

Catalysis of Silicon Alkoxide Transesterification by Early Transition Metal Complexes

Matthew D. Curran, Thomas E. Gedris, and A. E. Stiegman*

Department of Chemistry, Florida State University, Tallahassee, Florida 32306

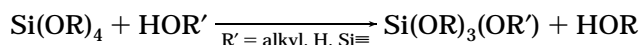
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The transition metal alkoxides $\text{Ti}(\text{OPr}^i)_4$ and $\text{OV}(\text{OPr}^i)_3$ are shown to catalyze the transesterification of tetramethyl- and tetraethyl orthosilicates: $\text{Si}(\text{OR})_4 + \text{R}'\text{OH} \leftrightarrow \text{Si}(\text{OR})_3(\text{OR}') + \text{ROH}$. A detailed study of metal-catalyzed transesterification reactions and the factors that affect their efficiency and selectivity are presented. ^{29}Si NMR techniques were used to quantify the extent of transesterification of the two different silicon alkoxides under a variety of conditions while mechanistic aspects of the reaction were probed using ^{51}V NMR. It was found that tetramethyl and tetraethyl orthosilicates, when reacted with smaller, less sterically demanding alcohols, are substituted to a similar extent by both metals. However, transesterification of bulkier alcohols (2-propanol) revealed dramatic differences in their reactivity, with titanium being significantly more efficient than vanadium. The catalytic process and the differences in reactivity between the two metals are explained in terms of a mechanism involving ligand migration between the metal and the silicon. A comparison of the catalytic activity of these Lewis acids with a strong Brønsted acid (triflic acid) showed the latter to have far greater catalytic activity.

Introduction

Currently, there is considerable interest in the development of multicomponent transition metal/silica glasses by the sol–gel process.¹ This interest is driven by their many potential applications including optical materials, heterogeneous catalysts, and chemical sensors.² These useful characteristics are often dictated by the chemical and physical properties of the metal centers as they occur in the silica matrix.³ As revealed in a number of studies, the chemistry of the sol–gel process in the presence of metal ions such as vanadium, titanium and aluminum is complex.^{4,5,6} The specific metal species distributed in the matrix are greatly affected by the particular conditions under which the sol–gel process is run. In turn, the metal can strongly affect the hydrolysis and condensation rates of the silicon alkoxide and, hence, the properties of the resultant glass.⁷

Broadly speaking, much of the reaction chemistry of silicon alkoxides can be thought of as ligand metathesis:



For example, when the reactant is an alcohol, this process represents transesterification,⁸ and when it is water or a silicate, it represents the hydrolysis and condensation steps, respectively, of the sol–gel process.⁹ These reactions are affected by a number of factors including the addition of Brønsted acids and bases which are commonly used as catalysts. Significantly, all of these reactions occur during the sol–gel process, and all contribute, in varying degrees, to the properties of the final sol–gel-derived glass (xerogel). In the production of multicomponent, transition metal/silica xerogels, the effect of the transition metal on these primary metathesis processes might be expected to have a significant impact on the overall sol–gel reaction. As part of our efforts to understand the chemistry of the multicomponent sol–gel process, we report here a detailed study of the transition metal catalyzed transesterification of silicon tetraalkoxides. In particular, we report the effect of Ti(IV) and V(V) alkoxides on alkoxy exchange in tetramethyl and tetraethyl orthosilicate under a variety of conditions. The transesterification reaction is significant because it occurs during the sol–gel process, and when the solvent alcohol differs from the alkoxy group on the silicon, it can effect the overall properties of the gel. This fact has been used success-

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fully to control spinability in pure silica sol-gel-derived films and,¹⁰⁻¹³ more recently, to control the transparency and homogeneity of aluminosilicate gels.⁶ More fundamentally, however, it is a relatively simple reaction with which to investigate reactivity differences between metal centers and the effect of factors such as steric and inductive effects on the metathesis process.

Experimental Section

Tetramethyl orthosilicate (TMOS; 99+%) and oxovanadium triisopropoxide were purchased from Gelest. Tetraethyl orthosilicate (TEOS; 98+%), titanium tetraisopropoxide, trifluoromethanesulfonic acid (triflic acid), vanadium oxytrichloride (VOCl₃), and chromium acetylacetonate (Cr(acac)₃) were purchased from Aldrich. Tetraisopropyl orthosilicate was obtained from TCI and used as received. Methanol, ethanol, *n*-propanol, 2-propanol, and acetonitrile were purchased from Fisher. Tetramethyl and tetraethyl orthosilicate were distilled under a nitrogen atmosphere immediately prior to use. Oxovanadium triisopropoxide and titanium tetraisopropoxide were distilled under vacuum immediately prior to use. Methanol, ethanol, *n*-propanol, 2-propanol, and acetonitrile were all refluxed over calcium hydride for 24 h under a nitrogen atmosphere and distilled immediately prior to use. Triflic acid and tetraisopropyl orthosilicate were used as received. In all distillations a forerun comprising ~10% of the total volume was collected and discarded, while a similar fraction was left in the distillation flask at the end of the distillation. Only the intermediate fraction, collected at constant temperature, was used in the experiments.

Nuclear magnetic resonance experiments were performed on a Brüker AC 300 NMR spectrometer. Measurements were performed in glass 10 mm NMR tubes. The broad-band probe was tuned to 59.6 MHz for the ²⁹Si nucleus. A 45° pulse width was used with a 3-s repetition rate for 250 transients. The probe was then tuned to 78.9 MHz for the ⁵¹V nucleus. A 45° pulse width was used with a 0.1-s repetition rate for 2500 transients. All ²⁹Si NMR peaks were secondarily referenced to tetramethylsilane (TMS), and all ⁵¹V NMR peaks were referenced to vanadium(V) oxytrichloride (VOCl₃). The resonance from the silicon in the NMR tube itself was a broad band further upfield than the resonances of the silica species of interest; therefore, the signal from the NMR tube did not interfere with our experiments. Due to the extremely long relaxation times of the ²⁹Si nucleus, Cr(acac)₃ (0.015 M) was introduced into those samples to act as a relaxation agent. Control experiments showed no reactivity between the Cr(acac)₃ and the metal alkoxide or the silicate esters.

For all of the measurements except the 2-propanol substitution of TEOS, the molarity of the silicon alkoxides was kept constant at 2.05 M with a catalyst

concentration of 0.01 M for each sample. In the case of 2-propanol substitution, it was not possible to add a stoichiometric amount of the alcohol to TEOS and still keep the total volume of the sample constant. To compensate for this and still maintain a valid comparison between tetramethyl and tetraethyl orthosilicates, we lowered the molarity of both to 1.36M and lowered the catalyst concentration to 0.007 M, thereby keeping the Si:catalyst ratio the same. Finally, to ascertain whether residual silicon chloride impurities, resident in the orthosilicates, contributed to the transesterification rate by generating HCl, we measured the chloride content of the solutions using ion chromatography. In all working solutions the chloride concentration was ≤50 μM. We believe that this concentration is sufficiently low that HCl did not contribute substantially to the catalyzed transesterification rate; however, it may be responsible for some of the transesterification in the uncatalyzed control.

Assignments for the chemical shifts of the ²⁹Si resonances for the substituted orthosilicates were made on the basis of previous literature assignments tabulated in Table 1. In the case of isopropoxy substitution of TMOS, which has not been previously assigned, the assignments were made, by analogy to the other substituted tetraalkoxyorthosilicates, in the following way. The spectrum of the substitution products consisted of five lines commencing at -78.5 ppm for tetramethyl orthosilicate and ending at -85.3 ppm for tetraisopropyl orthosilicate (obtained from an authentic sample). Between these two extremes are three resonances, each separated by 1.8 ppm, which we assign, in ascending order, to mono-, di-, and triisopropyl-substituted tetramethyl orthosilicate.

Results and Discussion

The transesterification of silicon tetraalkoxides can be described by the sequential reactions shown in Scheme 1 in which the alkoxy group of a reacting alcohol (HOR') exchanges with an alkoxy group (OR) on the silicon. Each of these reactions, over time, will reach an equilibrium defined by the general expressions for the equilibrium constant, *K*, given by the equation

$$K^{(x+1)} = \frac{[\text{Si}(\text{OR})_{3-x}(\text{OR}')_{x+1}][\text{HOR}]}{[\text{Si}(\text{OR})_{4-x}(\text{OR}')_x][\text{HOR}']} \quad x = 0-3$$

Ligand-exchange reactions between various reacting alcohols and tetramethyl and tetraethyl orthosilicate (TMOS and TEOS) were carried out in the presence of added titanium tetraisopropoxide and oxovanadium triisopropoxide (0.01 M). The progress of the reactions was monitored by ²⁹Si NMR spectroscopy with measurements taken approximately 2 h after the samples were prepared and again at 5 and 12 days. The concentrations of all of the substituted silicon species observed in the reactions were determined from the integrated intensities of their characteristic ²⁹Si NMR resonances. Table 1 gives the chemical shifts, relative to tetramethylsilane (TMS), of all the relevant substitution products. For each alcohol/silicon alkoxide system studied, two different ratios of reacting (OR') and parent (OR) alkoxy groups were used. The first contained a 4/1 ratio of the reacting alcohol to the silicon alkoxide

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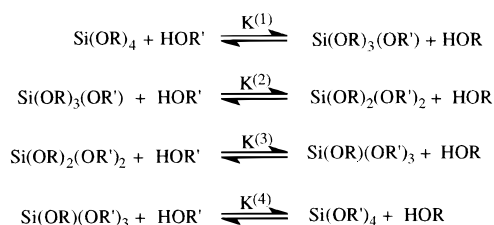
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Table 1. ^{29}Si Chemical Shifts of Relevant Silicon Alkoxides

silicon species	^{29}Si chemical shift (ppm rel. to TMS)	ref
$\text{Si}(\text{OMe})_4$	-77.9 ± 0.3	10
$\text{Si}(\text{OMe})_3(\text{OEt})$	-78.8 ± 0.3	12
$\text{Si}(\text{OMe})_2(\text{OEt})_2$	-79.6 ± 0.3	12
$\text{Si}(\text{OMe})(\text{OEt})_3$	-80.5 ± 0.3	12
$\text{Si}(\text{OEt})_4$	-81.4 ± 0.3	12
$\text{Si}(\text{OMe})_3(\text{OPr}^n)$	-79.2 ± 0.3	10
$\text{Si}(\text{OMe})_2(\text{OPr}^n)_2$	-80.1 ± 0.3	10
$\text{Si}(\text{OMe})(\text{OPr}^n)_3$	-81.0 ± 0.3	10
$\text{Si}(\text{OPr}^n)_4$	-81.9 ± 0.3	10
$\text{Si}(\text{OMe})_3(\text{OPr}^i)$	-79.6 ± 0.3	this work
$\text{Si}(\text{OMe})_2(\text{OPr}^i)_2$	-81.5 ± 0.3	this work
$\text{Si}(\text{OMe})(\text{OPr}^i)_3$	-83.4 ± 0.3	this work
$\text{Si}(\text{OPr}^i)_4$	-85.3 ± 0.3	17
$\text{Si}(\text{OEt})_3(\text{OPr}^i)$	-82.5 ± 0.3	17
$\text{Si}(\text{OEt})_2(\text{OPr}^i)_2$	-83.4 ± 0.3	17
$\text{Si}(\text{OEt})(\text{OPr}^i)_3$	-84.4 ± 0.3	17

Scheme 1R = ethyl, methyl; R' = ethyl, methyl, *n*-propyl, *i*-propyl

which provides equimolar amounts of both alkoxy groups ($[\text{OR}']/[\text{OR}] = 1$). The solution was diluted in varying amounts of a noncompeting solvent (acetoni-

trile) to maintain a constant molarity of the silicon alkoxide (2.05 M). The second ratio has an excess of the reacting alkoxy group ($[\text{OR}']/[\text{OR}] > 1$) obtained by using the reacting alcohol as the diluting solvent. For purposes of comparison, Brønsted acid catalyzed samples, using trifluoromethanesulfonic acid (triflic) as the proton source, and control samples containing no added catalyst were also monitored for certain transesterification reactions. In all cases, the reaction solutions were kept scrupulously anhydrous to avoid any possible contribution to the ligand-exchange process from hydrolytic intermediates; consistent with this, no hydrolyzed or condensed species were observed in any of the uncatalyzed or metal-catalyzed solutions after 12 days. However, triflic acid catalyzed samples showed small amounts (<1%) of condensation products (Si–O–Si) after 12 days presumably from alcohol dehydration. The distributions of substitution products, expressed as a mole fraction of total silica, for all of the transesterification reactions at ~2 h and at 5 and 12 days are tabulated in Table 2.

Both titanium tetraisopropoxide and oxovanadium triisopropoxide catalyze the transesterification of silicon alkoxides. Figure 1 shows ^{29}Si NMR spectra for tetramethyl orthosilicate (TMOS) in the presence of a 4-fold excess of ethanol ($[\text{OEt}]/[\text{OMe}] = 1$) collected shortly after mixing (~2 h) and at 5 and 12 days. The solutions containing no metal complexes showed no reaction at 2 h, while at 5 days about 73% of the silicon remained as TMOS, with the remainder having been converted to $\text{Si}(\text{OMe})_3(\text{OEt})$ (26%) and $\text{Si}(\text{OMe})_2(\text{OEt})_2$ (1%). Conversely, the solutions containing oxovanadium

Table 2. Product Distribution for Transesterification of Tetraalkoxyorthosilicates with Alcohols^a

		2 h, $x =$					5 days, $x =$					12 days, $x =$					
		0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	
		$\text{Si}(\text{OMe})_{4-x}(\text{OR}')_x$															
$[\text{OR}']/[\text{TMOS}]^b$	$[\text{OEt}]/[\text{OMe}]$																
	1	Ti	0.08	0.29	0.39	0.20	0.04	0.10	0.28	0.36	0.21	0.05	0.08	0.27	0.37	0.22	0.06
		V	0.17	0.53	0.28	0.02	0.00	0.10	0.30	0.37	0.20	0.04	0.09	0.29	0.37	0.20	0.05
		H ⁺	0.09	0.28	0.36	0.22	0.06	0.08	0.26	0.37	0.23	0.06	0.06	0.25	0.38	0.25	0.06
		control	1.00	0.00	0.00	0.00	0.00	0.73	0.26	0.01	0.00	0.00	0.42	0.48	0.08	0.00	0.00
		stat.	0.06	0.25	0.38	0.25	0.06	0.06	0.25	0.38	0.25	0.06	0.06	0.25	0.38	0.25	0.06
1.5		Ti	0.05	0.20	0.37	0.29	0.08	0.05	0.20	0.37	0.29	0.10	0.04	0.20	0.35	0.31	0.11
		V	0.05	0.30	0.48	0.17	0.00	0.04	0.20	0.37	0.30	0.09	0.04	0.20	0.37	0.30	0.10
		$[\text{OPr}^n]/[\text{OMe}]$															
1		Ti	0.07	0.29	0.44	0.21	0.00	0.08	0.25	0.35	0.25	0.08	0.08	0.24	0.35	0.26	0.07
		V	0.60	0.34	0.07	0.00	0.00	0.09	0.23	0.35	0.25	0.08	0.06	0.24	0.37	0.26	0.07
		control	1.00	0.00	0.00	0.00	0.00	0.72	0.26	0.02	0.00	0.00	0.50	0.44	0.07	0.00	0.00
1.2		Ti	0.06	0.20	0.35	0.29	0.04	0.06	0.19	0.33	0.29	0.13	0.05	0.20	0.36	0.30	0.10
		V	0.26	0.52	0.21	0.00	0.00	0.07	0.22	0.33	0.28	0.11	0.05	0.20	0.36	0.30	0.10
		$[\text{OPr}^i]/[\text{OMe}]$															
1		Ti	0.24	0.68	0.09	0.00	0.00	0.07	0.37	0.54	0.03	0.00	0.07	0.32	0.52	0.09	0.00
		V	1.00	0.00	0.00	0.00	0.00	0.85	0.15	0.00	0.00	0.00	0.65	0.34	0.02	0.00	0.00
		control	1.00	0.00	0.00	0.00	0.00	0.96	0.04	0.00	0.00	0.00	0.93	0.08	0.00	0.00	0.00
1.1		Ti	0.14	0.70	0.16	0.00	0.00	0.04	0.30	0.57	0.09	0.00	0.06	0.29	0.53	0.12	0.00
		V	1.00	0.00	0.00	0.00	0.00	0.79	0.22	0.00	0.00	0.00	0.59	0.39	0.02	0.00	0.00
		$\text{Si}(\text{OEt})_{4-x}(\text{OR}')_x$															
		$[\text{OR}']/[\text{TEOS}]^b$															
		$[\text{OMe}]/[\text{OEt}]$															
1		Ti	0.48	0.27	0.14	0.08	0.03	0.05	0.24	0.38	0.26	0.07	0.05	0.24	0.38	0.26	0.07
		V	0.25	0.25	0.23	0.19	0.08	0.08	0.24	0.37	0.25	0.07	0.05	0.23	0.37	0.27	0.08
		H ⁺	0.05	0.23	0.38	0.27	0.08	0.05	0.24	0.38	0.27	0.07	0.05	0.22	0.37	0.26	0.10
		control	1.00	0.00	0.00	0.00	0.00	0.90	0.09	0.01	0.00	0.00	0.67	0.24	0.07	0.02	0.00
1.6		Ti	0.09	0.16	0.27	0.32	0.17	0.01	0.13	0.33	0.37	0.16	0.01	0.13	0.33	0.38	0.15
		V	0.07	0.15	0.29	0.33	0.15	0.01	0.12	0.33	0.38	0.16	0.02	0.12	0.34	0.38	0.15

^a Product distributions are presented as mole fractions (moles of product/total moles of silicon); errors in all values are 0.01. ^b $[\text{TMOS}] = [\text{TEOS}] = 2.05 \text{ M}$.

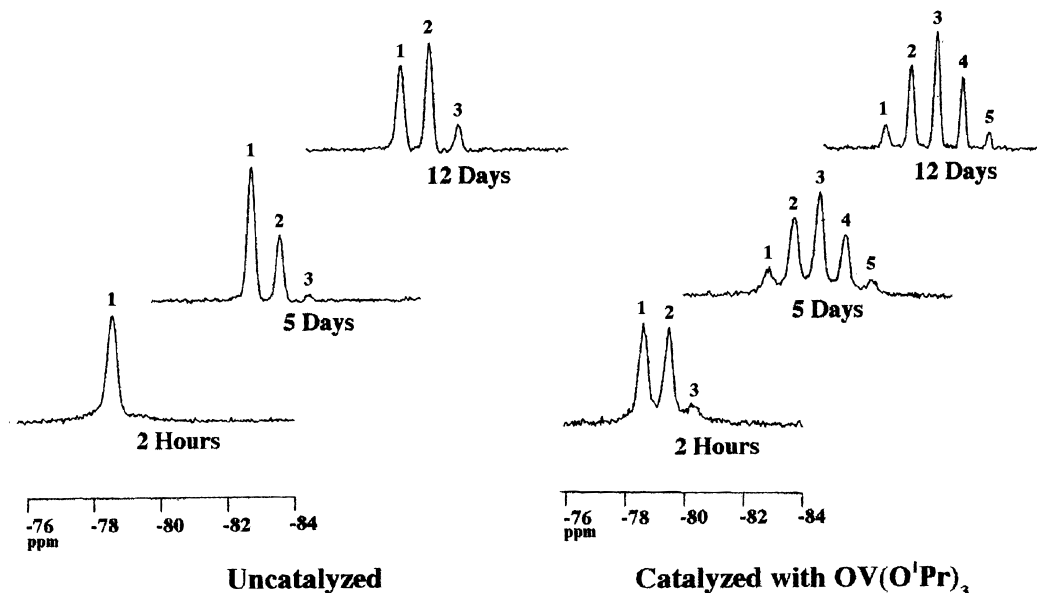


Figure 1. ^{29}Si NMR spectra of uncatalyzed (left) and oxovanadium triisopropoxide catalyzed (right) transesterification of tetramethylorthosilicate (1) with 4 equiv of ethanol ($[\text{OMe}] = [\text{OEt}]$) at 2 h and at 5 and 12 days showing the growth of mono- (2), di- (3), tri- (4), and tetraethoxy-substituted species (5) over time.

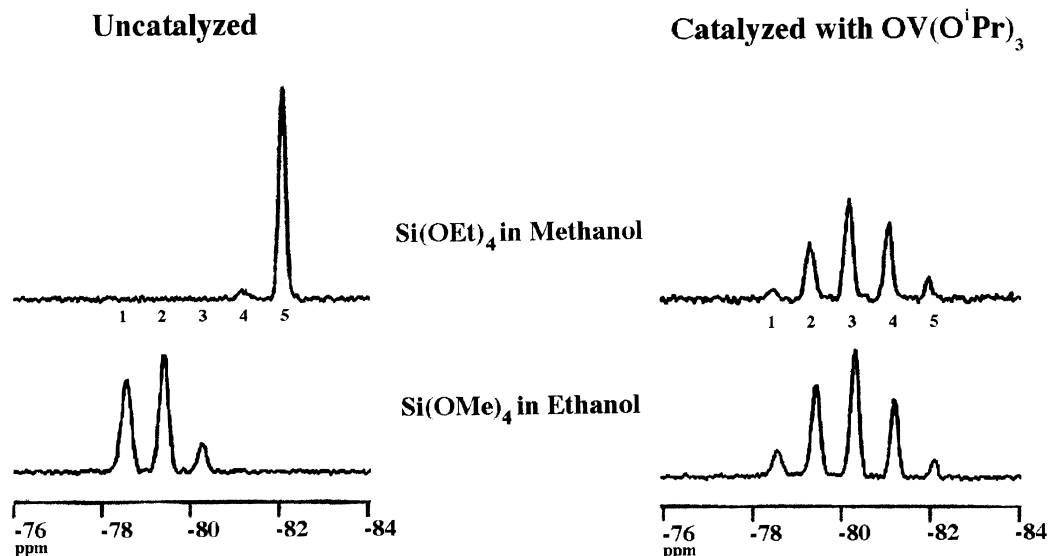


Figure 2. ^{29}Si NMR spectra of uncatalyzed and oxovanadium triisopropoxide catalyzed transesterification of tetramethylorthosilicate with 4 equiv of ethanol and of tetraethylorthosilicate with 4 equiv of methanol ($[\text{OMe}] = [\text{OEt}]$) after 12 days. In the spectra tetramethylorthosilicate is designated (1) with mono-, di-, tri-, and tetrasubstitution products designated 2, 3, 4, and 5, respectively.

triisopropoxide (Figure 1) showed significant exchange after only 2 h, while at 5 days about 10% of the silicon remained as TMOS, with the rest having been converted to all of the substitution products including TEOS.

A number of trends can be observed in the data presented in Table 2. For the uncatalyzed substitution of TMOS by ethanol and TEOS by methanol ($[\text{OR}]/[\text{OR}] = 1$) it was observed that TMOS is much more readily substituted, with 26% of it having been converted to $\text{Si}(\text{OMe})_3(\text{OEt})$ after 5 days. Under the same conditions only 9% of the TEOS was converted to $\text{Si}(\text{OEt})_3(\text{OMe})$ (Figure 2). Even with *n*-propanol, TMOS shows a much higher degree of substitution than TEOS does with methanol. This suggests that, within this range of reacting alcohols, the nature of the silicon alkoxide dominates the kinetics. For TMOS, the degree of uncatalyzed substitution with ethanol and that with

n-propanol are essentially identical, while significant inhibition is ultimately observed with 2-propanol, for which only a small amount (8%) of monosubstitution is achieved after 12 days.

The preferential substitution of TMOS over TEOS, observed in the uncatalyzed reactions, is not apparent in the metal-catalyzed reactions. In fact, as shown in Table 2 and illustrated for V(V) in Figure 2, the metal-catalyzed substitution of TEOS by methanol is more facile by a small but statistically significant amount, as evidenced by the greater amounts of higher substitution products present at both 5 and 12 days. This result, which is directly counter to the uncatalyzed case, seems to suggest that the steric constraints inherent to the silicon alkoxide are overcome, to an extent, by the metal. Interestingly, the relative product distributions suggest that the substitution of TMOS with *n*-propanol is more

facile than it is with ethanol. This is a somewhat anomalous, albeit reproducible, result that is not easily rationalized by either steric or electronic arguments. With 2-propanol as the reacting alcohol, the degree of metal-catalyzed substitution over time declines significantly for both silicon alkoxides, but it is still much greater than in the uncatalyzed case.

Most previous studies of silicon alkoxide transesterification have used Brønsted acids as catalysts. For direct comparison to the metal systems and so that comparisons with previous work can be made, we catalyzed several of the reactions with trifluoromethanesulfonic acid (triflic) in an amount equal to the concentration of metal used. This acid was used so that anhydrous conditions could be maintained. In general, triflic acid catalyzed transesterification reactions are orders of magnitude faster than those catalyzed by the metals. Significant transesterification was observed after only 2 h for both TMOS/ethanol and TEOS/methanol, with over 90% of the starting silicon concentration converted to substitution products during this period. For TEOS/methanol, the reaction was essentially complete after 2 h, with little further change in the product distribution observed after 5 days. For TMOS/ethanol the reaction was not quite as fast; however, changes in the product distribution between 5 and 12 days were within experimental error, and by this criterion, the system was judged to have reached equilibrium. This rapid equilibrium time is consistent with observations made by Hasegawa for (anhydrous) acid-catalyzed transesterification of TEOS by butyl alcohols.¹⁴ For the metal-catalyzed systems, the TEOS/methanol and TMOS/*n*-propanol transesterifications were judged to be at equilibrium after 12 days by the criterion outlined above. For the case of TMOS/ethanol, however, small but statistically significant changes in product distribution were observed between 5 and 12 days, making it less certain that equilibrium had been reached. Notably, since TEOS/methanol and TMOS/ethanol transesterifications are the forward and reverse of the same reaction, there is a simple inverse relationship between the equilibrium constants (e.g., K^1 for TMOS/ethanol = $(K^4)^{-1}$ for TEOS/methanol) which should hold if the systems are at equilibrium. In the case of these two metal-catalyzed systems at 12 days, the agreement is reasonably good, suggesting that both systems are essentially at equilibrium. The equilibrium constants for all of the transesterification reactions are tabulated in Table 3.

Scrutiny of the product distributions (Table 2) and equilibrium constants (Table 3) suggests that, for a given substitution, the equilibrium lies slightly to the right for TEOS/methanol and slightly to the left for TMOS/ethanol. This would be consistent with decreased steric crowding upon substitution in the former case and increased crowding in the latter. It should be emphasized, however, that this difference in equilibrium position is small and not always statistically significant so that, in effect, both systems come to extremely similar equilibrium positions for each substitution. In fact, all of these equilibria are quite close to a statistical distribution; this has been noted previously for ethanol

Table 3. Equilibrium Constants^a for Transesterification Reactions

	K^1	K^2	K^3	K^4
TMOS/EtOH ^b				
Ti	3.0(1)	1.2(1)	0.54(2)	0.26(2)
V	2.8(1)	1.1(1)	0.47(2)	0.20(2)
H ⁺	4.3(1)	1.5(1)	0.65(2)	0.22(2)
TMOS/Pr ⁱ OH				
Ti	3.1(1)	1.5(1)	0.74(2)	0.29(2)
V	4.1(1)	1.6(1)	0.73(2)	0.28(2)
TEOS/MeOH				
Ti	5.2(2)	1.7(1)	0.77(2)	0.29(2)
V	4.8(2)	1.7(2)	0.81(2)	0.30(2)
H ⁺	5.7(2)	2.0(1)	0.81(2)	0.45(2)

^a Calculated as

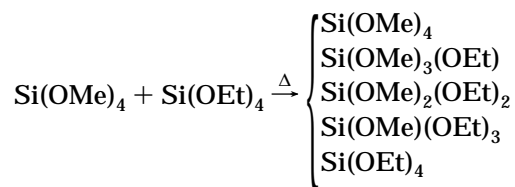
$$K^{(x+1)} = \frac{[\text{Si}(\text{OR})_{3-x}(\text{OR}')_{x+1}][\text{HOR}]}{[\text{Si}(\text{OR})_{4-x}(\text{OR}')_x][\text{HOR}']}, x = 0-3.$$

^b May not have quite achieved equilibrium.

transesterification of TMOS catalyzed by aqueous HCl.¹⁵ Also, for these less sterically crowded systems, there appears to be little difference in the final product distribution between Brønsted and metal (Lewis acid) catalysis, though the rate of reaction is much faster for the former. Substitution of 2-propanol is inherently difficult regardless of the catalyst, but as with the other reactions, the triflic acid is a much more efficient catalyst and is the only catalyst capable of generating Si(OPrⁱ)₄ during the 12-day period.

As outlined above, there are a number of trends in the transesterification of silicon alkoxides that can be generalized to both Ti(IV) and V(V). Notably, however, there are distinct differences between these two metals in terms of their ability to induce transesterification. For the reaction of TMOS with ethanol and *n*-propanol and of TEOS with methanol, both metals appear to behave analogously giving very similar product distributions at 5 and 12 days. In the case of 2-propanol substitution, the reactivity differences between the two metals become striking, with titanium observed to be overwhelmingly more efficient than vanadium in catalyzing the process (Figure 3). At 5 days titanium had consumed 93% of the TMOS and 72% of the TEOS achieving trisubstitution for TMOS and disubstitution for TEOS. Conversely, vanadium had converted only 15% of the TMOS to monosubstituted product, [Si(OMe)₃(OPrⁱ)], and had not substituted TEOS at all. At 12 days, the reaction lay only slightly further to the right for both metals with a small amount (2%) of disubstituted TMOS appearing for the vanadium-catalyzed samples. Substitution of TEOS with 2-propanol could not be accomplished with vanadium.

The cross-transesterification of TMOS and TEOS was



also investigated. As shown in Figure 4, an equimolar mixture of TMOS and TEOS showed no reaction after

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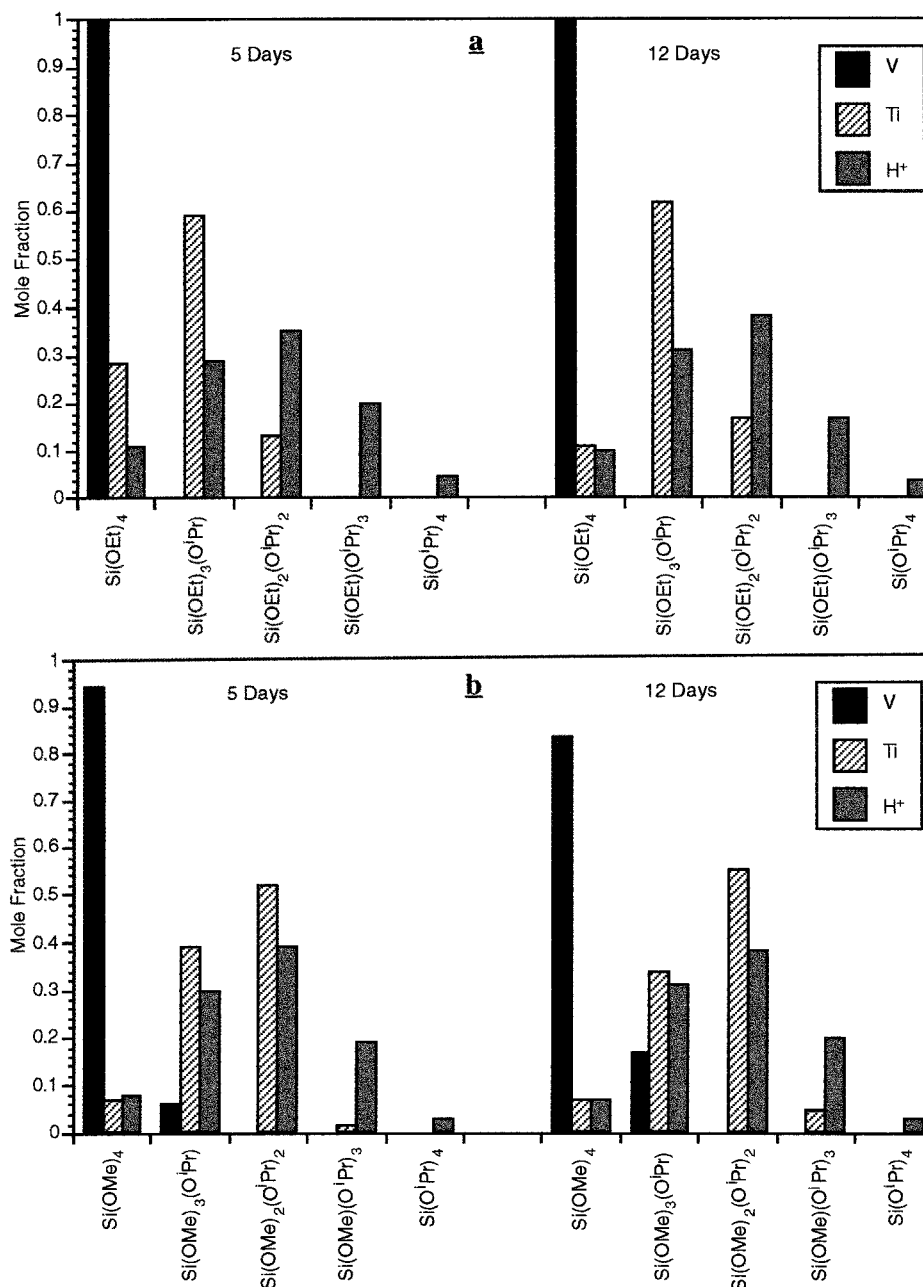


Figure 3. Distribution of isopropoxy substitution products (in mole fraction of total silicon) of (a) tetraethyl- and (b) tetramethylorthosilicate ($[TMOS] = [TEOS] = 1.36$ M) at 5 and 12 days as catalyzed by triflic acid, titanium tetrakisopropoxide, and oxovanadium triisopropoxide.

a period of 2 h either in the absence of catalyst or in the presence of 0.01 M oxovanadium triisopropoxide. As in the 2-propanol transesterification reactions, Ti(IV) is the more efficient catalyst, producing equimolar amounts of monosubstituted products $Si(OMe)_3(OEt)$ and $Si(OEt)_3(OMe)$ along with a small amount (5.6%) of disubstituted product $Si(OEt)_2(OMe)_2$ in the first 2 h. After 1 day (Figure 4), however, both metal-catalyzed systems had reached a statistical distribution of substitution products, while the uncatalyzed reaction still had not substituted. Further studies of this cross reaction revealed a rather dramatic temperature effect. Freshly made solutions, equimolar in TMOS and TEOS and containing either V(V) or Ti(IV) (0.01 M), were plunged for 5 min into an 85 °C thermostated water bath, at which point the solution had reached a temperature of 82 °C. ^{29}Si NMR spectra, run immediately

after immersion, showed complete scrambling of the alkoxy groups giving almost exactly a statistical distribution of products, which suggests that equilibrium had been reached (Figure 3). No reaction was observed for the uncatalyzed sample treated under identical conditions. The fact that equilibrium for the cross-transesterification was reached so quickly under such mild heating suggests the existence of a relatively small activation barrier for this process.

Transesterification is generally believed to proceed via the nucleophilic attack of an alcohol on the silicon alkoxide.¹⁶ Brønsted acids are thought to catalyze this reaction by protonating the oxygen on the alkoxide group thereby making it a better leaving group (Scheme 2).

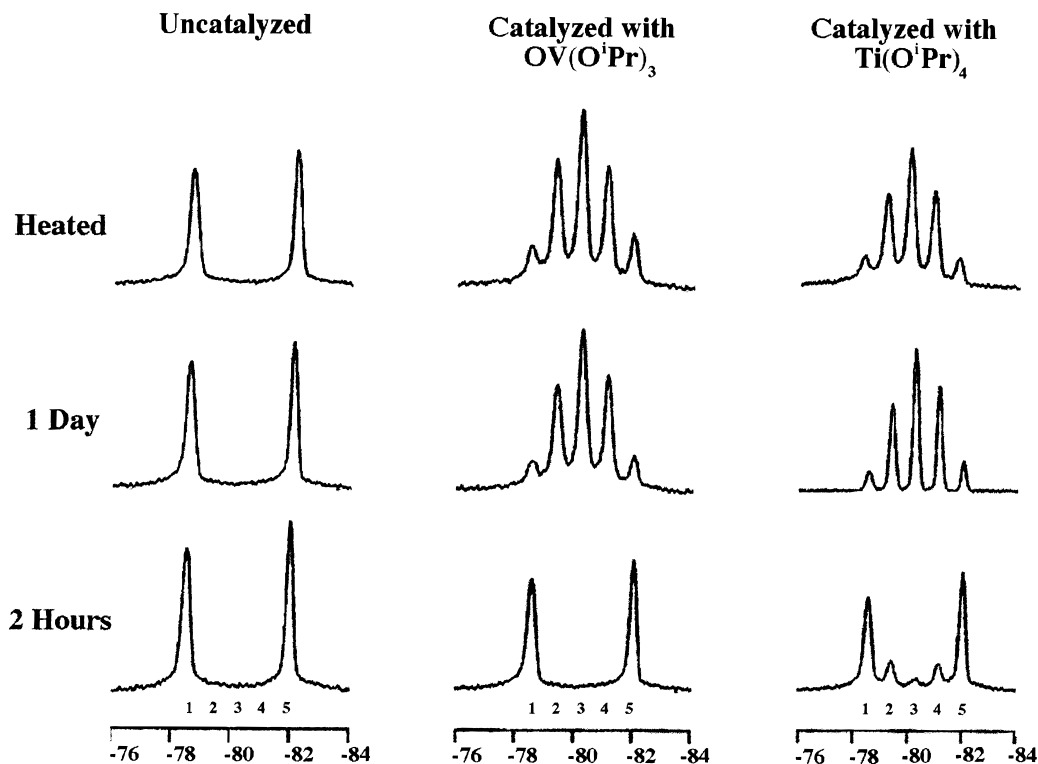
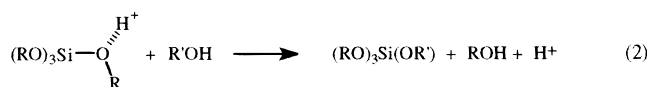
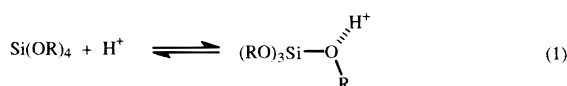
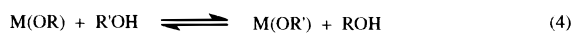
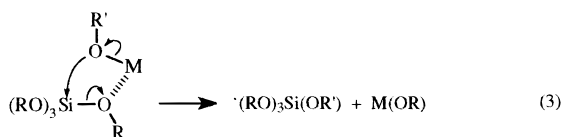
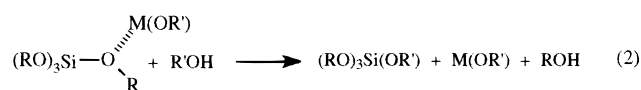
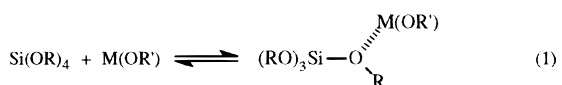


Figure 4. ^{29}Si NMR spectra of uncatalyzed, oxovanadium triisopropoxide catalyzed, and titanium tetraisopropoxide catalyzed cross-transesterification of equimolar concentrations of tetramethyl- and tetraethylorthosilicate at 2 h, 1 day, and after being heated at 85 °C for 5 min.

Scheme 2



Scheme 3



For Lewis acids such as V(V) and Ti(IV), a similar interaction can be postulated whereby the nonbonding electrons on the alkoxide oxygen form a coordinate bond with empty d orbitals on the metal. This coordination process, written as an equilibrium in Scheme 3, rxn 1, generates an activated complex, which is substitutionally labile. Unlike the proton-catalyzed reaction, however, alkoxide metathesis at the activated complex can occur by two possible mechanisms. The first (Scheme 3, rxn 2), which is analogous to proton catalysis, involves

nucleophilic attack of the silicon by the entering alcohol. The second (Scheme 3, rxn 3) is a unimolecular reaction in which alkoxides exchange between the metal and the silicon in the activated complex. This complex then decomposes into the observed products with the metal center subsequently exchanging with more of the entering alcohol to regenerate the catalysts (Scheme 3, rxn 4). In this mechanism, which is unique to metal-catalyzed transesterification, the inherent lability of the metal center to alkoxide exchange acts to shuttle alkoxy groups between the silicon and the metal.

For the vanadium-catalyzed systems, key steps in the overall mechanism can be probed directly by ^{51}V NMR spectroscopy. For the conditions under which the transesterification reaction is carried out, the metal alkoxide exchanged immediately with the excess alcohol present in the solution (Scheme 3, rxn 4).¹⁷ In particular, the ^{51}V NMR spectrum of oxovanadium triisopropoxide dissolved in 2-propanol showed a single sharp resonance at -631 ppm (relative to VOCl_3) (Figure 5a).¹⁸ Addition of small amounts ($[\text{R}'\text{OH}]/[\text{V}] = 3$) of methanol or ethanol resulted in the immediate appearance of broad peaks at -606 and -621 ppm (Figure 5b,c), which we assigned to mixed oxovanadium isopropoxide-methoxide and -ethoxide partial substitution products, respectively. The observed downfield shift in the ^{51}V NMR resonances, in conjunction with the significant broadening, is attributed to dimerization or oligomerization of the resulting vanadium alkoxide species.^{18,19} This association occurs with the addition of methoxide or

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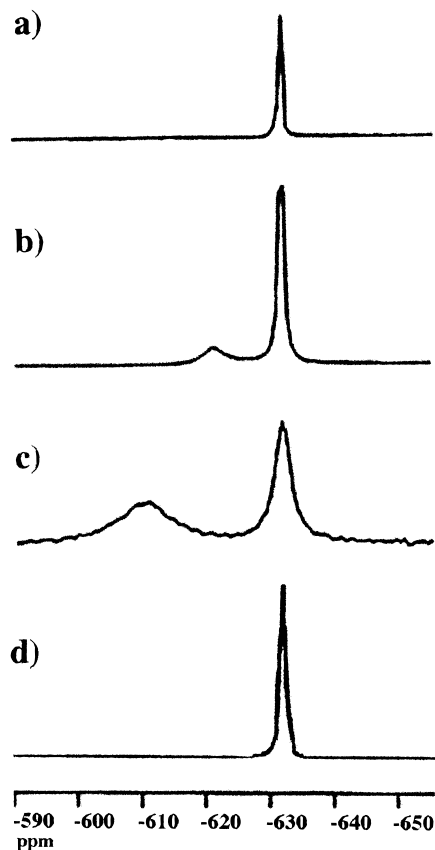


Figure 5. ^{51}V NMR of oxovanadium triisopropoxide in 2-propanol (a) and after the addition of 3 equiv of (b) ethanol, (c) methanol, and (d) 4.6 M tetramethylorthosilicate.

ethoxide to the coordination sphere due to the decrease in steric constraints. Notably, this does not occur at all with isopropoxide, which remains essentially monomeric in dilute solution. Addition of excess methanol or ethanol to the solution produces peaks at -458 and -443 ppm associated with the complete substitution products, oxovanadium trismethoxide and trisethoxide, respectively.¹⁹ This result not only verifies that the catalyst regeneration reaction shown in Scheme 3 (rxn 4) occurs but it further suggests that the active catalyst may differ depending on the nature of the entering alcohol. While we have indicated that the catalyst is monomeric in Scheme 3, it may in fact be a dimer or a higher order oligomer, all of which could have different catalytic properties. Furthermore, this observation also suggests that as the alcoholic composition of the solution changes over time, so does the nature of the active catalyst.

Direct evidence for the formation of the activated complex (Scheme 3, rxn 1) was not observed by ^{51}V NMR. In general, ligand/metal systems with strong coordination interactions, such as acetonitrile and VOCl_3 , give complexes with new resonances well upfield (e.g., -114 ppm for the acetonitrile/ VOCl_3 adduct) from the uncoordinated species.¹⁸ Vanadium alkoxides, however, show relatively modest chemical shifts even in coordinating solvents such as acetonitrile and tetrahydrofuran, suggesting that such interactions are weaker for these species. Addition of TMOS to attain concentrations of 0.6, 1.2, 2.3, and 4.6 M in a 0.02 M solution of oxovanadium triisopropoxide in 2-propanol resulted in

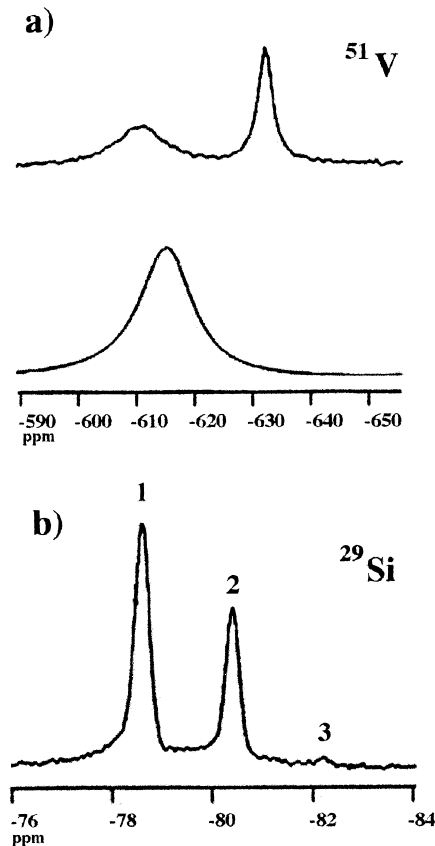


Figure 6. (a) ^{51}V NMR of oxovanadium triisopropoxide in 2-propanol (top) after the addition of 3 equiv of methanol and (lower) mixed in an equimolar amount with tetramethylorthosilicate. (b) ^{29}Si NMR of a solution containing equimolar amounts of oxovanadium triisopropoxide and tetramethylorthosilicate (1) showing the formation of mono- (2) and disubstituted (3) products.

no new peaks, nor was there any broadening or shift in the existing -631 ppm resonance. The formation of an activated complex which is a true intermediate (Scheme 3, rxn 1) implies a relatively strong interaction. Therefore, the absence of any perturbation in the ^{51}V NMR spectrum, even at high concentrations of silicon esters, suggests either that the steady-state concentration of the intermediate is small or that the reaction may proceed via a transition state rather than a true intermediate. In the latter case, the ligand transfer from the metal to the silicon, and vice versa, occurs concomitant with association so that, in effect, rxns 1 and 3 in Scheme 3 occur as a single concerted process. In either case, this would imply that the proposed bimolecular reaction between the activated complex and an entering alcohol (Scheme 3, rxn 2) is unlikely.

Ligand exchange between the vanadium and the silicon can be observed directly by both ^{29}Si and ^{51}V NMR (Figure 6). Addition of oxovanadium triisopropoxide to TMOS (1:1) in the absence of solvent shows formation of $\text{Si}(\text{OMe})_3(\text{OPr}^i)$ and $\text{Si}(\text{OMe})_2(\text{OPr}^i)_2$ on the basis of their characteristic ^{29}Si resonances at -79 and -81 ppm, respectively (relative to TMS). Conversely, ^{51}V NMR of solutions containing TMOS and the vanadium complex at equimolar ratios shows the formation of a broad peak at -614 ppm (Figure 6) which lies between those of oxovanadium triisopropoxide (-631 ppm) and the mixed isopropoxide/methoxide species

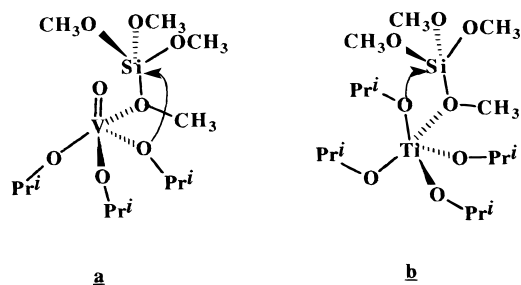


Figure 7. Proposed mechanism for alkoxide exchange in (a) oxovanadium trisopropoxide and (b) titanium tetraisopropoxide.

(−606 ppm) observed previously and, as such, represents the superposition of these resonances.

In the case of titanium-catalyzed transesterification, similar reaction steps have been reported. In particular, the cross-transesterification of titanium tetraisopropoxide and TEOS were studied thoroughly by Diré and Babonneau, whose observations directly parallel ours for vanadium.²⁰ Spontaneous ligand exchange between the titanium and silicon centers, yielding products of mixed substitution, was observed via ²⁹Si and ^{47,49}Ti NMR. Also observed was the subsequent complexation of the titanium into dimeric and oligomeric species as steric crowding was reduced with ligand exchange.

As discussed, titanium is a more facile transesterification catalyst than vanadium. This difference in reactivity is evident in all the systems studied but becomes dramatic in the case of 2-propanol substitution. It is difficult to rationalize this difference on electronic grounds since the vanadium, with its higher oxidation state, would be expected to activate the silicon to a greater extent and, hence, be more reactive. Given that the differences in reactivity become much more pronounced when substitution with bulky alcohols is attempted, steric factors seem to clearly dominate. In the case of vanadium and titanium metathesizing the same substrate, differences in reactivity must be due to differing steric environments around the metal. Structurally, the vanadium and titanium complexes differ primarily by the presence of the short terminal oxygen on the vanadium. This group is present regardless of

the degree of oligomerization of the complex and affords a region of low steric congestion. In forming the activated complex (or transition state) the silicon alkoxide is likely to orient preferentially into this region and away from the alkoxides bonded to the metal (Figure 7a). While this is a lower energy structure, it is not a favorable geometry for ligand migration and, hence, would make the process less efficient. The preferential orientation of the silicon substrate would be more pronounced with bulky groups such as isopropoxides around the metal, which is consistent with the data. The titanium complexes would not strongly favor any particular orientation, and any activated complex or transition state formed would have the alkoxy groups in close proximity for metathesis (Figure 7b).

Conclusions

Early transition metal complexes, specifically titanium and vanadium alkoxides, catalyze the transesterification of silicon alkoxides. These Lewis acid species accelerate the metathesis markedly over the uncatalyzed reaction. They are significantly less efficient, however, than equivalent amounts of strong Brønsted acids. Mechanistically, the transesterification appears to occur, at least in part, by ligand transfer between the metal and silicon centers. The consequences of this are that steric factors strongly influence the rate of the process and that differences in the coordination geometry around the metal centers strongly affect the efficiency of the catalyst.

From the standpoint of making mixed metal/silica materials via the sol–gel process, these results suggest that the presence of early, high-valent transition metals such as these is likely to affect reaction processes of the silicon. In mixed alcohol systems, the transesterification process will change the alkoxide group on the silicon thereby altering the kinetics of hydrolysis. These results also suggest that other metathesis reactions central to the sol–gel process such as hydrolysis and its reverse, alcoholysis, may also be catalyzed by these metals.

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CM970803U

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