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Building block syntheses of site-isolated vanadyl groups in silicate oxides†

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Cross-linking of the cubic silicate building block, Si_8O_{20} with vanadyl chloride leads to porous solids in which a homogeneous dispersion of isolated vanadyl groups is maintained throughout the matrix even at high loadings of vanadium.

The preparation of homogeneous dispersions of metal species on the surfaces of porous, high surface area supports such as SiO_2 or Al_2O_3 has been a goal of heterogeneous catalyst scientists for many years. Many strategies have been applied to this problem.[1] One of the most commonly used procedures involves the impregnation of the support with an aqueous solution of a catalyst precursor.[2] Working in aqueous media, however, limits the number of synthetically accessible species and distributions of aggregated species often result.[3]

More recent approaches to the problem of simultaneously controlling dispersity as well as aggregation in supported catalysts have involved the incorporation of metals into zeolites and mesoporous supports using hydrothermal and sol–gel technologies.[4] Additionally, thermolysis of single source metal–silicon containing complexes has produced various metal silicate xerogels.[5]

Silica supported vanadium complexes have recently attracted interest as catalysts for a variety of important chemical reactions.[6–8] The development of a simple synthetic methodology for the preparation of homogeneously dispersed vanadium on metal oxide supports which can accommodate high loadings of vanadium is, however, still a challenge.[9] Additionally, the ability to choose from a wider variety of precursors than allowed either by aqueous based strategies, vapour deposition or thermolyses would be of great utility in the design of new supported catalysts. An approach to this problem that we are developing involves the controlled coupling of silicate based molecular building blocks to construct the support while simultaneously incorporating various catalysts onto the support surface. In this communication, we describe results from initial investigations into the linking of the cubic Si_8O_{20} spherosilicate unit with vanadyl chloride ($VOCl_3$). In these investigations we have been able to alter the connectivity of vanadium to the silicate support while maintaining monodispersed vanadium centres throughout the matrix.

Trialkyltin groups bound to silicon through oxygen are known to undergo facile reaction with high valent metal chlorides to yield a soluble trialkyltin chloride by-product and M-O-Si bonds.[10]

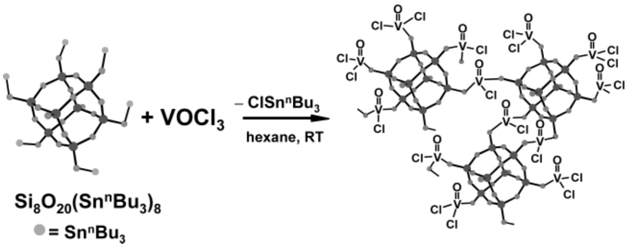
$$\equiv \text{Si–O–SnR}_3 + \text{Cl–ML}_3 \rightarrow \equiv \text{Si–O–ML}_n + \text{ClSnR}_3$$

When the octakis(tri-*n*-butyltin) spherosilicate ($Si_8O_{20}(Sn^nBu_3)_8$ "tin cube") reacts with $VOCl_3$, amorphous, 3-dimensionally linked solids result in which site isolated vanadyl (V=O) groups link cubes together as shown in Scheme 1.

Two initial experiments were performed to explore the nature of the cross-linking in the products of these reactions. In the first experiment (referred to as *normal addition*), a solution of $VOCl_3$ in hexane was slowly added to a solution of tin cube in hexane until an excess of $VOCl_3$ was achieved (V : tin cube = 8 : 1). The off white, water sensitive solid that formed was isolated, washed and dried under vacuum. An *inverse addition* sequence was used in the second experiment wherein a hexane solution of the tin cube was added to $VOCl_3$ in hexane. The final V : tin cube stoichiometry and workup procedures were the same as in the first experiment.

All of the solid products in these reactions are porous having broad pore size distributions with a significant component in the mesoporous range (typical specific surface area: 100–200 $m^2\ g^{-1}$). IR spectra show strong bands of almost equal intensity at 1180 and 950 cm^{-1} which are assigned to Si–O–Si and V–O–Si stretches, respectively.[5,9] Raman spectra show a broad band centred around 1017 cm^{-1} and no signs of bands associated with V_2O_5 domains.[9,11] Both IR and SSNMR (^{13}C, ^{119}Sn) spectra indicate that no tributyltin groups are left in any of the solid products from these reactions. Si and V elemental analysis of the solids give a Si : V ratio of approximately two.

^{51}V SSNMR (magic angle spinning) spectroscopy has been used to characterize the vanadyl linking groups in the solid products. When $VOCl_3$ is added slowly to the tin cube in hexane (*normal addition*) the spectrum of the solid product gives evidence of two isotropic peaks at $\delta = -292$ and -540 ppm (Fig. 1). Based upon several literature studies, the resonance at -292 ppm can be assigned to "capping" ($\equiv$ SiO)$VOCl_2$ groups while the -540 ppm signal arises from vanadyl groups linking two silicate cubes (($\equiv$SiO)$_2$VOCl).[12–14] The series of spinning sidebands associated



Scheme 1

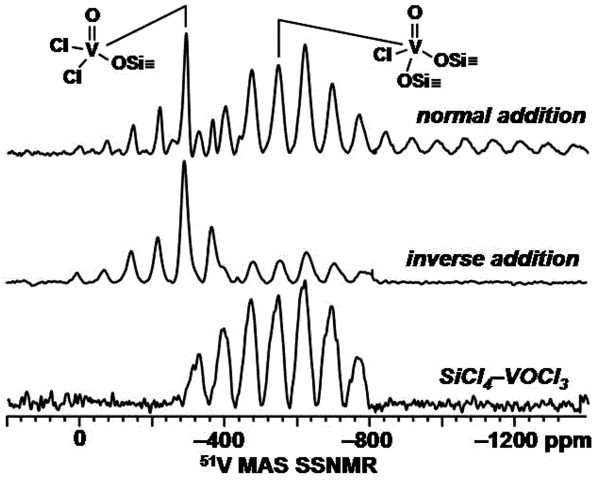


Fig. 1 ^{51}V MAS NMR spectra for vanadyl linked samples described in text. Isotropic peaks are indicated based on variable speed MAS spectra (not shown).

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† Electronic supplementary information (ESI) available: summary of experimental procedures, ^{51}V NMR collection parameters, BET, IR and Raman data. See http://www.rsc.org/suppdata/cc/b3/b316184f/

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with the isotropic peak at −540 ppm extends well into those observed for the isotropic peak at −292 ppm. Deconvolution of the two MAS sideband patterns observed in the spectrum of this sample and summation of the integrated intensities indicate that the manifold for the isotropic peak at −540 ppm has more intensity than the one for the isotropic peak at −292 ppm.

When an *inverse addition* sequence is used (tin cube added to excess $VOCl_3$) the solid product gives rise to the second ^{51}V MAS spectrum shown in Fig. 1. Here the signal at −292 ppm is more intense than the signal at −540 ppm. Neither spectrum shows evidence for vanadyl groups which are bound to three oxygen atoms from Si_8O_{20} cubes (the isotropic peak for $(\equiv SiO)_3VO$ groups is expected at approximately −750 ppm).[5] Thus, the last chloride ligand on vanadium appears not to react with the tributyltin groups under the reaction conditions described above.

The *normal* and *inverse addition* experiments provide simple, first order illustrations of how the distribution of vanadyl species can be altered in these highly loaded samples (> 20 wt% V) while maintaining site isolation. When vanadyl chloride is slowly added to a solution of the tin cube as in the *normal addition* experiment, reaction of the tin groups with V–Cl moieties initially yields oligomers consisting of two cubes bound to single vanadyl chloride groups $(\equiv SiO)_2VOCl)$. As more vanadyl chloride is added these oligomers in turn become 3-dimensionally cross-linked together. 3-Dimensional cross-linking should cause the matrix to become increasingly rigid as it grows. In this situation many of the remaining tin groups on cubes become spatially isolated from one another. At this point the additional $VOCl_3$ reacts with these groups to form capping $(\equiv SiO)VOCl_2$ groups (to complete the removal of tin from the matrix) without cross-linking the matrix any further.

In the *inverse addition* experiment as the tin cube is slowly added to an excess of vanadyl chloride, a preponderance of capping $(\equiv SiO)VOCl_2$ groups should form initially until enough tin cube is added for cross-linking to begin. In this case, the final distribution of vanadyl groups in the solid should favor capping positions, whereas, in the case of normal addition linking groups should be favored as observed by ^{51}V SSNMR.

The experiments described above do not realize the goal of obtaining isolated catalyst centres of a single type, but a simple extension of the strategy above to a combination of two linking moieties comes much closer. In this case a robust, non-catalytically active linker, such as $SiCl_4$, is first used to initiate the cross-linking process. Small soluble oligomers of cubes linked together with $SiCl_n$ groups form. In the second step, a limiting amount of $VOCl_3$ is added to the reaction mixture continuing the cross-linking process and causing precipitation. A final exposure to more $SiCl_4$ is utilized to remove the remaining tributyltin groups from the matrix.

^{51}V MAS NMR (Fig. 1) of the solid now shows an isotropic peak and sideband pattern consistent with the presence of linking vanadyl chloride groups $(\equiv SiO)_2VOCl$ throughout the matrix. The Si : V atom ratio in this sample is estimated to be approximately 30.

Feher and Weller[10] described the reaction of the trimethyltin building block precursor, $Si_8O_{20}(SnMe_3)_8$ with linking reagents (Si, P, Ti-based linkers) similar to the vanadyl chloride reactions described here. In their investigations residual trimethyltin groups were left in the solids they produced. By using larger ratios of $VOCl_3$: $^nBu_3Sn–O–Si\equiv$ groups we have been able to remove all tin from the final products. Furthermore, the experiments described herein illustrate a general synthetic strategy for producing multi component, nanostructured metal oxides. The basic tenets of the strategy are: 1) the use of one or more structural building blocks, 2) the use of complementary functionalities on both building blocks and linking reagents so that linking reactions can only produce cross-links between building blocks and linking groups, thus ensuring isolation of the catalyst sites,[15] and 3) the use of multiple linking agents to control the dispersity of the catalyst centres in the matrix as it is formed.

Irreversibility of the linking reactions under the conditions utilized in this strategy will generally lead to random cross-linking patterns around building blocks and amorphous solids. Consistent with this prediction is the observation that none of the solids described here exhibit Bragg diffraction. Regardless of the lack of long range order in these samples, the local environments around the catalytic centres exhibit nanostructuring. Simple combinations and sequences of appropriate linking agents can be used to create materials containing tailored distributions of catalytically active centres in a robust, nonreactive cross-linked matrix of structural building blocks. The utilization of building blocks in this strategy pushes structural properties of the final materials, such as the separation of catalytic sites and the pore size distributions, into the nanometre regime.

Finally, the reaction of a trialkyltin group bound to a support through oxygen with a high valent metal or main group chloride group is quite general. Current work is directed toward expanding the results described here to other metal halides, metal clusters and new building blocks.

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