



The targeted synthesis of single site vanadyl species on the surface and in the framework of silicate building block materials

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ABSTRACT

A new synthetic methodology for the targeted preparation of single site, atomically dispersed vanadyl groups in silicate matrices is described. This methodology requires functionalized silicate building blocks $\text{Si}_8\text{O}_{20}(\text{OSnMe}_3)_8$ that become linked together through vanadyl ($\equiv\text{V}=\text{O}$) groups in the matrix. A sequential addition strategy is illustrated which allows the targeting of specific connectivities for the vanadyl group to the silicate building block matrix (i.e. the number of V–O–Si bonds linking the vanadyl unit). Silicate matrices containing exclusively 3-connected ($\text{OV}(\text{OSi}_{\text{cube}})_3$), 2-connected ($\text{OV}(\text{OR})(\text{OSi}_{\text{cube}})_2$) or 1-connected ($\text{OVCl}_2(\text{OSi}_{\text{cube}})$) vanadyl sites are described and characterized via a wide variety spectroscopic and physical techniques (gravimetric analysis, EXAFS, AA and solid state NMR (^{51}V , ^{29}Si , and ^{17}O)). We demonstrate how the combination of gravimetric, solid state NMR (SSNMR) and EXAFS data can be used to uniquely define the vanadyl sites in these matrices. Furthermore, the use of ^{17}O SSNMR (1D and MQMAS) is illustrated as an indirect spectroscopic probe to follow changes in the ligands bound to vanadium atom within the vanadyl groups in these matrices.

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1. Introduction

Methods by which homogeneous arrays of metal sites may be constructed on and within extended solid matrices are of great interest in many fields such as electronic solids and heterogeneous catalysis [1,2]. Supported metal based catalysts have shown a wide variety of fundamental and technologically interesting reactivity in solid acid chemistry [3,4], polymerization reactions and oxidation and reduction processes [5]. A key requirement in many such system is that homogeneous arrays of metal sites be constructed on and within extended solid matrices [1]. The most common methods of chemically binding metal species onto metal oxide support involve exposing the surface to a precursor of the desired metal species either in solution (wet impregnation) [6,7] or in the gas phase (CVD) [8–10]. Surface hydroxyl groups are the most obvious points of attachment for metal cations through simple metathesis reactions [11]. The high densities of this group on typical untreated metal oxide powders frequently requires some tailoring of these binding sites before reaction [12]. Thermal protocols are commonly used to remove potential interferences of physisorbed water as well as reduce the number of surface hydroxy groups via dehydration and reconstruction of the surface [13]. In this way supports may be

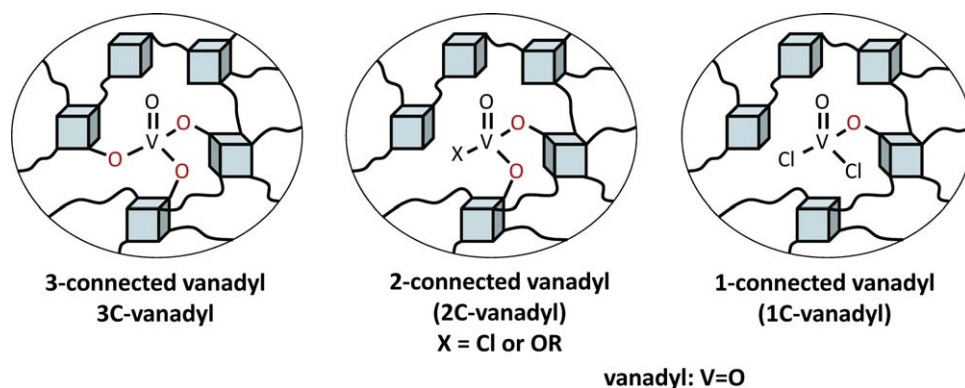
tailored to produce what are believed to be isolated metal catalyst sites on the surface of a metal oxide support.

All strategies which begin with polycrystalline/amorphous powders suffer first from the inability to predict exactly which surface species will result upon cation binding. Second, it is still quite difficult to target a single surface species even when average surface densities might indicate what attachments should result. Clustering of hydroxyl groups on metal oxide surfaces is well known [12] which, upon cation binding will produce multiple surface species that differ from what average measurements would suggest. Finally, the requirement of site isolation usually places rather low limits on site densities to avoid site–site interactions [14] or aggregated sites that exhibit different and frequently unwanted reactivities.

With these challenges in mind, a research program focused on developing new synthetic approaches to constructing what have been referred to as “next generation” catalysts was begun. Such catalysts must, by design, rigorously contain only a single active site. The goal of preparing well defined single site catalysts is not new and should in theory give rise to higher selectivities than systems with multiple sites. The definition of the active site “ensemble” is critical in the context of surface bound species. A metal site bound to the surface of a solid and in contact with a second fluid medium is defined to first order by all the ligands that are directly bound to the metal of which there are generally two types: those that terminate the support phase and hold metal cations in place on the surface

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Scheme 1.

and ligands that fill out the rest of the coordination sphere of the ensemble but are not associated with the support. In the past, much attention has been focused on empirical procedures that give rise to a specific number of metal-support bonds in the surface ensemble. However, in most procedures involving a preexisting solid support little control of the spatial geometry of metal-surface bonds can be affected and therefore a distribution of species results even if the desired average connectivity to the surface is achieved. This challenge was approached from a different perspective, namely that the metals which define the active site should participate in each step of the development of the metal-surface interface. The process of creating a surface “imprint” in the immediate environment of the active site should be a critical component of the definition of any single site catalyst [15,16].

Tailored surface binding pockets may also lead to more stable, long lived catalysts in the context of leaching reactions. Overall catalyst activity, however, is dependent on at least two other factors beyond the inherent activity and lifetime of the site itself. Both the number of sites in the system and mass transport processes can also limit activity [17]. Methodologies by which next generation catalysts are prepared should contain well defined strategies by which high site densities are achieved (while ensuring site isolation) as well as high surface areas and mass transport rates.

Two components are required to build such nanostructured matrices: (1) a rigid, nanometer or larger sized molecular building block that will be the main component of the support matrix and (2) two types of chemical linking agents: one that delivers the metal core of the final catalyst ensemble into the matrix and a second that will generate robust chemical linkages between building blocks [18]. With these precursors in hand, a well defined linking reaction must also be identified that involves complementary functionality on the building block and linking agents such that only cross-reaction can occur. Finally, by carefully adjusting both the stoichiometry and sequence of doses of linking reagents and building block, one can target specific connectivities between the building block and metal core of the active site. In this manner, the disposition of the catalyst ensemble can be varied by design from being completely within the framework of cross-linked building blocks to more exposed positions on the surface of a building block support platform.

Atomically dispersed vanadyl groups (VO_4 ; orthovanadate) on silica have been extensively investigated because of the interesting catalytic behavior exhibited in a number of selective oxidation and polymerization reactions [19–21]. A wide variety of conditions and procedures have been described in the literature to obtain vanadyl groups on support surfaces and much effort has been put into recognizing the distinct spectral signatures exhibited by different surface species that develop as a function of loading and synthetic strategy [22]. It has been reported that loadings between 1–5 wt.% vana-

dium on silica begin to yield mixtures of isolated orthovanadate centers (VO_4) and VO_x domains containing V–O–V bonds [22–24]. Herein we describe how the combination of building block materials synthesis together with a sequential addition strategy can be used to prepare silicate matrices containing high loadings of atomically dispersed vanadyl groups [25]. Using this strategy, specific connectivities for the orthovanadate groups in these matrices may be targeted (Scheme 1). The synthesis and characterization of isolated 1-, 2- and 3-connected vanadyl centers on the surfaces and in the framework of silica building block solids is described. Finally, an efficient synthetic route for the incorporation of ^{17}O into the bridging oxygen positions around vanadyl groups in these matrices is described. Subsequent ^{17}O SSNMR spectra illustrate how this spectroscopic probe can be used to identify the different types of vanadyl groups present.

2. Materials and methods

2.1. Materials

Experiments with air-sensitive materials were performed under high vacuum or in a nitrogen atmosphere glove box. Diethyl ether, hexanes and toluene were dried over Na/K alloy and distilled. Methylene chloride was dried using calcium hydride and distilled. Vanadylchloride (VOCl_3 , 99.995%), chlorotrimethylsilane (TMSCl, 98%), and dimethyl-dichlorosilane (Me_2SiCl_2 , 99%) were obtained from Aldrich. Tetrachlorosilane ($\text{SiCl}_4 > 99.5\%$) was obtained from Fisher Scientific. SiCl_4 , TMSCl, and Me_2SiCl_2 were distilled and stored in Teflon sealed solvent bulbs and capillaries under vacuum. Solvent and reactants were delivered to reaction flasks using vapor transfer methods. Amounts delivered were determined gravimetrically. All glassware was pretreated with TMSCl to remove hydroxyl groups on glass surfaces prior to use.

2.2. NMR spectroscopy

Solution ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were collected at 7.05 T (Varian Mercury). ^{29}Si solution NMR spectra were acquired at 9.4 T on a Bruker Avance wide-bore multinuclear NMR spectrometer. ^{51}V and ^{29}Si solid state NMR experiments were conducted at 9.4 or 16.4 T, respectively at spin rates of 5–15 kHz on a Varian INOVA 400 and 700 spectrometers. Samples were placed in 5-mm pencil rotors in a nitrogen atmosphere dry box and sealed with paraffin wax. Solid state chemical shifts were referenced externally to ^{29}Si (Me_3Si) $_8\text{Si}_8\text{O}_{20}$: 11.72 ppm; ^{51}V (VOCl_3): 0 ppm. Solid state ^{17}O NMR spectra were acquired on a 16.4T Varian spectrometer at a resonance frequency of 94.9 MHz. The spectrometer is equipped with a Varian console and Varian 3.2 mm MAS probe. Samples were typically spun at 20 kHz. One pulse experiments used

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