carbon of the cation. This carbonyl species has a sufficient lifetime to undergo CO dissociation before undergoing heterolytic cleavage to the most stable cation-anion combination. Eventually homolytic cleavage leads to the final bimetallic complexes.

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Olefin Polymerization by Vanadium-Containing Polyhedral Oligometallasilsesquioxanes

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Numerous catalysts have been developed, studied, and commercialized for the production of polyolefins.[1] A large fraction of these catalysts, especially the industrially relevant ones, are heterogeneous systems prepared by the deposition of soluble Ti, Zr, or Cr-containing precursors on high surface area supports, such as silica or alumina. Recently, however, silica-supported vanadium catalysts have attracted attention as olefin-polymerization catalysts because their excellent hydrogen response and high comonomer incorporation potentially allow greater control over the properties of the polymer.[2]

We recently reported[3] the synthesis and characterization of several vanadium-containing polyhedral oligometallasilsesquioxanes (POMSS) as part of our efforts to develop homogeneous models for silica-supported catalysts.[4,5] In this paper we report that the reaction of one such complex (i.e., **2**) with trialkylaluminum reagents produces a catalyst that is capable of polymerizing or copolymerizing α-olefins. Although the active catalyst in this system has yet to be identified, the similarity between **2** and surfaces sites that have purportedly been identified on monodisperse silica-supported vanadates[6] suggests that detailed studies of vanadium-containing POMSS may provide new insights into mechanisms by which silica-supported vanadium catalyzes the polymerization of olefins.

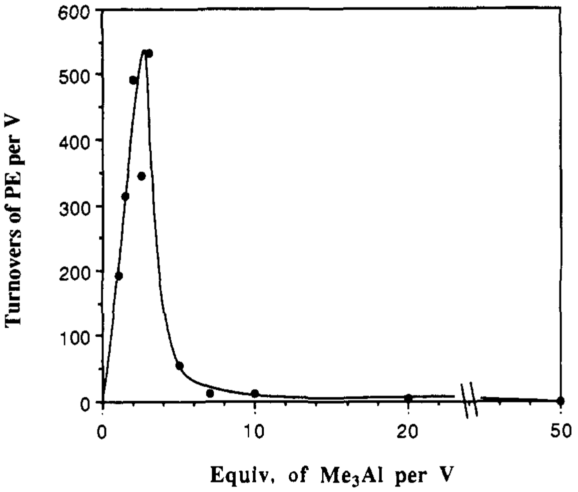
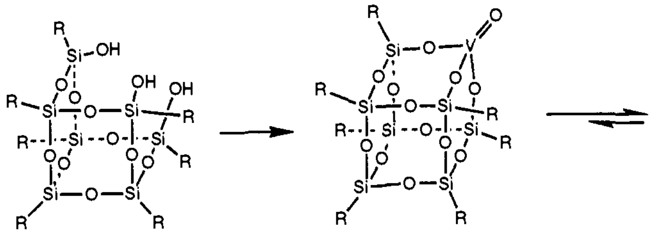
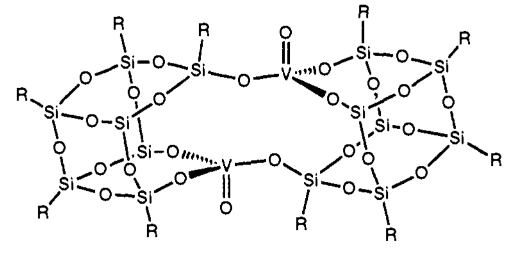


Figure 1. A plot illustrating the dependence of ethylene polymerization activity (i.e., average number of turnovers[7c] per V) on the number of equivalents of Me_3Al added to **2**. All reactions were performed under identical conditions (33.7 μmol of **2** in 10 mL of C_6H_6, 25 °C, 720 Torr of C_2H_4) and quenched with 2-propanol after 3 h.

As reported previously,[3] vanadates **2** and **3**, which can be prepared from the reaction of **1** with $(n\text{-PrO})_3VO$, $(Me_3SiCH_2)_3VO$, or $VOCl_3$, are components in a monomer/dimer equilibrium ($\Delta H° = -6.02 \pm 0.27$ kcal/mol and $\Delta S° = -17.1 \pm 0.2$ eu). The dimerization of **2** is enthalphically favored, but at concentrations less than 10 mM and/or temperatures greater than 25 °C, the major (>95%) V-containing species is **2**.



1 R = c-C_6H_{11} 2



3

The addition of Me_3Al (1-5 equiv/V) to benzene or hexane solutions containing **2** at 25 °C produces straw-colored solutions which readily polymerize ethylene.[7] At 25 °C, ethylene pressures of 1 atm, and vanadium concentrations of 3 mM, ethylene polymerization typically proceeds for 1000-1500 turnovers[7c] before gelation of the solution prevents further uptake of ethylene and

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[7] (a) Matheson polymerization grade ethylene and propylene were purified by slow bubbling through tri-*n*-octylaluminum, followed by two freeze-pump-thaw (-196 °C/10^{-3} mTorr/25 °C) degas cycles. (b) Except were indicated, each polymerization reaction reported in this paper was performed by the addition of Me_3Al (1.03 M in toluene) to **2** (35 mg, 0.0337 mmol) in 10-50 mL of solvent. Reactions were quenched by the addition of excess 2-propanol/hexane. The crude polymers were stirred overnight in 2-propanol/hexane and then collected by filtration or decantation and dried in vacuo (~60 °C, 10^{-5} Torr, 1-2 days). Evaporation of the 2-propanol/hexane washes typically afforded silsesquioxane residues, but small amounts of oily polymers or oligomers were obtained from the reactions with propylene. (c) The "number of turnovers" was defined as (grams of PE/28)/(total moles of V present in the reaction mixture). (d) The reaction of **1** with Me_3Al affords an interesting siloxy-bridged complex[4c] which does not initiate olefin polymerization.

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leads to deactivation of the system. GPC analysis of the polymer indicated M_n and M_w values of 21 000 and 47 900 daltons (Da), respectively, and a DSC curve for the polymer exhibited no detectable exotherm prior to the onset of crystalline melting at 131.6 °C. In contrast, the reactions of $(Ph_3SiO)_3VO$ and $(n\text{-}PrO)_3VO$ under identical conditions gave no polyethylene; the only observable reaction (by ^{51}V NMR) was metathesis of alkyl ligands on Al for alkoxide ligands on V.[7d,8] We have not extensively explored the use of other cocatalysts with **2**, but we have observed similar activities with Et_3Al and somewhat lower activities with $(Me_3SiCH_2)_3Al$.

A survey of the catalyst's reactivity indicates that other olefins can also be polymerized or copolymerized, although not as efficiently as ethylene. For example, the reaction of **2** and Me_3Al (3 equiv) in propylene (25 °C, ~8 atm, 3 h) gave a small amount (~125 turnovers) of atactic polypropylene[9] (MW < 10 000). Similarly, the copolymerization of ethylene (1%) in neat propylene produced small amounts (~350 turnovers) of copolymer, which contained 5–10% propylene (by ^{13}C NMR).[9] One olefin that is polymerized well by our catalyst is 1,3-butadiene; an ampule containing 50 mL of neat butadiene (bp −4.5 °C) completely solidifies within 30 min to create a partial vacuum inside the ampule. ^1H and ^{13}C NMR spectroscopy[10] indicated that the resulting product was >95% *trans*-1,4-polybutadiene.[11]

The activity of the catalyst is sensitive to the amount of Me_3Al used. As shown in Figure 1, polyethylene production (1 atm, 25 °C, 3 h) is maximized when approximately 3 equiv of Me_3Al is used as cocatalyst. Large excesses of Me_3Al lead to complete deactivation of the catalyst. Both observations are contrary to the behavior of typical "soluble catalysts"[12] prepared from trialkylvanadates, which typically require large excesses of alkylaluminum reagents (15–500 equiv) to initiate olefin polymerization.[13] In light of the narrow polydispersity measured for our polyethylene sample (2.28), these results suggest that a well-defined catalyst is being formed[14] and that this catalyst is fundamentally different from these conventional soluble V catalysts.

The presence and equilibration of both **2** and **3** in the starting solution greatly complicate mechanistic studies, but several polymerization reactions performed at −30 °C, where the equilibration of **2** and **3** is negligibly slow, indicate that the active catalyst is derived from the reaction of **2** with Me_3Al. Specifically, the addition of Me_3Al to an ethylene-saturated solution of **2** and **3** (~10:90 by ^{51}V NMR) at −30 °C initiates ethylene polymerization by slowly consuming **2**, but does not affect the amount of **3** in solution. Furthermore, ethylene polymerization is only initiated when the ^{51}V NMR resonance for **2** is initially present.

The active polymerization catalyst(s) in our system is (are) currently not known, and it would be inappropriate to speculate about its identity without additional data.[15] It is, however, important to note that this POMSS-based catalyst is capable of polymerizing olefins when stoichiometrically similar complexes (e.g., $(Ph_3SiO)_3VO$ and $(n\text{-}PrO)_3VO$) show little or no reactivity. Since our understanding of surface catalysis is both based upon and inherently limited by known reaction chemistry of solution complexes, the unique chemistry of V-containing POMSS may provide new insights into the chemistry of silica-supported vanadate catalysts. Efforts to elucidate the active polymerization catalyst(s) in this interesting system are currently in progress.

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(11) Neither pure **2** nor pure Me_3Al reacts with 1,3-butadiene, and only trivial amounts of 1,3-butadiene are polymerization by $(Ph_3SiO)_3VO/Me_3Al$ or $(n\text{-}PrO)_3VO/Me_3Al$ under identical conditions.

(12) The term "soluble" has been used quite loosely to describe catalyst solutions that appear to remain homogeneous.[13b] In many instances, serious questions can be raised regarding the apparent homogeneity of the catalyst.

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(15) A referee has suggested that a V(IV) species might be the active catalyst. This is clearly a reasonable hypothesis, but we have prepared $[(c\text{-}C_6H_{11})_7Si_7O_{12}V(CH_2SiMe_3)]$ and found that it does not initiate ethylene polymerization. The synthesis of this complex and the results from our other efforts to elucidate the identity of the polymerization catalyst(s) will be reported in a subsequent article.

2D Nuclear Magnetic Resonance Study of the Structure of the Fullerene C_{70}

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Geodesic structures were developed by R. Buckminster Fuller[2] on the basis of his insight into their structural economy and stability. In 1985, similar considerations led Smalley, Kroto, et al.,[3] to propose that C_{60}, observed in carbon cluster beam experiments,[3,4] possessed the geometry of a soccer ball, and they named it "Buckminsterfullerene". Their prediction of the stability of this molecule, as well as other fullerenes, has been stunningly verified by the recent synthesis of macroscopic amounts of C_{60} and C_{70}.[5-8] This development has sparked intense research activity in the production and characterization of these materials.[8-18] Raman[9,18]

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