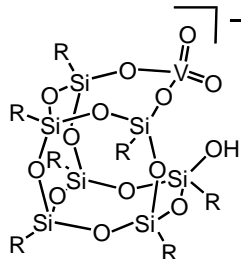
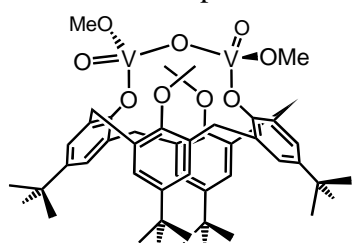


Oxovanadium complexes inspired by the surfaces of V_2O_5/SiO_2 catalysts

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While in comparison to homogeneous catalysts the employment of heterogeneous catalysts has certain advantages with respect to the product separation, stability and technical issues, the unequivocal identification of their surface constitution and the active sites poses problems. These are usually studied by techniques that involve bulk measurements, whose sensitivity is often inadequate to obtain accurate data of the various sites that are present on the surface in low concentration. Furthermore, even if the active sites are known, the clarification of mechanistic questions is far more difficult for the heterogeneous than for the homogeneous phase. Naturally, information gathered concerning the functioning of a heterogeneous catalyst provides a stimulus for the synthesis of molecular models: these can then be investigated in the homogeneous phase and on the one hand may serve to support or defeat structural, spectroscopic or mechanistic proposals. On the other hand such models can in turn prove themselves as novel homogeneous catalysts, independently of the heterogeneous process that led to their synthesis. Various different surface species have been discussed as being active during the V_2O_5 -catalysed oxidative dehydrogenation (ODH) of light alkanes and methanol in one way or the other, and hence these structural motifs represent an inspiration for attempts to mimic them in molecular compounds. This contribution deals with model complexes based on the calixarene and silsesquioxane ligand systems. While



silsesquioxane complexes were investigated to analyze spectroscopic features inherent to vanadyl-support interactions [1] calixarene complexes were examined as functional models [2]: indeed they catalyze the ODH of alcohols – dinuclear

complexes more efficiently than mononuclear representatives [3] and thiacalixarene complexes with higher activities than complexes containing “classical” calixarene ligands [4]. In case of the thiacalixarene complexes mechanistic studies led to the isolation and characterization of intermediates within the catalytic cycles, whose constitution permits inferences concerning the catalysts function [4]: μ -oxo ligands represent more favorable oxidation sites than terminal oxo ligands, and in dinuclear cores the two vanadium atoms cooperate during the oxidation process so that higher turnover frequencies are achieved.

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