

Nonhydrolytic Surface Synthesis of a Heterobimetallic V–Ti Alkoxide Complex on Silica

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A nonhydrolytic low-temperature route to ternary V–Ti–Si catalysts has been developed. The vanadium overlayer is deposited first, by the complete reaction of VOX_3 (X is Cl or OⁱPr) with the surface hydroxyl groups of pyrogenic silica. $\text{Ti}(\text{O}^i\text{Pr})_4$ migrates underneath the vanadium overlayer to give a heterobinuclear complex containing one Ti and one V, bound to the silica surface by an Si–O–Ti link. The heterobinuclear complex is not formed when TiCl_4 is used, nor can it be generated by first depositing $\text{Ti}(\text{OR})_4$.

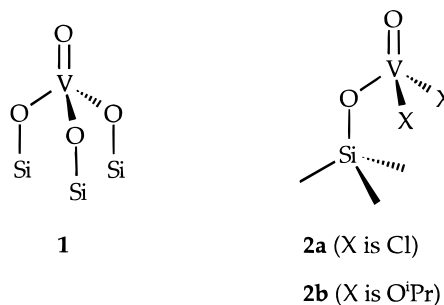
Introduction

Heterometallic oxides find wide application in materials science (for example, glasses and ceramics) and heterogeneous catalysis, due to the unique properties conferred by the synergy between different metal sites. Mixed oxides are usually prepared by classical co-impregnation or by sol–gel hydrolysis. Both methods suffer from the difficulty of controlling the precise composition and homogeneity of the precipitated oxide. A possible solution is the use of heterometallic alkoxide complexes as precursors to well-defined mixed oxides.¹ However, well-characterized bimetallic alkoxide complexes containing two transition metals are rare. Their potential in OMCVD processes has therefore yet to be developed.

One particularly important heterometallic oxide is the ternary V–Ti–Si catalyst. This material is made by wetness impregnation of high surface area silica with titania, followed by deposition from solution of vanadium oxide. It is reported to be more active and selective than any of the possible bimetallic combinations (i.e., V–Si, Ti–Si, or V–Ti) for the oxidation of *o*-xylene to phthalic anhydride,² and in the selective catalytic reduction of NO_x ,³ for which it is used in a commercial process.⁴ Anatase-like Ti overlayers on silica are thought to be much more active than rutile-like phases in V–Ti–Si selective oxidation catalysts, since the rutile phase has been associated with unselective oxidation.⁵ Unfortunately, the usual calcination/dehydration treatments for oxide catalysts prepared by hydrolytic routes are performed in the same temperature range as the anatase–rutile transition, which

has therefore been suggested as a major deactivation mechanism for the catalyst.⁶

The nature of the interfacial oxide–oxide interactions in the ternary catalyst is not known; however, the vanadium active sites were suggested to be dispersed as pseudotetrahedral monomers, anchored to the titania overlayer via three oxygen bridges.⁷ This model resembles the proposed active site on bimetallic V–Si oxide catalysts, **1**.⁸



Recently, thermal condensation of metal halides with metal alkoxides has been reported as a novel low-temperature nonhydrolytic sol–gel route to transition metal oxides and mixed oxides (eq 1).⁹ We have



synthesized and characterized a series of fully dispersed homogeneous surface complexes **2** by grafting VOX_3 onto partially dehydroxylated silica followed by ligand metathesis.^{10,11} In the course of our investigation of their reactivity, we discovered a stoichiometric CVD reaction that leads to a heterobinuclear V–Ti alkoxide complex attached to silica. Its composition makes it an interesting model for the ternary catalyst, as it may represent an intermediate in the hydrolysis–polycondensation reactions that lead to V–Ti–Si.

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Experimental Section

VOCl_3 , $\text{VO}(\text{O}^i\text{Pr})_3$, TiCl_4 , and $\text{Ti}(\text{O}^i\text{Pr})_4$ were purchased from Aldrich and transferred under N_2 into oven-dried glass reactors equipped with high-vacuum Teflon stopcocks. The liquids were subjected to several freeze–pump–thaw cycles to remove dissolved gases and then distilled trap-to-trap under vacuum to eliminate alcohol and HCl impurities. Each reagent was stored under vacuum and transferred into reactors via the gas phase (metal halides) or using breakseals (metal alkoxides).

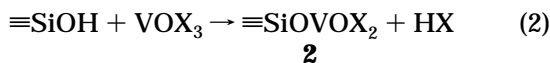
The silica used in all experiments was Degussa Aerosil-200, with a surface area of $200 \text{ m}^2/\text{g}$. The notation silica-500 indicates that the silica was partially dehydroxylated under dynamic vacuum at 500°C before reaction with the volatile transition metal complex. This pretreatment does not change the surface area of the silica, but it reduces the number of surface hydroxyl groups to ca. $1.2/\text{nm}^2$, or $0.40 \text{ mmol of OH/g}$.¹² The silica treatment follows strict high-vacuum protocol and has been described previously.¹⁰

All experiments were performed in sealed glass high-vacuum reactors. For reactions with metal halides, the reactors were equipped with Teflon stopcocks or glass stopcocks using the perfluorinated grease Krytox (which does not react with metal halides to generate HX). Samples were manipulated under vacuum and never exposed to air, solvents, or inert atmospheres during the experiments. Infrared spectra of thin self-supporting pellets and thin films¹⁰ were recorded in situ in a specially constructed cell. ^{51}V magic angle spinning (MAS) and static solid-state NMR spectra were recorded at 52.6 MHz in $5 \times 30 \text{ mm}$ Pyrex tubes sealed under vacuum and placed in zirconia rotors. Spectra were collected on a Bruker ASX-200 spectrometer using a $4.8 \mu\text{s}$ 90° pulse and a relaxation delay of 0.2 s . MAS spectra were first obtained at a spin rate of 4 kHz , and then the spin rate was varied to identify spinning sidebands. The ^{51}V MAS spectra were baseline-corrected with a spline fit. The ^{51}V solution NMR spectra were recorded in CDCl_3 at 78.9 MHz on a Varian XL-300 spectrometer using a $10 \mu\text{s}$ 90° pulse and a relaxation delay of 0.1 s . All ^{51}V spectra were referenced to external neat VOCl_3 .

The metal loading of the silica was determined by quantitative extraction at the end of each experiment. Metals were extracted by boiling $10\text{--}15 \text{ mg}$ of the modified silica in $1 \text{ M H}_2\text{SO}_4$ for 1 h , followed by addition of 0.1 mL of $30\% \text{ H}_2\text{O}_2$ and dilution with $1 \text{ M H}_2\text{SO}_4$ to 25 mL .¹³ Ti and V peroxide complexes absorb at 405 and 462 nm , respectively. The absorbance at each wavelength was measured, and the concentration of each metal calculated by solving simultaneously two equations with two unknowns. Organic products were identified and quantified by IR, GC, and GC/MS.

Results

The gas–solid reaction of excess VOX_3 with the surface hydroxyl groups of silica-500 is reproducible and produces a material that contains $2.2 \text{ wt } \%$ V, or 0.40 mmol V/g , and no residual hydroxyl groups.¹⁰ The surface reaction was formulated, based on IR and ^{51}V NMR,¹⁰ as well as isotope labeling studies,¹¹ as the formation of the chemisorbed complex **2** (eq 2).



Volatile HX is liberated in the reaction and completely removed by evacuation.

Reaction of $\equiv\text{SiOVCl}_2$ with TiCl_4 . Upon exposure of **2a** (X is Cl) to TiCl_4 vapor at room temperature,

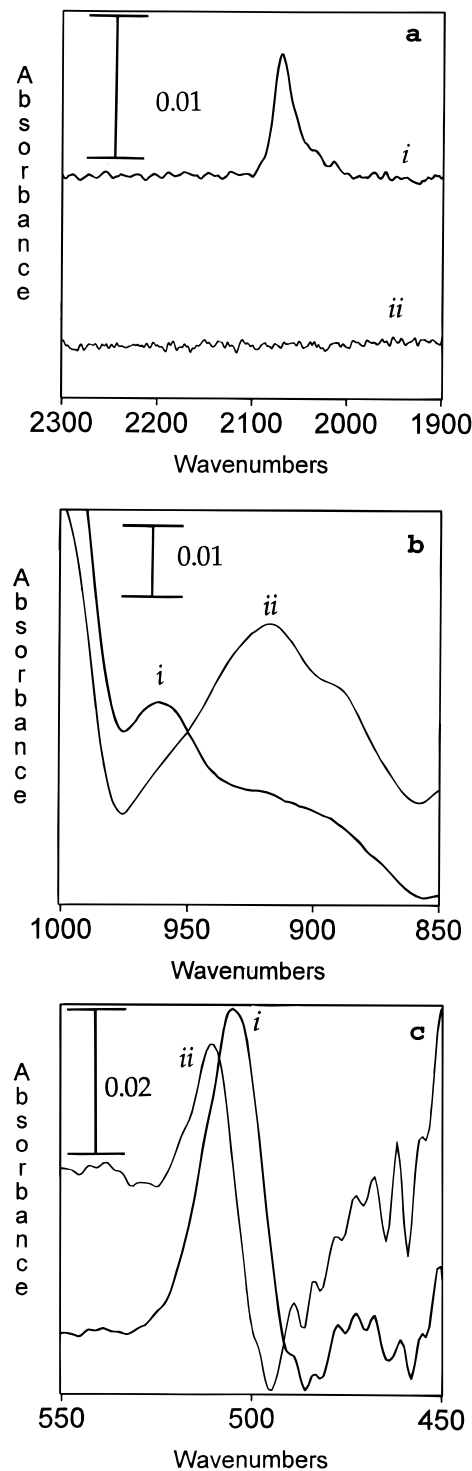


Figure 1. In situ IR spectra of (i) $\equiv\text{SiOVCl}_2$ (**2a**) and (ii) $\equiv\text{SiOTiCl}_3$ (**3**) formed by reaction of **2a** with TiCl_4 . The spectra are displayed as differences, i.e., the background spectrum of silica-500 was subtracted from each spectrum. The overtone region, shown in (a), was obtained from a thin self-supporting disk. The other spectral regions (b) and (c) are thin silica films supported on an IR-transparent ZnSe disk.

VOCl_3 was observed in the gas phase.¹⁴ In the infrared spectrum, bands characteristic of **2a**, i.e., the overtone $2\nu(\text{V}=\text{O})$ at 2070 cm^{-1} and $\nu(\text{V}-\text{O}-\text{Si})$ at 960 cm^{-1}

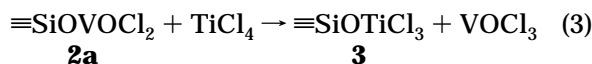
(14) VOCl_3 was readily identified by its characteristic gas-phase IR spectrum, with intense absorptions at $1043 \text{ (V}=\text{O)}$ and $508 \text{ (V}-\text{Cl)}$ cm^{-1} . Nakamoto, K. *Infrared spectra of inorganic and coordination compounds*, 2nd ed.; Wiley: New York, 1970.

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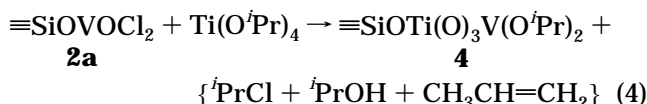
disappeared completely, while a new intense band appeared at 920 cm^{-1} . In addition, the band at 505 cm^{-1} , assigned to $\nu(\text{V}-\text{Cl})$, shifted slightly to 510 cm^{-1} , Figure 1. The final spectrum, stable under dynamic vacuum, is identical with that obtained by the direct reaction of TiCl_4 with the surface hydroxyl groups of unmodified silica-500.¹⁵ The 510 cm^{-1} band is associated with $\text{Ti}-\text{Cl}$ vibrations. The assignment of the 920 cm^{-1} band to the $\text{Si}-\text{O}$ vibration of a polarized $\text{Si}-\text{O}-\text{Ti}$ unit is less well-established,¹⁶ but it is always present in Ti -substituted silicas and zeolites.

Elemental analysis of the colorless product, after complete desorption of volatiles, gave $<0.1\text{ wt } \%$ V and $2.1\text{ wt } \%$ Ti, i.e., the amount (in moles) of chemisorbed Ti is equal to the initial amount of V present. We conclude that an exchange reaction has occurred, as shown in eq 3:



The possible formation of VOCl_3 by reaction of **2a** with adventitious HCl was verified separately and does not occur under these conditions, nor do $\text{VOCl}_2(\text{OR})$ complexes react with HCl in solution.¹⁷ The exchange reaction shown in eq 3 is not expected to regenerate any surface hydroxyl groups, nor are any observed by in situ IR.

Reaction of $\equiv\text{SiOVOCl}_2$ with $\text{Ti}(\text{O}^i\text{Pr})_4$. When **2a** was exposed to $\text{Ti}(\text{O}^i\text{Pr})_4$ vapor at room temperature, no hydroxyl groups reappeared but the IR spectrum of the product showed vibrations characteristic of 2-propoxide groups: $2880\text{--}2980\text{ cm}^{-1}$ ($\nu(\text{C}-\text{H})$), $1325\text{--}1465\text{ cm}^{-1}$ ($\delta(\text{CH}_3)$ and $\delta(\text{OCH})$), and 865 cm^{-1} . The bands of **2a** at 2070 and 505 cm^{-1} completely disappeared, while the band at 960 cm^{-1} shifted slightly to 945 cm^{-1} (Figure 2). The gas phase contained 2-propyl chloride, 2-propanol, and propene, but no HCl . Elemental analysis of the product **4** after prolonged desorption of volatiles under dynamic vacuum revealed the presence of V and Ti in a constant molar ratio V/Ti of 0.98 ± 0.07 (average of five experiments), Table 1). The number of isopropyl groups present was determined to be 2.1 ± 0.2 per V, by integration of the $\nu(\text{C}-\text{H})$ region of the IR spectrum.¹⁸ Calcination of the material at $700\text{ }^\circ\text{C}$ in 400 Torr of O_2 caused complete loss of surface hydrocarbyl groups with formation of H_2O and 7 ± 1 mol of CO_2 /mol of V, i.e., roughly two isopropyl groups per V. No HCl was detected by IR, even under these harsh conditions. To account for these observations, we propose the reaction shown in eq 4:



The ^{51}V MAS NMR spectrum of **4** consists of a weak resonance at -517 ppm , which is much decreased in

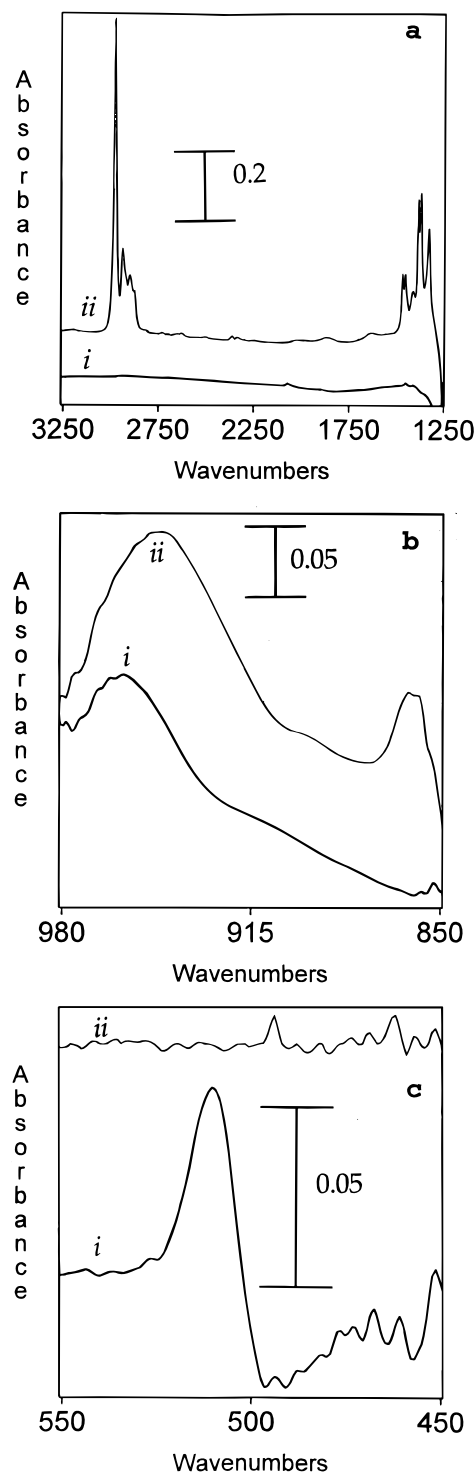


Figure 2. In situ IR spectra of (i) $\equiv\text{SiOVOCl}_2$ (**2a**) and (ii) $\equiv\text{SiOTi}(\text{O})_3\text{V}(\text{O}^i\text{Pr})_2$ (**4**) formed by reaction of **2a** with $\text{Ti}(\text{O}^i\text{Pr})_4$. The spectra are displayed as differences, i.e., the background spectrum of silica-500 was subtracted from each spectrum. The regions shown in (a) and (b) are the spectra of thin self-supporting disks. The other spectral region (c) was obtained from a thin silica film supported on an IR-transparent ZnSe disk.

intensity compared to the spectrum of the same amount of **2a**, -295 ppm ,¹⁰ when recorded with the same experimental parameters and data analysis (Figure 3).

When **2a** is exposed to enough $\text{Ti}(\text{O}^i\text{Pr})_4$ to wet the silica, a small amount ($<25\%$) of the surface vanadium is converted to the volatile forms $\text{VOCl}_2(\text{O}^i\text{Pr})$ and

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Table 1. Composition of Heterobimetallic Surface Complexes

reactants	wt % V	wt % Ti	V/Ti	volatile products
SiOVOCl ₂ + TiCl ₄	0.08	2.10		VOCl ₃
SiOVOCl ₂ + Ti(O'Pr) ₄	1.81	1.75	0.99	CH ₃ CHClCH ₃ , CH ₃ CH=CH ₂ , CH ₃ CH(OH)CH ₃
	2.06	2.07	0.95	
	1.75	1.74	0.97	
	1.86	1.96	0.91	
	1.79	1.59	1.06	
SiOVOCl ₂ + Ti(O'Pr) ₄ (large excess)	1.47	1.60	0.88	VOCl ₂ (O'Pr), VOCl(O'Pr) ₂ , CH ₃ CHClCH ₃ , CH ₃ CH=CH ₂ , CH ₃ CH(OH)CH ₃
SiOVO(O'Pr) ₂ + Ti(O'Pr) ₄	1.61	1.49	1.03	CH ₃ CH=CH ₂ , CH ₃ CH(OH)CH ₃
	1.94	1.69	1.09	

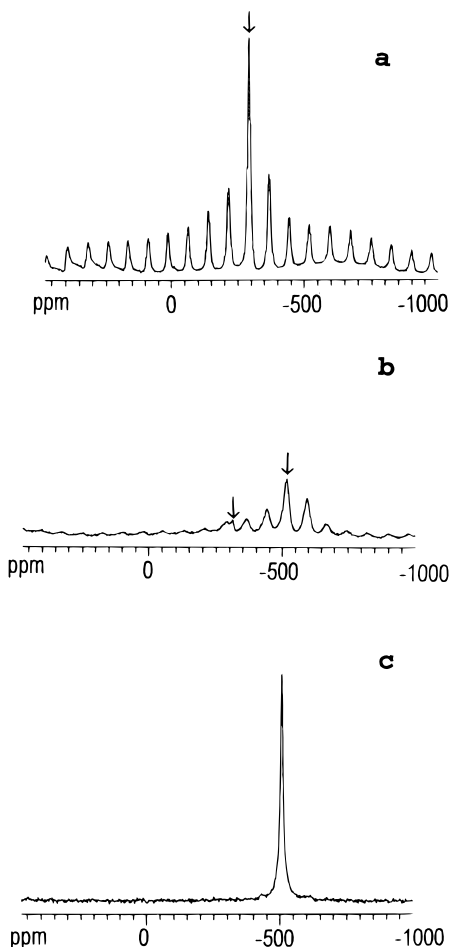


Figure 3. ⁵¹V NMR spectra of (a) ≡SiOVOCl₂ (**2a**) (b) ≡SiOTi(O)₃V(O'Pr)₂ (**4**) and (c) physisorbed VO(O'Pr)₂Cl on silica, produced by the reaction of **2a** with a large excess of Ti(O'Pr)₄. The MAS spectra in (a) and (b) were obtained at 4 kHz. The spectrum in (c) was recorded without spinning. In the MAS spectra peak positions are marked by arrows; all other bands are spinning sidebands.

VO(O'Pr)₂Cl. These complexes were identified in the ⁵¹V NMR spectra by their characteristic chemical shifts at -317 and -505 ppm,¹⁹ respectively. A small band at -317 ppm can be seen in Figure 3b. The formation of VO(O'Pr)₂Cl was observed in another NMR experiment, where the resonance at -505 ppm dominates the spectrum even when the sample is not spinning, indicating a highly mobile (not chemisorbed) species (Figure 3c). After prolonged desorption of volatiles, the metals analyses of these samples show reduced (<2%) vanadium content (Table 1).

Solution Reaction of VOCl₃ with Ti(O'Pr)₄. The ⁵¹V NMR spectrum of a roughly equimolar mixture of VOCl₃ with Ti(O'Pr)₄ contains two sharp resonances at -306 and -502 ppm, assigned to VOCl₂(O'Pr) and VOCl(O'Pr)₂, respectively. When the amount of Ti(O'Pr)₄ was increased relative to VOCl₃, the band at -306 disappeared while the band at -502 ppm increased in intensity.

Reaction of ≡SiOVO(O'Pr)₂ with Ti(O'Pr)₄. Since **4** contains no chloride, we attempted to prepare it independently by reaction of **2b** with Ti(O'Pr)₄. When **2b** was exposed to Ti(O'Pr)₄ vapor at room temperature, no change in intensity was observed in the hydrocarbon regions of the IR spectrum (implying no retention of additional 2-propyl groups on the surface). However, the band at 960 cm⁻¹ belonging to the ν(Si–O–V) mode of **2b** shifted to 945 cm⁻¹, which is consistent with the formation of **4**. Elemental analysis of the product revealed the presence of V and Ti, once again in a molar ratio of 1.1 ± 0.1 V/Ti (average of two experiments). The gas phase contained a mixture of 2-propene and 2-propanol.

To our surprise, we failed to prepare **4** by the (more logical) reversed order sequential CVD process. Although Ti(O'Pr)₄ reacts with unmodified silica to form a chemisorbed Ti complex,²⁰ we observed no subsequent reaction with VO(O'Pr)₃.²¹

Discussion

The preparation of multicomponent oxides by nonhydrolytic condensation reactions of metal alkoxides has recently been described;^{22,23} however, the mechanisms of the reactions are little known.²⁴ The first step in the formation of **4** from **2a** is likely the reversible coordination of TiX₄, a strong Lewis acid,²⁵ to the surface siloxo ligand. The latter becomes a 3e⁻ donor bridging the pair of metal atoms, as in the intermediate **5**.²⁶ TiCl₄ is known to form Lewis acid adducts with ethers²⁷ and

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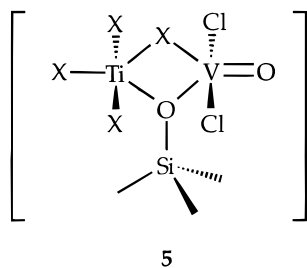
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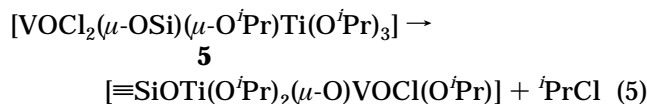
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alcohols.²⁸ When X is Cl, formation of a μ -Cl bridge between Ti and V is followed by cleavage of the heterobimetallic intermediate with liberation of volatile VOCl_3 and formation of a SiO-Ti bond to the surface. When X is O^iPr , the major reaction is the formation of the more stable μ -OR bridge,²⁸ yielding an oxo bridge by concerted elimination of 2-propyl chloride²² (eq 5).



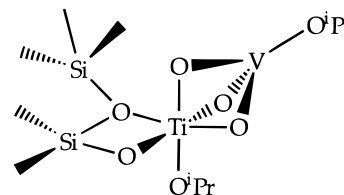
Heterolysis of the O-C bond of alkoxide ligands with formation of oxide bridges is promoted by coordination to strong Lewis acids in the synthesis of heterometallic alkoxide complexes.¹ A second such reaction would generate the product **4**, containing no chloride and two alkoxide ligands per surface complex. The absence of HCl among the volatile reaction products and the lack of reactivity of **2a** toward HCl are evidence for the nonhydrolytic nature of the condensation reaction. When the reactant is **2b**, we propose that the heterolysis of the bridging alkoxide ligand produces an incipient carbocation which loses a proton to form propene. The proton is captured by another alkoxide ligand to form 2-propanol.

The presence of propene and propanol among the reaction products when the starting material is **2a** suggests that ligand exchange between $\equiv\text{SiOVOC}_2$ and $\text{Ti}(\text{O}^i\text{Pr})_4$ is occurring to produce chemisorbed vanadium alkoxide complexes. Dissociation of **5** to yield volatile $\text{VOCl}_x(\text{O}^i\text{Pr})_{3-x}$ is a minor side reaction which can be minimized by using a small excess of $\text{Ti}(\text{O}^i\text{Pr})_4$ reactant. Facile ligand exchange is well-documented for $\text{TiCl}_4/\text{Ti}(\text{OR})_4$ mixtures²⁹ but not for $\text{VOCl}_x(\text{O}^i\text{Pr})_{3-x}$.³⁰ The reaction of **2** with a large excess of $\text{Ti}(\text{O}^i\text{Pr})_4$ to liberate chemisorbed vanadium implies that ready ligand exchange occurs on the surface between V and Ti. This conclusion is supported by our observation of ligand scrambling in solution (eq 6).



The exact nature of **4** is presently unknown, but a possible structure contains a tetrahedral VO_4 unit

sharing a face with octahedral TiO_6 :



In the proposed structure, the coordination sphere of Ti is completed by $2e^-$ donation from a surface siloxane bridge site. This model is consistent with all the available spectroscopic and analytical results, including the decrease in intensity of the ^{51}V MAS NMR signal due to the restricted mobility of the V site. The alkoxide ligands of **4** undergo metathesis with other alcohols without destroying its structure, i.e., without disruption of Si-O-Ti or desorption of V from the surface. An alternate structure, which has been proposed for V-Ti-Si active sites,³¹ contains pairs of terminal oxo ligands on a VO_2^{2+} unit, which is bound via bridging oxygen atoms to Ti. However, we see no IR evidence for V=O vibrations. Also, **4** fails to react with *p*-tolylisocyanate to form CO_2 , in a reaction characteristic of the terminal oxo ligands of vanadium.^{11,32}

The efficiency of formation of mixed metal oxides from molecular precursors has been quantified by their degree of condensation.²² For **4**, the degree of condensation is 0.78 and is similar to the best results in nonhydrolytic condensations which yield zirconium titanate.²³ Unlike **2**, which is thermally unstable above 70°C and readily decomposes in the presence of water vapor at room temperature,¹⁰ **4** is unreactive toward water at room temperature and can be heated in a vacuum to at least 120°C with no observable color changes. We suggest that the greater thermal and hydrolytic stability of the SiO-Ti linkage relative to SiO-V³³ may be responsible for these changes.

We were surprised that $\text{VO}(\text{O}^i\text{Pr})_3$ did not react with a preformed Ti overlayer on silica. The effect of the structure of the Ti overlayer on subsequent grafting of volatile V complexes is under investigation.

Conclusion

We suggest that the mixed V-Ti alkoxide complex on silica, **4**, may be a structural model for the active site on dehydrated V-Ti-Si catalysts. The selectivity and activity of these materials have been linked to the high dispersion of V, the absence of exposed Ti, and the silica support, which contributes high surface area, as well as thermal and mechanical stability.³⁴ The sequential CVD technique holds promise for the future "design" of well-defined isolated multifunctional active sites in heterometallic oxide catalysts.

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Supporting Information Available: Solution ^{51}V NMR spectra of mixtures of VOCl_3 and $\text{Ti}(\text{O}^i\text{Pr})_4$ (2 pages). See any current masthead page for ordering and Internet access instructions.

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