Metallasilsesquioxanes as Models for Heterogeneous Catalysis

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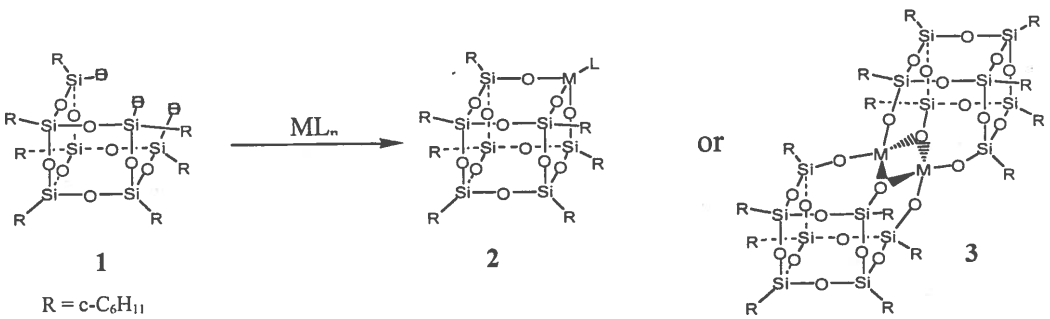
Heterogeneous catalysts are preferred industrially due to easy separation, high thermal stability, and easy regeneration. Unfortunately, they lack the selectivity observed in homogeneous systems. This difference in selectivity can often be attributed to the wide range of surface sites found in heterogeneous systems. The presence of different sites makes it difficult to identify the active site. This has led to the use of homogeneous models, such as polyhedral oligosilsesquioxanes (POSS), to obtain a better understanding of possible active sites found on heterogeneous catalysts.

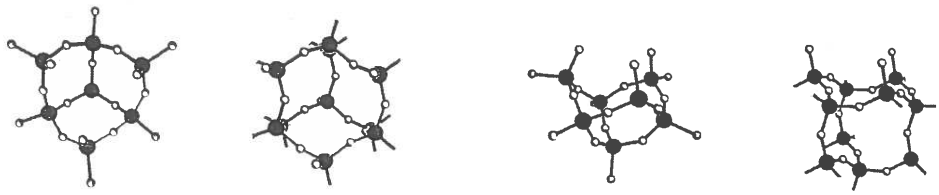
POSS are stable polyhedral organosilicates with the general formula $(RSiO_{1.5})_n$ (R = exo organic functional group) formed from the controlled hydrolytic condensation of $RSiY_3$ (Y = halide or alkoxide).[1] In 1965, Brown and Vogt discovered that the hydrolytic condensation of $(c\text{-}C_6H_{11})SiCl_3$ results in the slow formation of an incompletely condensed trisilanol silsesquioxane, $[(c\text{-}C_6H_{11})Si_7O_9(OH)_3]$ (**1**).[2] Recent research by Feher, *et. al.*, shows that incompletely condensed silsesquioxanes can be synthesized quickly from the base-catalyzed cleavage of POSS.[3]



1 R = c-C_6H_{11} **2** **3**

Trisilanol (**1**) can undergo a variety of corner-capping reactions with complexes of main group elements, early transition metals and lanthanides to form completely condensed metallasilsesquioxanes, **2** and **3**. Alkyl, alkoxide, and amine metal complexes undergo metathesis with **1** to form stable metallasilsesquioxanes.[4] Similarly, metal halides undergo base assisted metathesis with trisilanol to form the corresponding condensed metallasilsesquioxane. Anionic equivalents of trisilanol, formed from $SbMe_5$ or TlOEt, react with less active metal halides.[5]

Incompletely condensed trisilanol is structurally similar to two major silica (111) polymorphs, cristobalite and tridymite.[6] As shown in Figure 1, trisilanol and an idealized portion of cristobalite contain three terminal OH groups and a siliceous cavity, defined by an outer rim of six Si-O units. Tridymite consists of identical OH groups, but contains a channel in place of a cavity. Although the distances between the terminal OH groups vary, they share similar bonding characteristics and intermediate conformations. These similarities make trisilanol, and its derivatives, excellent models for short-range order on a silica surface and its use as a support.[7]



trisilanol along C_3 | cristobalite (111) | trisilanol side view | cristobalite side view

Figure 1

Several metallasilsesquioxanes can be synthesized to model heterogeneous olefin polymerization catalysts, such as CrO_3/silica (Phillip's Catalyst), VO_x/silica, and $ZrCp_2Cl_2$/MAO.[8-10] The local environment of the metal in Cr POSS, $[(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)CrO_2]$, V POSS, $[(c\text{-}C_6H_{11})_7Si_7O_{12}VO]$, and dimeric Zr POSS, $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]ZrCH_2Ph\}_2$, model a proposed site on their respective heterogeneous analogs.[11,12] All of the models are active olefin polymerization catalysts with low polydispersities. The use of trisilanol as a ligand allows the models to be characterized with multinuclear NMR spectroscopy and X-ray crystallography.

Recent work on Ti epoxidation catalysts has been aimed toward the heterogenization of homogeneous catalysts.[13] Understanding the active site in these systems would accelerate the design of new heterogeneous catalysts. Several Ti metallasilsesquioxanes, $[(c\text{-}C_6H_{11})Si_7O_{12}Ti(L)]$ (L = OPr^1, NMe_2, $OSiMe_3$, CH_2Ph), were synthesized to model different sites of Ti on the surface of silica.[14,15] The activity and selectivity of the model suggests that the active sites are related to a tripodal Ti site. Additionally, superior performance of the metallasilsesquioxane over Ti-MCM-41 catalysts suggests that fewer Ti sites are exposed in the heterogeneous system.

Current research is directed towards the reactivity of trisilanol with later transition metal complexes. The interaction of metal carbonyl complexes with trisilanol can be used to model chemisorption onto hydroxylated supports.[16] Other areas being investigated are lanthanide metallasilsesquioxanes and the immobilization of catalytically active metallasilsesquioxanes.

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