Final Technical Report

DOE Award Number: DOE-FG02-01ER15259

Name of Recipient: Craig E. Barnes

Project Title: Nanostructured Metal Oxide Catalysts via Building Block Syntheses

Principal Investigator: Craig E. Barnes

Date: March 5, 2013

Period Covered: November 1, 2010 – October 31, 2012

Executive Summary:

A broadly applicable methodology has been developed to prepare new single site catalysts on silica supports. This methodology requires of three critical components: a rigid building block that will be the main structural and compositional component of the support matrix; a family of linking reagents that will be used to insert active metals into the matrix as well as cross link building blocks into a three dimensional matrix; and a clean coupling reaction that will connect building blocks and linking agents together in a controlled fashion. The final piece of conceptual strategy at the center of this methodology involves dosing the building block with known amounts of linking agents so that the targeted connectivity of a linking center to surrounding building blocks is obtained. Achieving targeted connectivities around catalytically active metals in these building block matrices is a critical element of the strategy by which single site catalysts are obtained. This methodology has been demonstrated with a model system involving only silicon and then with two metal-containing systems (titanium and vanadium). The effect that connectivity has on the reactivity of atomically dispersed titanium sites in silica building block matrices has been investigated in the selective oxidation of phenols to benezoquinones. 2-connected titanium sites are found to be five times as active (i.e. initial turnover frequencies) than 4-connected titanium sites (i.e. framework titanium sites).

Accomplishments:

Proposed:

In the work supported by the BES program of the DOE we proposed to develop a methodology to prepare nanostructured complex oxide catalysts. There were three specific objectives to this research program:

1. To develop a general, broadly applicable synthetic methodology to prepare single site catalysts in a targeted fashion.
2. To obtain high densities of these sites on the support materials while maintaining strict site isolation.
3. To accomplish (1) and (2) on a porous, high surface area support with a distributed pore system composed of macro, meso and micropores to obtain high numbers of sites on a per unit mass or volume basis for the material.
4. To study the activity of these new nanostructured materials as catalysts in selective oxidation reactions.

Actual:

1. During an early phase of this research project objectives (1) and (2) were demonstrated and described for a model system (containing no active catalysis centers) in a publication that is given at the end of this technical report.[1]
2. This study was followed up by more detailed investigations involving titanium and vanadyl centers in silica building block matrices. The results of this work were recently reported in several publications given at the end of this technical report.[2-4]
3. More recently we have completed two additional studies focusing on how the porosity of these matrices changes with the synthetic stoichiometry used in their synthesis and the activity of single site titanosilicate catalysts in the selective oxidation of phenols to *p*-quinones. Short summaries of these two studies follow.

Silicate Catalysts: Targeted Mesoporous Systems without the Use of Templates

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Introduction

Nanostructured materials have many properties in common with supported catalysts.[1] Both frequently target creating an array of identical sites on the surfaces of a support. In addition to controlling active site identity, the surface area and porosity of the supported catalysts are two important properties that influence many aspects of catalysis and need to be tailored to intended application. High surface area supports bring with them the potential for more active sites in the matrix without having problems maintaining site isolation. The sizes of the pores in such matrices play critical roles in determining what substrates and products can access internal active sites and what products eventually escape. Naturally occurring and synthetic zeolites are good examples of how well ordered (crystalline) microporous materials function as molecular sieves but also can be combined with catalytic reactions that occur within the pores where size exclusion can be used to tailor substrate and product selectivity. This double door selection process has been exploited in numerous areas of solid acid and selective oxidation chemistry with zeolites.[2]

Limitations associated with microporous systems have led to an intense effort to develop high surface area mesoporous analogues to zeolites. Tremendous progress has been made in this area primarily through the development of surfactant templating theories of sol-gel derived matrices. From these efforts has come a vast array of mesoporous silicates and other metal oxides that have impacted a broad spectrum of scientific disciplines and technological areas of endeavor. However, as simple as templating strategies are in practice, they do require additional reagents (e.g. surfactants, block copolymers) that add to the cost and must be removed from these matrices before application. Furthermore, targeting and achieving specific dispersities of catalytically active metals on porous oxide supports is still quite challenging in this context because of the number of different processes that occur simultaneously which must be controlled in sol-gel systems.

We have approached the challenges described above from the context of producing single site, metal based catalysts on metal oxides using a different synthetic strategy. To simplify the number of reactions that must be controlled we use nonaqueous sol-gel reactions involving reagents that are already functionalized to react together and removed any solvolysis steps from the reaction matrix (**Figure 1**). Simplifying the linking strategy in this manner opens the door to the use of more complex building blocks to build up structures without worrying as much about solvolysis and fragmentation of the building block itself. The use of rigid building blocks with spatially well-defined arrays of linking points also allows some measure of control over how such matrices grow which, in theory, ought to be experimental parameters through which properties such as porosity and surface area may be controlled. In this presentation we will describe the results of an investigation of how the porosity and surface area of matrices based upon the cubic spherosilicate Si_8O_{20}, depend on the stoichiometric ratios of linking reagents to this building block as they react to form a cross-linked matrix. The results of this study can easily be rearticulated into a simple strategy for targeting specific types of porosity without compromising our parallel objective of developing methodologies for preparing single site catalysts.

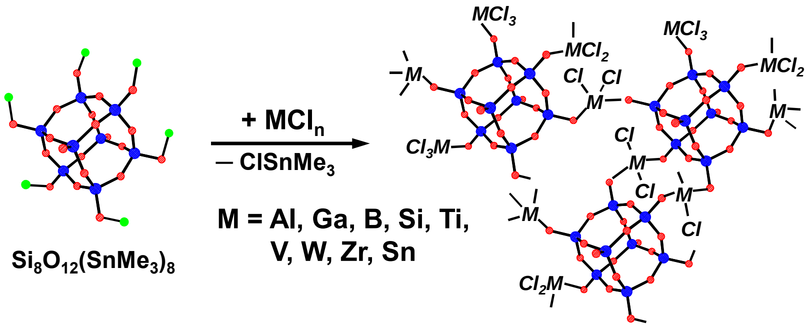

Figure 1 Building Block Solids based on the cubic silicate Si_8O_{20}

Experimental

All reagents and solvents were handled under air and water free conditions (Schlenk lines and N_2 glove box). Dry solvents were vapor transferred into reaction flasks under vacuum. The primary linking reagent used in these studies, the bis-pyridine adduct of silicon tetrachloride $SiCl_4py_2$ was prepared following a literature procedure.[3] $TiCl_4$ was distilled and stored in a Teflon sealed bulb. The trimethyl tin cube, $Si_8O_{20}(SnMe_3)_8$ (**1**) was prepared from the octaanion $[TMA]_8[Si_8O_{20}]$ and trimethyltin chloride.

Instrumentation and measurement protocols

Infrared spectra are collected using a Thermo Nicolet IR100 in a N_2 dry box. Nitrogen adsorption-desorption analyses were performed using a Quanta Chrome Nova 1000 instrument. BET surface area was calculated using adsorption data in the relative pressure range from 0.05 to 0.35.[4] t-plots or □$_s$-plots were used to determine micro- and mesoporosity of the materials.[5,6] The adsorption portion of the nitrogen gas adsorption/desorption isotherms was used to calculate the pore size distribution (BJH method) of the samples.

General Synthesis of Nanostructured Silicate Building Block Supports

Nanostructured silicate building block supports were synthesized following our previously reported procedure.[7] In general, $Si_8O_{12}(OSnMe_3)_8$ and $SiCl_4py_2$ are transferred to a Schlenk reaction vessel followed by the addition of approximately 30 mL of toluene. The solution is stirred at 80°C under static vacuum for up to 24 hours whereupon all volatiles (solvent, trimethyltin chloride, pyridine) are removed under vacuum. The resulting solid is used without further purification. Other metal chlorides (e.g. $TiCl_4$, $ZnCl_4$) are handled in an identical fashion except that all volatiles were removed from the initial oligomeric mixture after the first dose was administered the cube in toluene. Reexposing this residue to toluene for subsequent doses generally gave rise to suspensions of some undissolved material. However, we found that the final surface areas and pore size distributions that were observed for these materials followed the same trends described below and were not affected by an intermediate isolation step.

Results and Discussion

We are engaged in a program of research to develop new synthetic methodologies that focus on the targeted preparation of single site, supported catalysts. The basic elements of this strategy have been laid out recently for silicon, vanadyl and titanium based systems.[8-10] Therefore only a brief overview will be presented here. Controlling the number of bonds that bind a metal center to a support surface (*connectivity*) is a critical property in defining its reactivity and long term stability. To obtain atomically dispersed catalysts where all the metal centers have the same connectivity to a silicate support we begin by exposing the tin cube **1** to *limiting* amounts of an appropriate halide reagent MCl_n (**Figure 2**). All chloride ligands are replaced by links to surrounding silicate cubes as $ClSnMe_3$ is formed and eventually removed from the reaction mixture. Isolation of the oligomeric mixture at this stage for gravimetric analysis to verify achieved connectivity usually yields a low surface area residue. To create a high surface area solid a second dose of a chemically and thermally robust cross-linking reagent must be applied to this mixture to "knit" these oligomers together. The reagents that we use for this purpose are silyl chlorides which ultimately produce new silicate or siloxane bonds throughout the matrix.

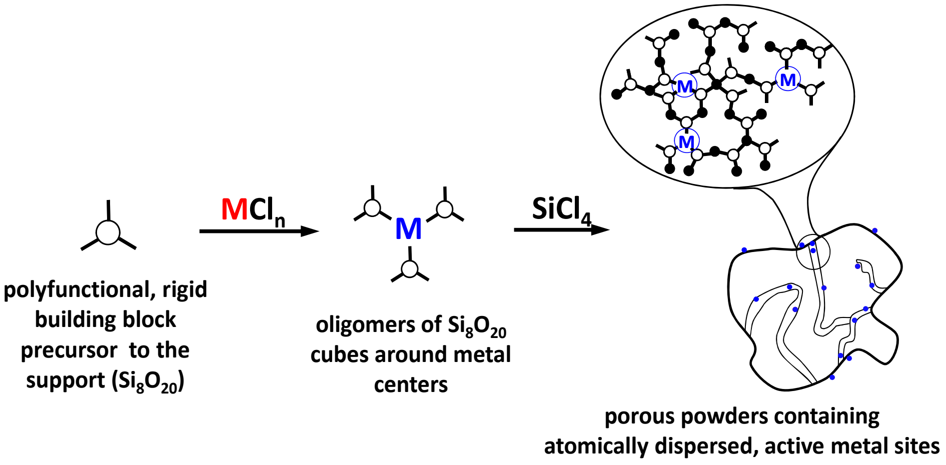

Figure 2 Dosing Sequence leading to porous, cross-linked building block matrices

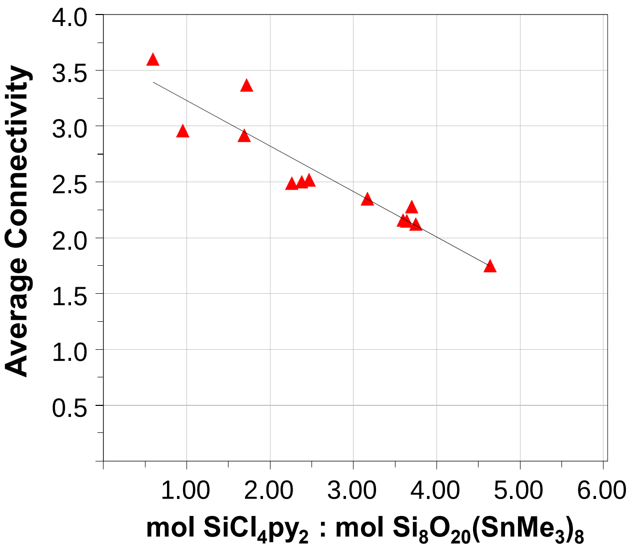

Figure 3 Achieved Connectivity vs. ratio of linker to cube

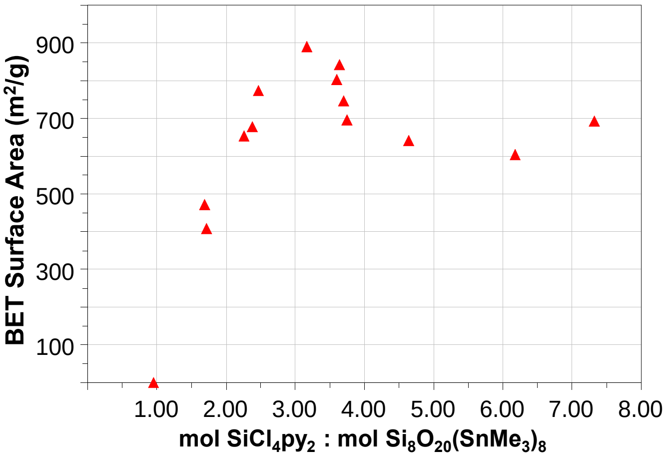

Figure 4 Dependence of surface area on stoichiometric ratio of linker to building block

The first cross linking step with metal based reagents is generally when the catalytically active centers are inserted into the eventual matrix and, as described above, their connectivity to the matrix is set. However, porosity is generally not observed until a higher *total* dose of cross-linking reagents is applied to the system. In previous studies our focus has been on establishing the single site nature of the catalyst ensembles that we created within the matrix of silicate cubes. Here we focus on when, how and what types of porosity develop in these same matrices. Ultimately we seek to understand this process well enough to extend our synthetic methodology to include the targeted synthesis of silicate matrices in which the porosity can be tailored to produce predominantly micro- to mesoporous products while maintaining the single site nature of the metal species on their surfaces.

Initially, a series of silicon cross-linked materials based on the Si_8O_{20} building block was synthesized varying the stoichiometric ratio of linking reagent to Si_8O_{20}-based cube (derived from the tin cube, $Si_8O_{20}(SnMe_3)_8$). **Figure 3** shows how the *average* connectivity of the linker varies with this ratio, progressively getting smaller as more linking reagent is used in the initial cross-linking does. For the purposes of making single site catalysts, we must tailor the dose of an analogous metal chloride reagent so that the connectivity achieved at this point is equal to the total number of chloride ligands initially present on the metal. When this occurs then all metal sites will have exactly the same connectivity and the first step in making a single site catalyst will have been fulfilled.

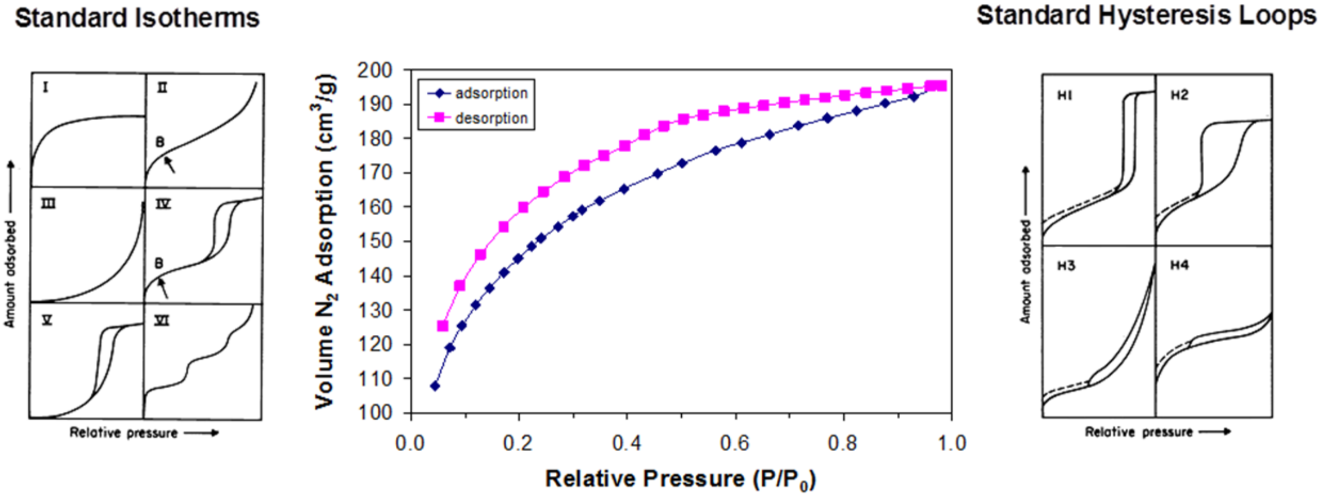

Figure 5 Nitrogen adsorption isotherm data for a sample prepared using a low ratio of $SiCl_4py_2$ to Si_8O_{20}. Representative plots of standard isotherms and hysteresis and their IUPAC recommended designations are provided left and right of the experimental data

Figure 4 summarizes how surface area varies with the same stoichiometric ratio described above. It is obvious that at the very low ratios of linker-to-cube required to achieve uniform connectivity, little to no surface area has been generated in these materials. The surface area of the solid products does rise abruptly as the ratio of linker-to-building block increases past two, to a maximum of between 800 and 900 m^2/g (N_2 BET). Between ratios of two and four a peak in the SA curve is observed after which a plateau at approximately 600 – 700 m^2/g is reached for higher stoichiometric ratios.

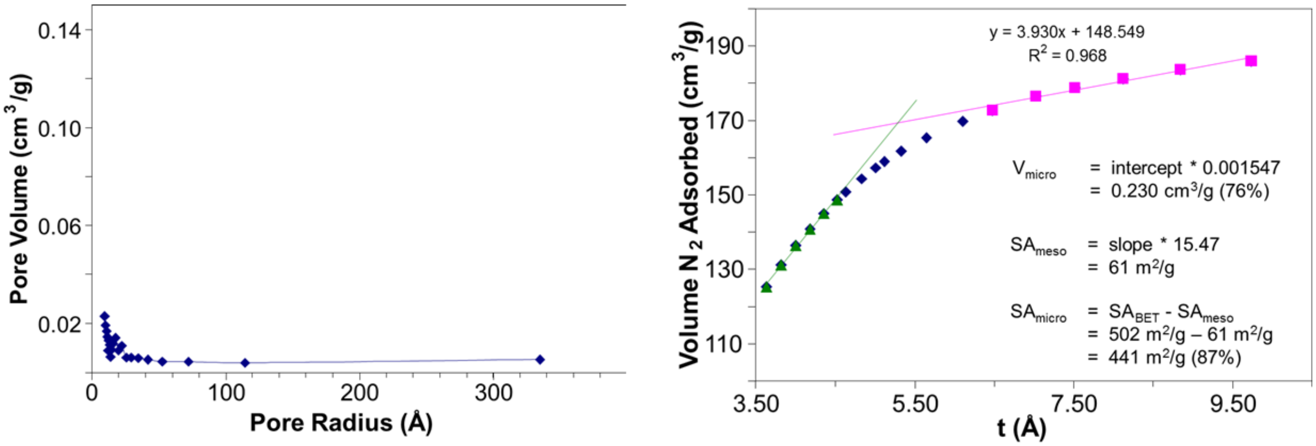

Figure 6 BJH pore size distribution and t-plot analyses for a sample prepared using a low stoichiometric ratio (1 – 3) in the reaction of the tin cube with $SiCl_4py_2$.

The pore networks underlying the significant surface areas exhibited by these materials were then characterized. Pore size distributions were investigated using two procedures. BJH pore size distributions were calculated according to standard algorithms. Additionally, t-test analyses were also performed on nitrogen adsorption data to determine the relative percentages of micro, meso and macropores present. Representative plots of nitrogen adsorption data, pore size distribution and a t-test analysis are shown in **Figures 5,** and **6**.

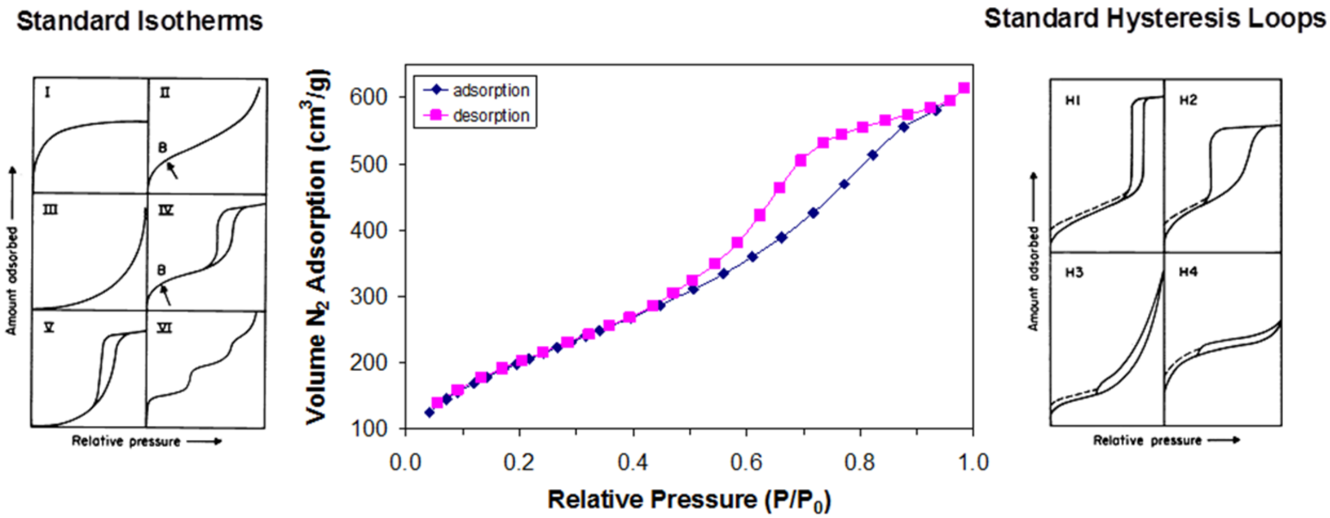

Figure 8 Nitrogen adsorption isotherm data for a sample prepared using a ratio of $SiCl_4py_2$ to Si_8O_{20} between three and five. Representative plots of standard isotherms and hysteresis and their IUPAC recommended designations are provided left and right of the experimental data

The data in **Figure 5** were collected for a sample prepared using a low stoichiometric ratio (~2) ($SiCl_4$: Si_8O_{20}) in the cross linking reaction. The shape of the adsorption data is typical of a microporous material. The BJH pore size distribution plot (**Figure 6**) reveals that very little of the pore volume for this sample (0.3 cm/g) is accounted for by mesopores in the sample but the adsorption data does not extend to low enough P/P_0 values to accurately present the micropore component in this sample. A t-plot analysis (**Figure 6**) is more revealing in that it gives a first-order estimate of the micro- and mesopore components in the sample. The plot bends significantly below the linear extrapolation of the data based on low P/P_0 data indicative of the presence of microporosity. Linear fits to the high and low t-plot data allow one to divide the total porosity into micro and meso components. As expected, based on the t-plot analysis, the

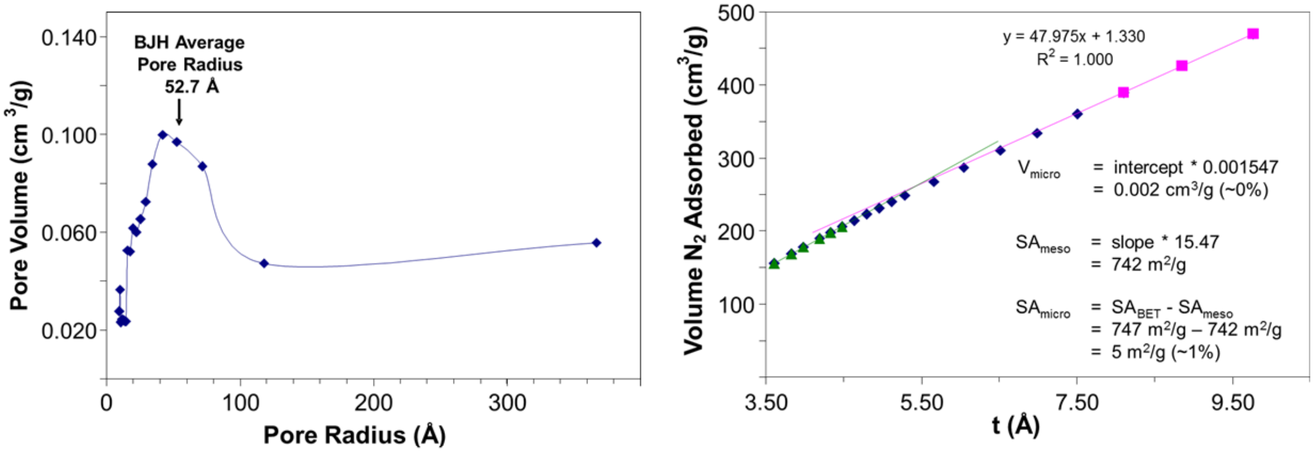

Figure 7 BJH pore size distribution and t-plot analyses for a sample prepared using a low stoichiometric ratio (3 – 5) in the reaction of the tin cube with $SiCl_4py_2$.

sample is almost 90% microporous.

Increasing the ratio of linker to Si_8O_{20} building block into the range of three to five causes the adsorption isotherm to change in its general appearance and the hysteresis exhibited between the adsorption and desorption legs (**Figure 7**). The gradual rise of the adsorption leg across the entire range of data can be classified as a type IV isotherm, indicative of a broad range of pore sizes beyond micropores. The BJH pore size analysis (**Figure 8**) indicates a significant mesopore component in the overall distribution. Finally the t-plot analysis for these data shows only a slight bending below the linear extrapolation of the low P/P_0 consistent with a material that has both micro and mesopores present. Combining these results with the total surface area obtained from the BET method allows the total surface to be divided into micro and meso components. As shown in **Figure 8** the porosity and surface area associated with this sample is composed primarily of mesopores.

At still higher linker-to-building block ratios a similar analysis of adsorption isotherm data indicates that while total surface area is maintained the pore size distribution shifts to larger and larger pores. This information concerning pore size distribution can be superimposed on Figure 4 to yield **Figure 9.** It should be noted that several other non-silicon linking atoms have been added to the plot in Figure 9. Zirconium and titanium data are derived from the analogous tetrachlorides so that the maximum connectivity that can be achieved around each of these linking atoms is the same as for silicon (four).

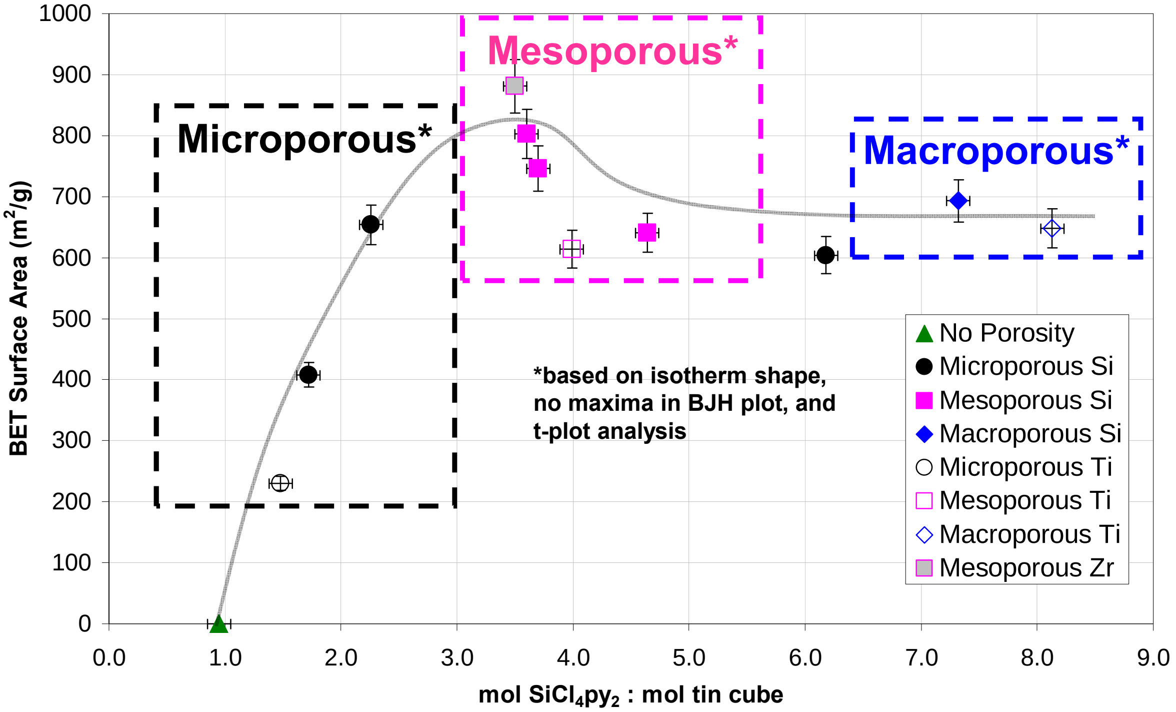

Figure 9 Plot of BET surface area versus linker-to-building block ratio with the primary pore size component indicated.

Conclusions

The surface area and porosity of a family amorphous solids built from the reaction of several four-connecting linking agents and the cubic silicate building block, Si_8O_{20} have been investigated as a function of the stoichiometric ration of linking agent to building block. At very low ratios (< 1) only distributions of small oligomers are formed where the limiting connectivity around the linking atom is achieved and no surface area is observed. At ratios between one and three macromolecular materials are formed which are primarily microporous and have surface areas as high as 900 m^2/g. As the ratio increases beyond three the major component of the pore size distribution initially changes to mesoporous and finally to macroporous. The correlation between linker-to-building block ratio and the surface area and porosity of the final matrix suggests a relatively easy way to tailor these properties while controlling connectivity of the linker to surrounding building blocks in the matrix.

Acknowledgements

We would like to acknowledge the Basic Energy Science program of the DOE (DE-FG02-01ER15259) for supporting this work.

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Nanostructured, Single Site Titanium-Silicate Catalysts with Varying Support Connectivities – Correlating Site Structure with Activity in the Oxidation of Trimethylphenol to Benzoquinone

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Introduction

The goals of preparing nanostructured materials are in many ways synonymous with longstanding efforts in catalysis science to prepare well defined, single site catalysts on the surfaces of support materials.[1] One picture of an ideal, single site, supported catalyst has a dense array of isolated, identical sites on a high surface area support material similar to nanopatterning. Traditional methods of binding metals to supports involving adsorption of catalyst precursors onto preexisting surfaces or sol-gel approaches to mixed metal oxides all face well known challenges in the context of preparing true single site catalysts.[2] For these reasons, many well-known catalysts used in industry are still not well characterized in the sense of having a precise and accurate picture of what the active site(s) that are responsible for their catalytic behavior.

Newer "soft" synthesis approaches have in a few cases yielded well defined catalysts but are usually quite limited in terms of targeting specific types of sites and the loadings that may be achieved before facing problems involving formation of separate metal oxide phases. Grafting and "hetero-genizing" strategies involving bifunctional reagents which tether homogeneous complexes to support surfaces frequently suffer from lowered activities and long term stability problems. Thus, there exists no simple, generally applicable synthetic strategy for targeting and preparing specific metal sites on the surfaces of metal oxide supports.

We have approached these challenges from a different perspective.[3] We begin with a suitable precursor containing the active metals and build up the support around the eventual active site in a controlled, stepwise manner. The essential elements of the "catalytic ensemble" that we target in this strategy are: 1) the nuclearity of the site, i.e. the number of metal atoms in each ensemble; 2) the number of covalent bonds that hold the collection of metal atoms on the support surface; and 3) the terminating ligands bound to the active metals that form the interface between the solid and fluid phases in the system. Beyond targeting a desired active site, it is essential to have a high density of sites while keeping all sites isolated from one another. High densities of surface sites generally require porous matrices with high surface areas. To avoid diffusional transport limitations we also want matrices with distributed pore systems with significant mesoporosity. All of these design requirements can be met with a *sequential addition* synthetic strategy involving non aqueous sol-gel linking reactions between a rigid silicate building block and metal halide precursors. Building blocks are readily cross-linked together around a wide variety of metals to form a distribution of small metal-building block oligomers (**Figure 1**). These oligomers form a second generation of building blocks which are subsequently linked together to form rigid, amorphous matrices with considerable void volume without the need for templating agents. Nitrogen gas adsorption measurements confirm that beyond specific stoichiometric ratios of linker to building block the final matrices exhibit high surface area (100 – 800 m^2/g) and are primarily mesoporous.

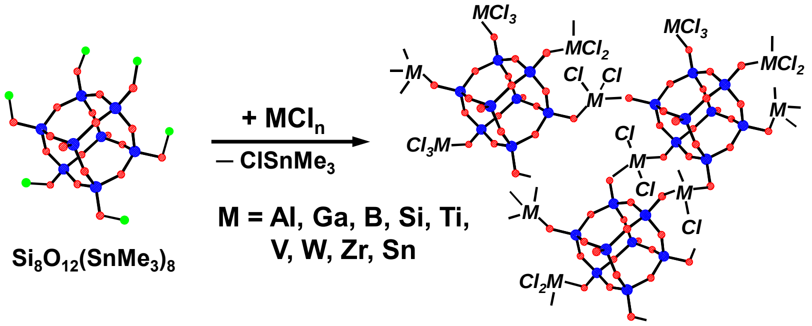
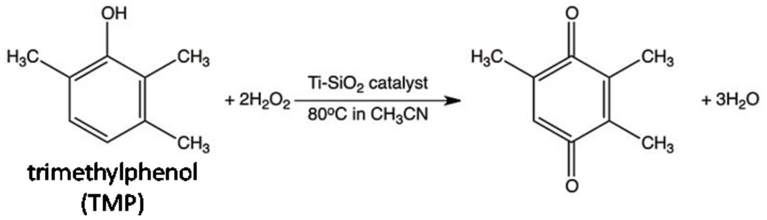


Figure 10 Building Block Solids based on the cubic silicate Si_8O_{20}

One of the more intensively studied families of silicate-supported catalysts involves titanium (IV) ions both on the surface and in the framework of the support. Within the context of potential single site systems, zeolitic TS-1 exhibits a wide range of oxidation chemistry and is one of the few Ti-SiO_2 systems able to utilize to aqueous peroxide without leaching.[4] Titanium loadings in most TS-1 syntheses are limited to ~2% (wt) before TiO_2 domains are formed with loss of activity. Thus it is widely believed that atomically dispersed titanium centers are responsible for many of the selective oxidation reactions observed for TS-1 and other titanosilicate catalysts.

At the same time, several studies have also implicated small, nanometer sized titania domains as potential catalytic species but the size and exact composition of these ensembles have been difficult to ascertain. A recent study by Kholdeeva et. al[5] sought to distinguish between the catalytic activities exhibited by atomically dispersed titanium sites and small ensembles of TiO_2 on the surface of silica in the reaction of trimethylphenol (TMP) with peroxide to form the corresponding benzoquinone (eq. 1).



eq. 1

Herein we describe the application of the synthetic approach outlined above to constructing titanium silicate matrices in which the "connectivity" of atomically dispersed titanium centers to Si_8O_{20}-based silicate supports is systematically varied from two to four and the relative catalytic activity of each measured in the oxidation of TMP to the benzoquinone. Furthermore, discrete tetranuclear titanium groups have also been incorporated into Si_8O_{20} matrices and their activity compared with that exhibited by atomically dispersed analogues.

Experimental

All reagents and solvents were handled under scrupulously air and water free conditions (Schlenk lines and N_2 glove box). Dry solvents were vapor transferred into reaction flasks under vacuum. $TiCl_4$ was distilled and stored in a Teflon sealed bulb. The trimethyl tin cube, $Si_8O_{20}(SnMe_3)_8$ (**1**) was prepared from the octaanion $[TMA]_8[Si_8O_{20}]$ (TMA: tetramethyl ammonium) and trimethyltin chloride. Titanium alkoxychloride reagents and tetranuclear complex, $Ti_4O_2Cl_6(O_2CPh)_6$ were prepared according to literature procedures.

Catalyst Synthesis Protocol: 1 – 2 g of the trimethyl tin cube, **1** was weighed into a Schlenk flask. Toluene was vapor transferred into the flask at 77K followed by a weighed amount of $TiCl_4$. After warming to room temperature the sealed reaction flask was heated with stirring at 80°C for 12 – 24 hr after which all volatiles were removed. In the cases of solid titanium alkoxychloride reagents, both the trimethyltin cube and titanium precursors were measured into the reaction vessel in a glove box before adding toluene and starting the reaction.

Gravimetric determination of the amount of trimethyl tin chloride byproduct formed after this first cross linking reaction gives rise to the connectivity achieved by titanium to surrounding Si_8O_{20} cubes. Toluene is again condensed into the reaction flask containing the intermediate off-white solid. A dose of $SiCl_4$ as a second cross linking reagent is added to the flask to further cross link the matrix and create a porous solid. After heating for 12 – 24 hours all volatiles were removed (solvent and $ClSnMe_3$). A measured amount of anhydrous methanol (slight excess of the estimated number of residual Si-Cl groups left in the matrix) was added to the reaction flask and allowed to react at 50°C for 1 hour. All volatiles were then removed to give an off-white solid residue. These titanosilicate materials were used *as is* in catalysis studies.

Catalysis Protocol: A procedure patterned after that described by Kholdeeva was used.[5] Typically a measured amount of the catalyst containing a known amount of titanium was put into a screwtop vial together followed by 2,3,6 trimethylphenol (TMP) and biphenyl as an internal GC standard and 5 mL of solvent (acetonitrile). Between 5 and 20 equivalents of aqueous peroxide (30 or 50% (wt)) solution were added to the catalysis reaction (t = 0). GC aliquots were removed periodically as the reaction progressed and analyzed by GC with a FID detector. Stir rates between 200 and 1000 rpm had no effect on the reaction kinetics. The amounts of TMP and corresponding quinone product (TMBQ) as a function of time were obtained relative to the biphenyl standard.

Results and Discussion

The preparation of single site titanosilicate catalysts described here follows directly the protocol laid out for vanadyl based systems recently described by us.[6] Therefore only a brief overview will be presented here. Controlling the number of bonds that bind a metal center to a support surface (*connectivity*) is a critical property in defining its reactivity and long term stability. To obtain atomically dispersed titanium catalysts where all the titanium centers have the same connectivity to the silicate support we begin by exposing the tin cube **1** to *limiting* amounts of the appropriate choroalkoxy titanium reagent. All chloride ligands are replaced by links to surrounding silicate cubes as $ClSnMe_3$ is formed and eventually removed from the reaction mixture. The alkoxy groups are unreactive in these reactions. Thus the number of chloride ligands bound to titanium sets the maximum connectivity for all titanium sites in the matrix. After reaction is complete, a second dose of a silyl chloride reagent cross links the oligomer distribution developed with titanium to produce a matrix of Si_8O_{20} cubes wherein all the titanium centers have the same number of bonds to surrounding cubes. In this manner 2C-, 3C-, and 4C-Ti catalysts are prepared. The final step in the synthesis involves exposure of the matrix to anhydrous methanol to remove any Si-Cl bonds as well as residual $SnMe_3$ groups (referred to as surface passivation) in the matrix. These catalysts require no further activation steps (e.g. calcination) and were used directly in the phenol oxidation reactions.

The catalyst containing tetranuclear titanium units (Ti_4O_2) was made in a similar manner starting from the $Ti_2O_2Cl_6(O_2CPh)_6$ complex. Analysis of the byproducts in the cross linking reaction indicates that four chloride and all benzoate ligands are lost as the tetranuclear cluster is incorporated into the Si_8O_{20} matrix.

Table 1 Analytical data on atomically dispersed titanium catalsyts

Ti Sample	Precursor	Ti : bb	Est. Connectivity	Actual Connectivity
4C-Ti	$TiCl_4$	0.5-0.7	4	4.0 ± 0.1
3C-Ti	$Ti(OiPr)Cl_3$	0.7-1.0	3	2.9 ± 0.1
2C-Ti	$Ti(OiPr)_2Cl_2$	1.0-2.0	2	1.8 ± 0.1

Ti Sample	Ti wt% $_{(theo)}$ (± 10%)	Ti wt% $_{(ICP)}$ (± 10%)	Sn wt% $_{(ICP)}$ (± 10%)	Ti : Sn (mol)
4C-Ti	3.5	3.2	1.8	4.4 : 1
3C-Ti	6.1	5.5	1.8	7.6 : 1
2C-Ti	8.0	7.6	0.32	59 : 1

Table 1 summarizes the analytical characterization data for these materials at different stages of their syntheses. The connectivity achieved based on gravimetric data mirrors the number of chlorides initially present in the limiting reagent and is strong evidence that *all* titanium centers have the same connectivity in the matrix. After the second cross linking reaction with $SiCl_4$ and passivation with methanol, ICP-OE data indicate that no titanium has been lost as the final matrix is built and that very little tin remains.

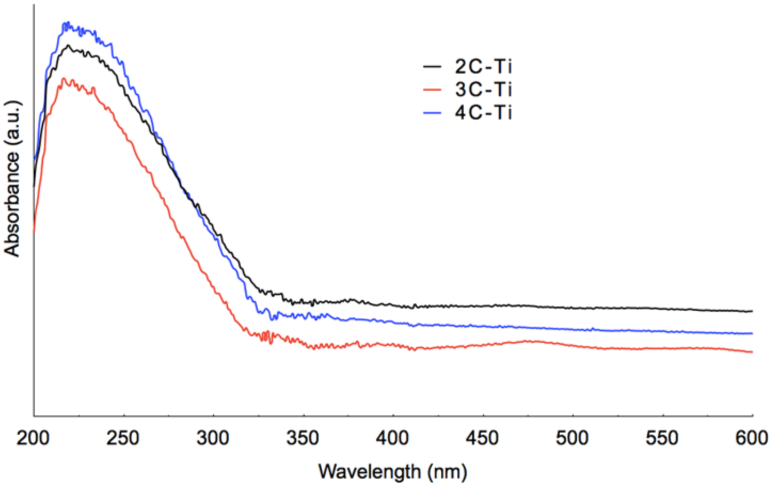


Figure 2 DRUV spectra for atomically dispersed titanium catalysts

DRUV spectra have been used to discern the disposition of titanium and other metals in silica.[7] An absorption maximum between 210 and 230 nm is generally interpreted as indicative of isolated, 4-coordinate titanium centers in crystalline silicate matrices. Band maxima between 230 and 250 nm indicate either presence of isolated titanium atoms with higher coordination numbers or small nanometer sized polynuclear Ti_xO_y domains. DRUV spectra for all the passivated catalysts prepared here are presented in **Figure 2**. Band maxima at 220 – 225 nm are consistent with the presence of 4-coordinate, pseudo tetrahedral titanium sites in all of these matrices. However, these bands are wider than normal, not reaching the baseline till after 300 nm. We ascribe this to the presence of site isolated titanium atoms in the matrix which have coordination numbers higher than four. The extra ligands around titanium are most likely picked up in the final passivation step where the matrix is exposed to methanol.

XANES data for some of these samples are summarized in **Table 2** and **Figure 3**. The preedge features for all atomically dispersed titanium catalysts are quite similar at all stages of their synthesis. A single preedge peak is observed after the initial reaction with cube. The combination of a second dose and passivation causes this band to broaden slightly and reduce its height relative to the edge jump. Reaction with aqueous peroxide causes a significant reduction in peak height for this main band as well as the appearance of two very weak bands above and below the main band.

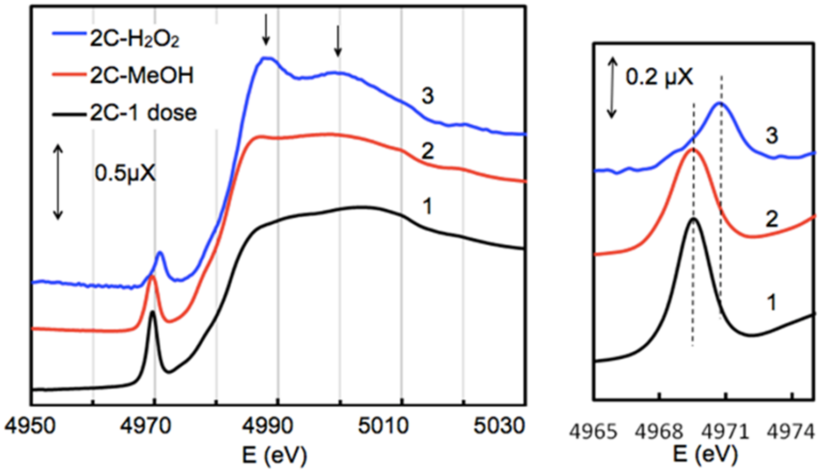


Figure 3 XANES region for 2C-Ti catalyst

The intensity of the preedge feature is a sensitive function of a number of factors, one of which is the presence of inversion symmetry (or pseudo inversion symmetry) around titanium.[7] Rigorous, well defined tetrahedral symmetry frequently leads to very narrow, intense preedge features while octahedral symmetry gives rise to multiple bands with much lower intensities. The XANES data for the 2C-, 3C-, 4C-Ti catalysts are consistent with 4- or 5-coordinate Ti centers. The broadening of their preedge features relative to TS-1 may in part be due to disorder around titanium in these amorphous matrices. The changes observed when peroxide is added are consistent with what has been described previously and are assigned to the formation of a 6-coordinate titanium site containing a peroxide ligand.

Table 2 Summary of XANES data for atomically dispersed titanium catalysts

Entry	Sample	Description	Pre-edge Peak Energy/eV	Peak Width FWHM/eV	[a]Peak Intensity/%	[b]Main Edge (eV)
1	2C-1 dose	$TiCl_2(OiPr)_2 + Si_8Sn_8$	4969.4	2.1	51	4980.8
2	2C-MeOH	methanol passivated catalyst	4969.4	2.3	34	4980.2
3	2C-H_2O_2	**2** + H_2O_2/H_2O	4970.8 (4968.8; 4973.8)[c]	2.3	20	4981.0
4	3C-1 dose	$TiCl_3(OiPr) + Si_8Sn_8$	4969.4	2.0	54	4980.7
5	3C-MeOH	methanol passivated catalyst	4969.4	2.1	49	4980.3
6	3C-H_2O_2	5 + H_2O_2/H_2O	4970.8 (4969.0, 4973.8)[c]	2.5	17	4980.5

7	4C-1 dose	$TiCl_4$ + Si_8Sn_8	4969.2	2.0	48	4980.8
8	4C-MeOH	methanol passivated catalyst	4969.2	2.2	37	4980.4
9	4C-H_2O_2	**8** + H_2O_2/H_2O	4970.8 (4969.0, 4973.8)[c]	2.7	21	4981.1
10	$Ti(OSiPh_3)_4$	4-connected Ti compound	4970	1.4	82	4980.4
11	TS-1	In vacuo	4967	1.4	79	
12	TS-1+H_2O_2	**10** + H_2O_2/H_2O	Not reported	3.4	9	

EXAFS data for all the atomically dispersed titanium catalysts are similar; the results for the 2C-Ti catalyst are shown in **Figure 4**. The titanium sites in 4C-Ti should approximate a tetrahedron of four equivalent oxygen around titanium while both 2C-and 3C-Ti materials could have two Ti-O back-scattering shells (Ti-OR and Ti-OSi_{cube}) at very similar atom separations. The expected Ti-O distance for a Ti(IV) center is 1.8 Å. One and two oxygen shell models were both applied to the data and gave essentially identical fits. In all cases the coordination number for oxygen around titanium refined to approximately four.

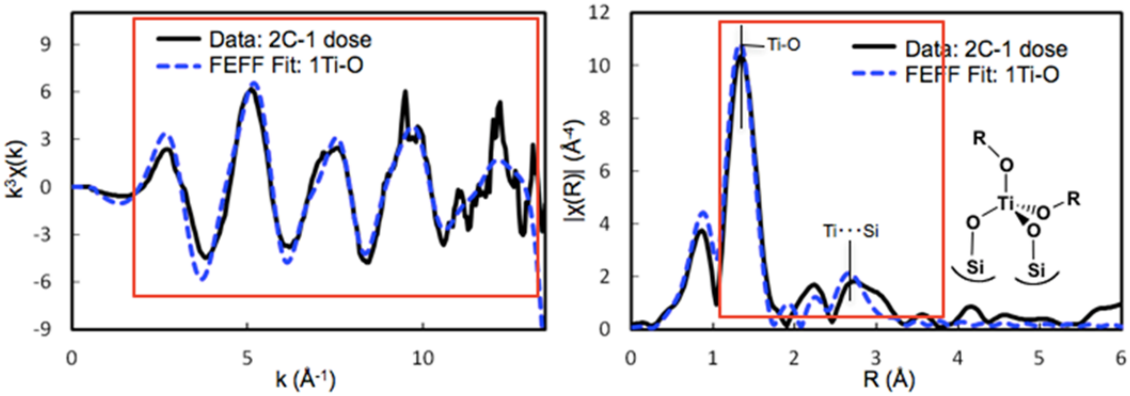


Figure 4 EXAFS data and fits for 2C-Ti atomically dispersed catalyst

The picture that emerges from analytical and spectroscopic characterization of these catalysts is in accord to expectations of our synthetic strategy. The essence of this strategy is to build a support of silicate building blocks around a targeted active metal site while controlling its connectivity and maintaining site isolation. The first step unambiguously sets the connectivity of the metal to the support. Subsequent steps further elaborate on the matrix, establishing porosity and passivating the surface. Utilizing this strategy, we have been able to make individual titanosilicate materials that have atomically dispersed titanium sites, the connectivity of which to surrounding cubes, has been systematically varied from two to four. We next conducted an initial screening of catalytic activity for each of these materials determine the effect that connectivity of the metal center has on catalysis.

Catalysis Studies

We have investigated the activity of the family of atomically dispersed catalysts described above (2C, 3C, 4C-Ti) as well as tetranuclear supported catalyst derived from the chloride benzoate complex, $Ti_4O_2Cl_6(O_2CPh)_6$ in the reaction of 2,3,6 trimethylphenol (TMP) to the corresponding *p*-benzoquinone (eq. 1) When aqueous peroxide is added to an acetonitrile solution containing TMP and a titanium containing catalyst the solid immediately changes color from white to bright yellow. Within five minutes, the solution also turned yellow as the quinone is produced. Aliquots taken over the course of the reaction show the smooth disappearance of phenol from the solution. **Table 3** summarizes the results of a quantitative GC analysis over the course of the reaction for the catalysts prepared here as well as controls and two titanosilicates from the literature.

Table 3 Activity and Selectivity

Ti catalysts	TMP Conversion% (± 3 %)	TMBQ Selectivity% (± 3 %)	TMBQ Yield%	Initial TOF (min^{-1})
TS-1	18	37	7	0.25
Ti-MCM-48	56	73	41	0.75
4C-Ti	26	43	11	0.35
3C-Ti	23	36	8	0.51
2C-Ti	90	80	73	1.58
Ti_4	96	93	89	1.72
No catalyst	0	-		
Silica, fumed	1	-		
$SiCl_4$ platform	3	-		

The control experiments (no catalyst, silica, Si_8O_{20}-building block material with no titanium) clearly show that all catalysis is derived from the presence of titanium in these samples and that any traces of residual tin do not show any significant activity. Microporous TS-1 and mesoporous Ti-MCM-48 (3.5 wt% Ti) were tested along with the new catalysts described here. As has been observed previously, TS-1 is neither effective nor selective in the oxidation of TMP to TMBQ because the micropores are too small for it to access the titanium sites in the zeolite matrix. Surfactant templated MCM-type catalysts contain larger mesopores and the titanium atoms in these matrices are accessible and active in the oxidation reaction. The family of atomically dispersed titanium-building block catalysts that are described here exhibit an interesting trend in reactivity. The 4C-Ti catalyst, where the titanium centers are "embedded" in the silicate cube matrix is the least reactive and exhibits the poorest selectivity for the desired benzoquinone product. The 2C-Ti catalyst, however, is a much better catalyst in terms of both activity and selectivity. Initial turnover frequencies for the 2C-Ti catalyst are higher than either 4C- and 3C-Ti catalysts by factors of 5 and 3, respectively.

Table 4. Stability of titanosilicate catalysts

Sample	Ti wt%		
	Initial Cat.	Recycled Cat.[a]	Mother Liquor[a,b]
2C-Ti	2.7	2.5	0.01
	7.6	6.8	0.10
3C-Ti	5.5	5.1	0.05
	4.2	3.9	0.03
4C-Ti	2.1	1.9	0.02
	3.2	2.6	0.02
Ti_4	5.1	4.5	0.04
	9.0	8.1	0.11

[a] Recycled catalyst and mother liquor collected after 4 - 6 cycles of reaction
[b] Titanium (mg) / recycled catalyst (mg) × 100%

It is also twice as active as and more selective than the well-known mesoporous Ti-MCM-48 catalyst.

Of particular interest in **Table 3** is the behavior of the tetranuclear site material, Ti_4 which displays both the highest activity and selectivity for forming the desired benzoquinone. The turnover frequency given in the table has been calculated on a per titanium atom basis. If it is assumed that the active site involves the tetranuclear unit then the TOF should be multiplied by a factor of 4 to give almost 7 min^{-1}. This "per site" activity is 20 times greater than what is observed for the atomically dispersed, 4C "embedded" titanium catalyst.

The stability of a supported catalyst is also question of importance in evaluating its efficacy in application. This issue has been addressed repeatedly in the past and we have followed the suggestions of Sheldon and coworkers[8] in recycling catalysts after hot filtrations during the course of reaction. **Table 4** summarizes ICP data following the presence of titanium in the recycled solid materials isolated after 4 – 6 cycles and in the reactant solution. All of the title catalysts showed reasonable to good stability against leaching of the metal into solution during reaction. After 4 – 6 cycles of catalysis in all but one case, the new titanium silicate building block catalysts retained 90% or more of the titanium in the matrix. The Ti_4 catalyst was the one exception losing 10% of the original titanium present in the matrix when higher loadings were used.

In many studies of titanosilicate catalysts it has been assumed that at least "tripodal" (3-connectivity) binding of the metal to the support was necessary for stability. However, based on the discussion above, 2C-Ti centers appear to be at least as stable as either 3C or 4C-Ti materials. Consistent with leaching studies described above, the 2C-Ti catalyst maintains good activity and remains selective for the desired quinone over four cycles of catalysis (**Figure 5**).

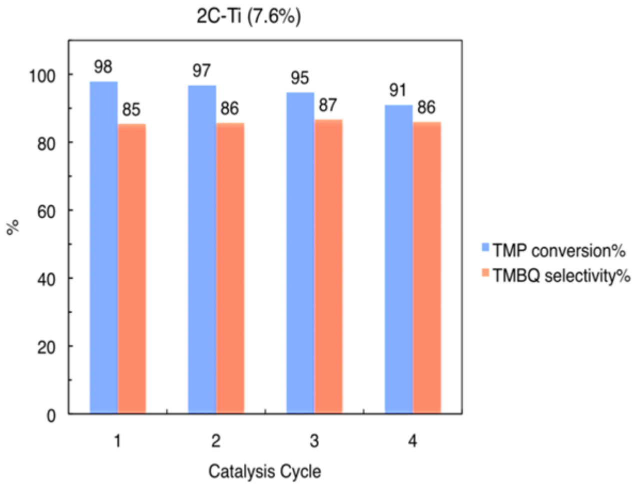


Figure 5 Recyclability of 2-connected titanium catalyst

Conclusions

A family of titanosilicate materials has been prepared through the cross-linking of cubic Si_8O_{20} building blocks with chloroalkoxy titanium reagents. The connectivity of titanium can be targeted simply by adjusting the number of chloride ligands initially present on titanium. Detailed analytical and spectroscopic characterization of the titanium sites in each of these materials are consistent with the presence of only a single type of site in each case with the targeted titanium connectivity to surrounding silicate cubes. A clear correlation of catalytic activity with metal connectivity is observed for atomically dispersed titanium catalysts in the oxidation of trimethylphenol to the corresponding quinone. The most exposed, 2C-Ti catalyst is the most active member of the family with the embedded analogue (4C-Ti) being 5 times slower and significantly less selective. Finally embedded, tetranuclear titania domains are the most active catalysts studied here being very selective and between 5 and 20 times more active than atomically dispersed catalysts prepared using the same synthetic strategy.

Acknowledgements

We would like to acknowledge the support of the Basic Energy Sciences program of the DOE (DE-FG02-01ER15259) for this work. Also we acknowledge the support of the DOE C3Bio EFRC (DE-SC0000997) for supporting our investigations of new single site catalysts that may be used for cellulose and lignin utilization.

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Cost Status:

Approved Budget: $405,000
Actual costs incurred: $403,900

Products Produced:

Publication derived from the support of the DOE BES program:

(1) Clark, J. C.; Barnes, C. E., *Reaction of the* $Si_8O_{20}(SnMe_3)_8$ *Building Block with Silyl Chlorides: A New Synthetic Methodology for Preparing Nanostructured Building Block Solids*, *Chem. Mater.* **2007**, *19*, 3212-18.

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