

Part I. Synthesis and Thermolysis of $\text{CpMoO}_2(\text{OR})$ and $\text{Cp}^*\text{MoO}_2(\text{OR})$
 Part II. Structural Characterization of Polysilicate
 Intermediates Formed During Sol-Gel Polymerization

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Final Seminar

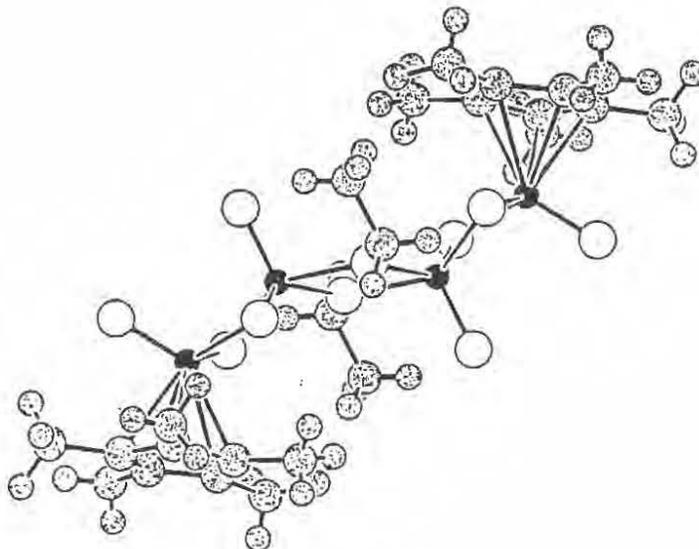
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Part I. Molybdenum trioxide is used commercially as a catalyst for the partial oxidation of methanol to formaldehyde (eq. 1) [1]. It has been



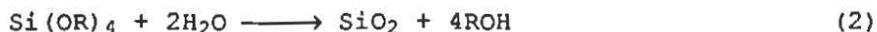
shown that the alcohol is chemisorbed to form surface molybdenum methoxides and then, in the rate limiting step, the C-H bond is cleaved and formaldehyde is released [2]. The thermolytic behavior of a series of model compounds for alkoxides on a MoO_3 surface, $[(\text{P}_3\text{O}_9)\text{MoO}_2(\text{OR})]^{2-}$, indicated that, contrary to previously proposed mechanisms [3], oxidation of surface alkoxides could occur at one molybdenum center [4].

In order to elucidate further the mechanism of β -H transfer in molybdenum(VI) dioxo alkoxides, the compounds $\text{LMoO}_2(\text{OR})$ ($\text{L} = \eta^5\text{-C}_5\text{H}_5$, $\text{R} = \text{Et}$, $i\text{-Pr}$; $\text{L} = \eta^5\text{-C}_5\text{Me}_5$, $\text{R} = \text{Me}$, Et , $i\text{-Pr}$) were prepared and their thermal reactivities compared with those of the $[(\text{P}_3\text{O}_9)\text{MoO}_2(\text{OR})]^{2-}$ complexes. The $\text{CpMoO}_2(\text{OR})$ compounds were prepared by addition of alcohol and an equivalent of base to CpMoO_2Br . The $\text{Cp}^*\text{MoO}_2(\text{OR})$ compounds were prepared by the transesterification of $(\text{Cp}^*\text{MoO}_2)_2\text{O}$ with an excess of alcohol. Single crystal X-ray diffraction studies revealed that the Mo-O bond lengths in $\text{CpMoO}_2(\text{OEt})$ and $\text{Cp}^*\text{MoO}_2(\text{OEt})$ were about 0.025 Å longer than those in $[(\text{P}_3\text{O}_9)\text{MoO}_2(\text{OEt})]^{2-}$. The Oxygen-17 NMR chemical shifts of the terminal oxygens showed that electron donation increased in the order $(\text{P}_3\text{O}_9)^{2-} < \text{Cp} < \text{Cp}^*$. Thermolysis of $\text{CpMoO}_2(\text{O-}i\text{-Pr})$ at 55°C in CD_3CN produced, after a 10 minute induction period in which no organic products were observed, equal amounts of acetone and 2-propanol. Thermolysis of $\text{CpMoO}_2(\text{OEt})$ produced ethanol and small amounts of acetaldehyde. Acetaldehyde was found to react readily with $\text{CpMoO}_2(\text{OEt})$ to produce acetal and $(\text{CpMoO}_2)_2\text{O}$. Thermolysis of $\text{Cp}^*\text{MoO}_2(\text{OEt})$ at 80°C in CD_3CN resulted in the formation of half an equivalent of ethanol, half an equivalent of tetramethylfulvene, and 1/4 equivalent of $[(\text{Cp}^*\text{MoO}_2)_4(\text{OEt})]_2$ (see A).

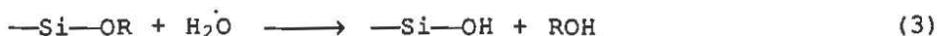


The thermal decomposition pathways of $\text{CpMoO}_2(\text{OR})$ and $\text{Cp}^+\text{MoO}_2(\text{OR})$ stand in contrast to the thermal decomposition of $[(\text{P}_3\text{O}_9)\text{MoO}_2(\text{OEt})]^{2-}$, which at 180°C in CD_3CN produced, with no induction period, half an equivalent of acetaldehyde and half an equivalent of ethanol [4]. Since comparable reactivity was not observed between these systems, no new conclusions could be reached regarding the mechanism of the oxidation of alcohols over MoO_3 .

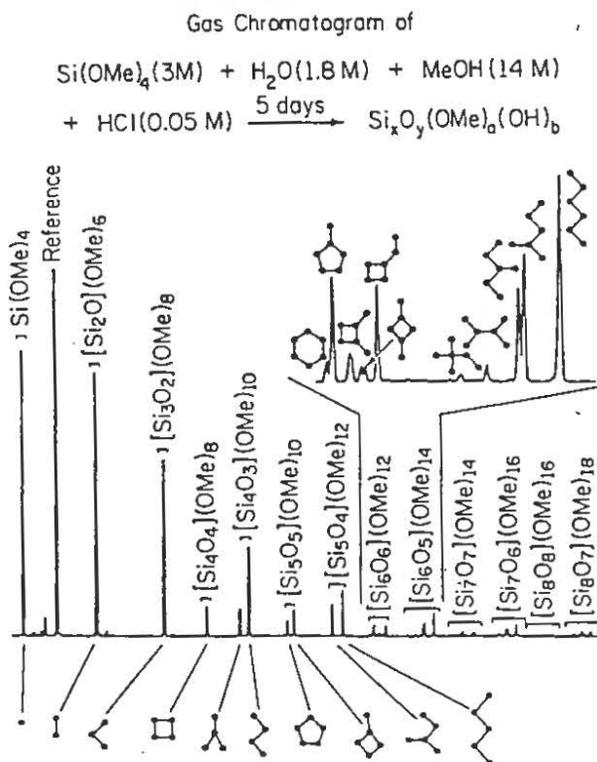
Part II. The synthesis of silica by sol-gel polymerization (eq. 2) is a promising technique for the preparation of glass coatings or for applica-



tions where conventional high temperature processing is undesirable [5]. Silica sol-gel polymerization proceeds by silicate ester hydrolysis (eq. 3) and condensation (eq. 4) [6].



In order to understand the process of sol-gel polymerization more completely, the molecular growth pathways operating in the hydrolysis and condensation of tetramethylorthosilicate have been examined [7]. This study required the quantitative identification of the silicate ester oligomers $[\text{Si}_n\text{O}_m](\text{OR})_{4n-2m}$, $\text{R} = \text{H}$ or CH_3 , which were present in the solution during sol-gel polymerization. To accomplish this goal, complex silica sol-gel mixtures were separated into several simpler samples which were characterized by gas chromatography and mass spectrometry [8]. The contents of each



sample were structurally characterized and quantified by $^{29}\text{Si}\{^1\text{H}\}$ NMR techniques (1-pulse, 1D-INADEQUATE and 2D-INADEQUATE) [9]. By comparing the NMR data with the gas chromatographic data, structural assignments were made and response factors were calculated for each of the components separated by gas chromatography. The structural assignments are summarized in B. In this figure each dot represents a Si atom and the interconnecting lines represent bridging oxygens. Terminal methoxy groups, which are not shown, are present which satisfy the tetravalency of the silicon centers.

References

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