acid is unique within this system or whether it can be replaced by other carboxylic acids, so that perhaps the catalysts robustness or activity can be increased even further. A corresponding investigation showed that indeed other acids can be employed, but only a small range of pK_s values (4–5) comes into question: If the acids employed are too acidic, they induce the formation of polyoxovanadates, and at pK_s

values above 5 the resulting catalysts are significantly less active than **2** (the pK_s value of cinnamic acid amounts to 4.44). Hence, acetic acid ($pK_s=4.76$) and pivalic acid ($pK_s=5.05$) were successful candidates: An activity similar to the one of cinnamic acid was reached with acetic acid, and pivalic acid only led to a slight decrease in activity, while the resulting system showed an enhanced stability against water (note that catalysis typically requires the presence of molecular sieves to immediately remove water where formed and $\text{NBu}_4[\text{O}_2\text{V}(\text{O}_2\text{C}t\text{Bu})_2]$ (**2'**) even functions in the absence of molecular sieves). However, these two acids did not significantly improve the long term stability, so that in the case of **2**, probably decarbonylation and not reactions of the $\text{C}=\text{C}$ unit antagonize it.

The catalytic cycle: As mentioned above, oxovanadium calixarene complexes were also found to be active in the catalytic oxidation of alcohols. For these complexes we observed that the oxidation of one alcohol molecule can be achieved by one catalyst molecule (via V^{III}), but is preferably accomplished by two cooperating V^{V} centers (via V^{IV}). To check whether the catalytic cycle of **2** involves one or two molecules of **2**, kinetic studies with varying catalyst concentrations were performed, which unfortunately did not produce unequivocal results. Therefore we decided to investigate the oxidation state of the reduced catalyst. A mixture of 9-hydroxyfluorene, **2** (2 mol %), and excess molecular sieves in CH_3CN was heated to 80°C and stirred for 10 min. After cooling to room temperature an EPR measurement of the filtrated solution at 77 K was performed (see Figure 8).

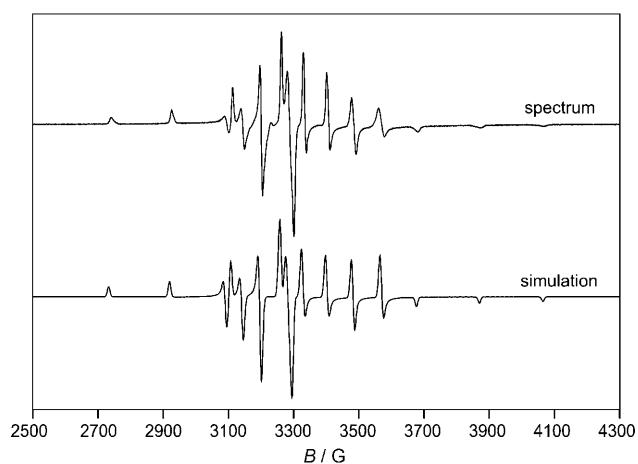
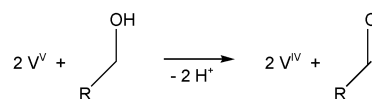


Figure 8. EPR spectrum of the reduced catalyst in CH_3CN at 77 K and its simulation. Simulation parameters: $A_{xx}=190.0$ G, $A_{yy}=68.0$ G, $A_{zz}=68.0$ G, $g_x=1.940$, $g_y=1.975$, $g_z=1.975$, linewidth: $x: 8$ G, $y: 10$ G, $z: 10$ G.

The EPR spectrum unambiguously proves the presence of a mononuclear V^{IV} species after alcohol oxidation and thus points to a mechanism featuring two molecules of **2** that perform single-electron oxidations (Scheme 3). Subsequently the rate-determining step was further investigated.



Scheme 3. Illustration of the alcohol oxidation with V^{V} via V^{IV} .

As observed for the oxovanadium calixarene complexes, the turnovers reached by **2** seemed to correlate with the strengths of the $\text{C}-\text{H}$ bonds inherent to the alcohols employed (a strength of 350 kJ mol^{-1} still leads to acceptable conversions), and in line with that a kinetic isotope effect of 3.9 (Figure 9) was observed for 9-deutero-9-hydroxyfluorene: Considering that the maximum isotope effect reachable at 80°C amounts to about 5, the value of 3.9 is certainly indicative of a rate-determining step with significant involvement of the $\text{C}-\text{H}$ bond, and a quite symmetric transition state along the hydrogen-transfer coordinate, $\text{O}\cdots\text{H}\cdots\text{C}$. This finding is also consistent with a recent investigation concerning the hydrogen-atom abstraction reactivity of cationic $[\text{O}_2\text{VL}_2]^+$ complexes.^[18]

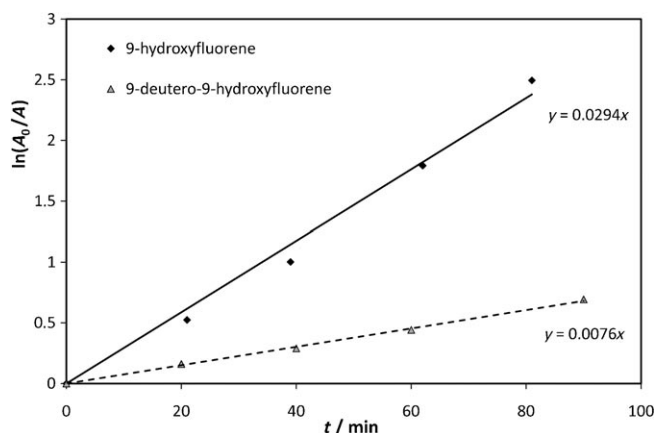


Figure 9. Logarithmic plot of the oxidation of 9-hydroxyfluorene and 9-deutero-9-hydroxyfluorene with catalyst **2** [alcohol (2 mmol), **2** (5 μmol) and molecular sieves (1 g, 3 \AA) in CH_3CN (4 mL) were heated to 80°C in an O_2/Ar atmosphere]. Dashed line: best fit for 9-deutero-9-hydroxyfluorene, solid line: best fit for 9-hydroxyfluorene.

Combining these results suggests an initial hydrogen-atom abstraction to yield a V^{IV} species and an alkyl radical that undergoes a single-electron oxidation (combined with a proton abstraction) with a second equivalent of **2** to yield the carbonyl compound. This poses the question, how is the V^{IV} species formed reoxidized by contact with O_2 ? As water is generated in this process, in-situ NMR studies to address this point (that had to be carried out in the absence of molecular sieves) were performed with the more robust $\text{NBu}_4[\text{O}_2\text{V}(\text{O}_2\text{CR})_2]$ system with $\text{R}=t\text{Bu}$ (**2'**; vide supra): **2'** (5 μmol) was dissolved in CH_3CN (0.5 mL) and CD_3CN (0.1 mL) and treated with 9-hydroxyfluorene (50 equiv) at 80°C to fully reduce it (**2'_{red}**). Then O_2 was added at -10°C and a ^{51}V NMR spectrum was recorded, which is shown in Figure 10.

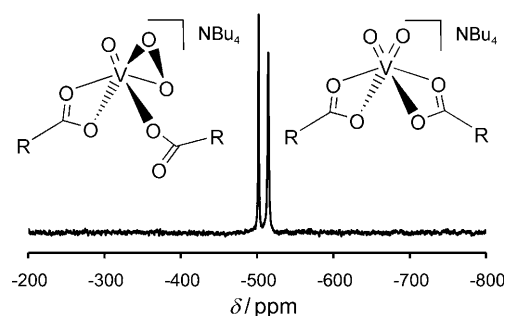
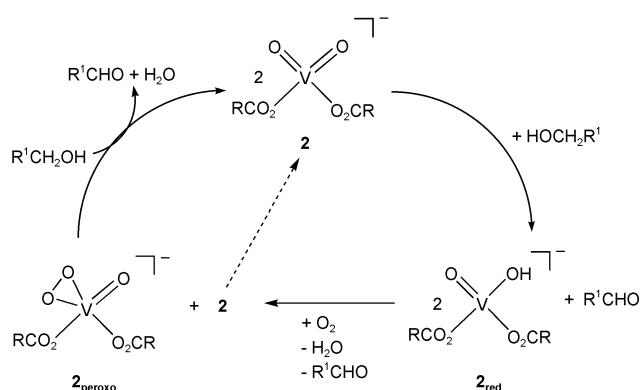


Figure 10. ^{51}V NMR spectrum after reoxidation of the reduced catalyst ($\text{R} = \text{CMe}_3$).

In addition to a signal for $\mathbf{2}'$, a second one at -501 ppm was observed (integral ratio of 1.3:1), which could be assigned to the peroxo compound $\text{NBu}_4[(\eta^2\text{-O}_2)(\text{O})\text{V}(\text{O}_2\text{CR})_2]$, $\mathbf{2}'_{\text{peroxo}}$, by comparison with a sample prepared independently from $\mathbf{2}'$ and H_2O_2 (see the Supporting Information). Such kind of reactivity in contact with O_2 has been known for vanadium(IV) complexes since 1999.^[17] In a further NMR experiment it could be shown, that $\mathbf{2}'_{\text{peroxo}}$ reacts with an equimolar amount of 9-hydroxyfluorene to give fluorenone and $\mathbf{2}'$. This might be the pathway, by which the catalytic cycle is closed.

Altogether, the following mechanism (see Scheme 4) could explain these results: Doubtlessly, the rate-determining step is an hydrogen-atom transfer from the alcohol to



Scheme 4. Proposed mechanism (NBu_4^+ ions have been omitted).

one of the terminal oxo atoms of $\mathbf{2}$,^[18] employed as such or prepared in in-situ. Perhaps prior to this step an addition of the alcohol across a $\text{V}=\text{O}$ bond of a second molecule of $\mathbf{2}$ occurs; such additions are often suggested in the literature as initial, fast steps.^[15,19] In the latter case a V^{V} species with a coordinated alkoxy radical would be formed that would collapse into the carbonyl compound and $\text{NBu}_4[(\text{O})(\text{OH})\text{V}(\text{O}_2\text{CR})_2]$ ($\mathbf{2}_{\text{red}}$); in the former case a free alcohol radical would form that could be oxidized by a second equivalent of $\mathbf{2}$. In both cases two equivalents of $\mathbf{2}$ react, one after another, with one equivalent of alcohol to give the corresponding carbonyl compound and two equivalents of $\mathbf{2}_{\text{red}}$. These

are reoxidized by O_2 to give a 1:1 mixture of $\mathbf{2}$ and $\mathbf{2}_{\text{peroxo}}$, which quickly oxidizes a second equivalent of alcohol to yield back $\mathbf{2}$, thus closing the catalytic cycle.

This mechanistic proposal is plausible, as it accounts for all four oxidation equivalents of O_2 , and at the same time it is supported by 1) the EPR investigation of the reduced catalyst, 2) the determination of the kinetic isotope effect for the substrate 9-hydroxyfluorene, 3) the identification of $\mathbf{2}_{\text{peroxo}}$ as an intermediate, and 4) the investigation of the reactivity of $\mathbf{2}_{\text{peroxo}}$ in contact with alcohols.

Conclusion

Our results show that the Si-O-V moieties of oxovanadium silsesquioxane complexes are sensitive to an attack by carboxylic acids and get cleaved to yield Si-OH functions and vanadyl carboxylates. These findings should be transferable to heterogeneous processes in which the over-oxidation of hydrocarbons at silica-supported vanadiumoxide catalysts produces carboxylic acids, that is, these should lead to leaching. In the course of corresponding studies we were also able to develop an efficient vanadium-based catalyst system ($[\text{O}_2\text{V}(\text{O}_2\text{CR})_2]^-$ salts in combination with HO_2CR) for the ODH of activated alcohols, which can be readily prepared in-situ starting from easily accessible starting materials. They react by means of a hydrogen-atom transfer from an alcoholic C-H unit to a $\text{V}=\text{O}$ group in the rate-determining step, and O_2 is needed to reoxidize the resulting reduced vanadium(IV) species. This leads, inter alia, to a peroxide intermediate which is capable of oxidizing a second alcohol equivalent.

Experimental Section

General remarks: All manipulations were carried out in a glove-box, or else by means of Schlenk-type techniques involving the use of a dry argon atmosphere. The ^1H , ^{13}C , ^{29}Si , and ^{51}V NMR spectra were recorded on a Bruker AV 400 NMR or DPX-300 spectrometer at 20°C . The ^1H NMR spectra were calibrated against the residual proton and natural abundance ^{13}C resonances of the deuterated solvent, the ^{29}Si NMR spectra against TMS, and the ^{51}V NMR spectra against VOCl_3 as standards. Coupling constants are given in Hz. Microanalyses were performed on a Leco CHNS-932 or HEKAtech Euro EA 3000 elemental analyzer. Infrared (IR) spectra were recorded using samples prepared as KBr pellets with a Shimadzu FTIR 8400S FTIR-spectrometer. ESR spectra were measured on ERS 300 (ZWG/Magnettech GmbH, Berlin-Adlershof, Germany). Pure $[\text{NBu}_4][\text{VO}_3]^{20}$, $[\text{Ph}_4\text{P}][\text{VO}_2\text{Cl}_2]$,^[21] and $(\text{C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OSiPh}_2\text{Me})(\text{OH})_2$ ^[7c] were prepared according to the literature procedure. Alcohols and acids were used as delivered without any purification.

Synthesis of 1: $[\text{PPh}_4][\text{VO}_2\text{Cl}_2]$ (0.18 g, 0.37 mmol) and $(\text{C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OSiPh}_2\text{Me})(\text{OH})_2$ (0.40 g, 0.37 mmol) were dissolved in THF (40 mL). After addition of Et_3N (1.0 mL, 7.2 mmol) the mixture was stirred for 15 h at room temperature. All volatiles were removed and the resulting solid was extracted with THF (20 mL). Removing of all volatiles from the extract afforded a grey powder. Recrystallization from a THF/n-hexane mixture afforded **1** (0.24 g, 0.16 mmol; 43%) in form of colorless crystals. ^1H NMR (400 MHz, CDCl_3 , 25°C , TMS): $\delta = 0.83$ (s, 3H; SiCH_3), 0.77–1.09 (m, 7H; CH), 1.27–1.79 (brm, 56H; CH_2), 7.20–7.28 (m, 6H; SiPh), 7.55–7.64 (brm, 12H; SiPh/ PPh_4^+), 7.70–7.78 (m, 8H;

SiPh/PPH₄⁺, 7.79–7.87 ppm (m, 4H; PPH₄⁺); ¹³C{¹H} NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = −0.5 (s, SiCH₃), 22.6, 22.7, 23.6, 23.9, 24.5 (s, CH), 27.0, 27.0, 27.1, 27.1, 27.4, 27.6, 27.6, 27.9 (CH₂), 117.5 (d, ¹J(C,P) = 90.1 Hz, PPH₄⁺), 127.4 (s, SiPh), 128.8 (s, SiPh), 130.7 (d, ²J(C,P) = 13.4 Hz, PPH₄⁺), 134.4 (s, SiPh), 134.4 (d, ³J(C,P) = 10.7 Hz, PPH₄⁺), 135.6 (d, ⁴J(C,P) = 3.6 Hz, PPH₄⁺), 138.5 ppm (s, SiPh); ²⁹Si{¹H} NMR (79.5 MHz, CDCl₃, 25 °C, TMS): δ = −69.0, −66.6, −66.5, −65.7, −62.8 (s), −10.5 ppm (s, SiMePh₂); ⁵¹V{¹H} NMR (105 MHz, CDCl₃, 25 °C, VOCl₃): δ = −574 ppm; IR (KBr): $\tilde{\nu}$ = 3058 (vw), 2948 (s), 2863 (m), 1437 (w), 1245 (vw), 1107 (vs), 1035 (m), 998 (sh), 947 (m), 935 (s), 756 (w), 722 (w), 526 (m), 488 cm^{−1} (m); elemental analysis calcd (%) for C₇₂H₉₆O₁₄Si₈V (1492.1): C 57.96, H 6.48; found: C 57.34, H 6.59.

Synthesis of 2: [NBu₄][VO₃] (1.00 g, 2.96 mmol) was dissolved in CH₂Cl₂ (10 mL) and molecular sieves (3 Å, 2.30 g) were added. Subsequently cinnamic acid (0.88 g, 5.94 mmol) dissolved in CH₂Cl₂ (10 mL) was added dropwise. After stirring of the mixture for 20 min at room temperature it was filtrated. The solution was concentrated under reduced pressure to a volume of 5 mL. Et₂O (25 mL) was added to the resulting yellow solution and the mixture was stirred for 30 min. The mixture was filtrated and the beige residue was washed with Et₂O (15 mL) and dried under high vacuum over night. This yielded **2** (1.49 g, 2.40 mmol, 81%) in the form of a beige powder. ¹H NMR (300 MHz, CD₃CN, 25 °C, TMS): δ = 0.95 (t, ³J(H,H) = 7.4 Hz, 12H; CH₃), 1.34 (m, 8H; CH₂-CH₃), 1.59 (m, 8H; CH₂-CH₂N), 3.09 (m, 8H; NCH₂), 6.51 (d, ³J(H,H) = 15.9 Hz, 2H; CH), 7.35–7.45 (m, 6H; C_{ar}H), 7.57–7.69 ppm (m, 6H; 4 C_{ar}H, 2 CH); ¹³C{¹H} NMR (75.5 MHz, CD₃CN, 25 °C, TMS): δ = 13.7 (s, CH₃), 20.3 (s, CH₂), 24.2 (s, CH₂), 59.2 (t, ¹J(N,C) = 2.8 Hz, NCH₂), 121.6 (s, CH), 128.9 (s, 2 C_{ar}), 129.7 (s, 2 C_{ar}), 130.8 (s, C_{ar}), 135.9 (s, C_{ar}), 144.2 (s, CH), 177.3 ppm (s, CO₂); ⁵¹V{¹H} NMR (105 MHz, CD₃CN, 25 °C, VOCl₃): δ = −511 ppm; IR (KBr): $\tilde{\nu}$ = 2955 (m), 2930 (m), 2872 (m), 1707 (vw), 1641 (vs), 1596 (w), 1576 (s), 1551 (w), 1496 (w), 1487 (m), 1448 (w), 1382 (s), 1285 (vw), 1262 (vw), 1231 (m), 1179 (vw), 1153 (vw), 1109 (vw), 1073 (vw), 1027 (vw), 978 (m), 946 (s), 931 (vs), 886 (vw), 874 (vw), 868 (vw), 804 (vw), 777 (m), 745 (m), 722 (w), 687 (w), 620 (vw), 610 (w), 593 (vw), 490 (vw), 441 cm^{−1} (w); elemental analysis calcd (%) for C₃₄H₅₀NO₆V (619.7): C 65.90, H 8.13, N 2.26; found: C 66.05, H 8.10, N 1.98.

Synthesis of 2': [NBu₄][VO₃] (1.00 g, 2.96 mmol) was dissolved in CH₂Cl₂ (10 mL) and molecular sieves (3 Å, 2.00 g) were added. Subsequently pivalic acid (0.60 g, 5.91 mmol) dissolved in CH₂Cl₂ (10 mL) was added dropwise. After stirring of the mixture for 20 min at room temperature it was filtrated. All volatiles were removed under reduced pressure, Et₂O (25 mL) was added, and the mixture was stirred for 30 min. It was then filtrated, and the beige residue was dried under high vacuum over night. This yielded **2'** (1.28 g, 2.43 mmol, 82%) in the form of a beige powder. ¹H NMR (400 MHz, CD₃CN, 25 °C, TMS): δ = 0.95 (t, ³J(H,H) = 7.6 Hz, 12H; CH₃), 1.14 (s, 18H; 2C(CH₃)₃), 1.35 (m, 8H; CH₂-CH₃), 1.61 (m, 8H; CH₂-CH₂N), 3.10 ppm (m, 8H; NCH₂); ¹³C{¹H} NMR (75.5 MHz, CD₃CN, 25 °C, TMS): δ = 13.7 (s, CH₃), 20.3 (s, CH₂), 24.3 (s, CH₂), 27.5 (s, C(CH₃)₃), 39.6 (s, C(CH₃)₃), 59.2 (t, ¹J(N,C) = 2.8 Hz, NCH₂), 191.1 ppm (s, CO₂); ⁵¹V{¹H} NMR (105 MHz, CD₃CN, 25 °C, VOCl₃): δ = −512 ppm; IR (KBr): $\tilde{\nu}$ = 2960 (s), 2874 (m), 1646 (w), 1586 (m), 1562 (m), 1481 (s), 1457 (m, sh), 1407 (m), 1375 (w), 1358 (m), 1261 (vw), 1220 (m), 1170 (vw), 1153 (vw), 1107 (vw), 1069 (vw), 1029 (vw), 948 (s), 927 (vs), 900 (s), 813 (w), 788 (vw), 743 (vw), 623 (m), 451 cm^{−1} (w); elemental analysis calcd (%) for C₂₆H₅₄NO₆V (527.2): C 59.18, H 10.32, N 2.65; found: C 59.32, H 10.38, N 2.45.

X-ray diffraction studies: The crystals were mounted on a glass fiber and then transferred into the cold nitrogen gas stream of the diffractometer Stoe IPDS using MoK_α radiation. The structures were solved by direct methods (SHELXS-97)^[22], refined versus F² (SHELXL-97)^[23] with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model. CCDC-761674 (**1**) and CCDC-761673 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for 1·2CH₂Cl₂: C₇₄H₁₀₀Cl₄O₁₄Si₈V, M_r = 1661.97, T = 100(2) K, λ = 0.71073 Å, orthorhombic, space group Pca2₁, a = 18.0987(6),

b = 22.3975(8), c = 20.3594(10) Å, α = β = γ = 90°, V = 8253.0(6) Å³, Z = 4, ρ_{calcd} = 1.338 Mg m^{−3}, μ = 0.444 mm^{−1}; 53885 reflections measured, 10991 unique (R_{int} = 0.0881); final R indices [I > 2σ(I)] R = 0.0648, wR = 0.1435
Crystal data for 2: C₃₄H₅₀NO₆V, M_r = 619.69, T = 100(2) K, λ = 0.71073 Å, monoclinic, space group P2₁/c, a = 9.8460(8), b = 9.9584(4), c = 33.969(2) Å, α = 90, β = 93.604(6), γ = 90°, V = 3324.1(4) Å³, Z = 4, ρ_{calcd} = 1.238 Mg m^{−3}, μ = 0.341 mm^{−1}; 33527 reflections measured, 4974 unique (R_{int} = 0.1434); final R indices [I > 2σ(I)] R = 0.0911, wR = 0.2491.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft, the CRC546, the Fonds der Chemischen Industrie, and the BMBF for financial support. We thank C. Knispel and E. Hoppe for X-ray determination and C. Jankowski for the preparation of starting materials. We also thank P. Kläring, C. Lehmann, R. Schiwon, F. Pfaff and N. Manicke for their very ambitious work in our laboratory.

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Received: January 21, 2010
Published online: May 12, 2010