

## BUILDING BLOCK-BASED CATALYSTS: TAILORING NEXT GENERATION TITANOSILICATES

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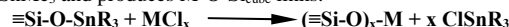
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### Introduction

Heterogeneous catalysis is at a crossroads in terms of catalyst development. The need for higher selectivity with high activity is the current focus in catalysis science and specifically in selective oxidation catalysis. The general consensus on achieving high selectivity with high activity is through spatially dispersed single-site catalysis.<sup>1-4</sup> However, only recently have general methodologies been developed to produce single site catalysts. A broadly applicable approach to the preparation of single site catalysts that does not add time or complexity is still needed. The building block approach to catalysis design allows for maximum control throughout the synthetic process to obtain spatially isolated catalytic sites. In this methodology, the catalytically active metal atom is allowed to tailor its immediate environment as it links building blocks together forming a rigid matrix. This level of control allows the tailoring of active sites to optimize the activity. Furthermore, the type of catalytic site, whether surface or embedded, can be selected by adjusting when the metal is added in the synthesis. This allows not only the tailoring of the catalyst toward high selectivity but also the correlation between the catalyst structure and the observed activity. We report here the synthesis of titanosilicates via the building block approach, EXAFS characterization, and catalytic activity toward isopropanol dehydration/oxidative dehydrogenation.

### Results and Discussion

**Catalyst Synthesis.** The cubic spherosilicate building block  $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$  is mixed with a high valent metal or main group chloride (e. g.  $\text{TiCl}_4$ ) in an aprotic solvent such as toluene or methylene chloride. Reaction between the building block and metal chloride linking reagents releases  $\text{ClSnMe}_3$  and produces  $\text{M-O-Si}_{\text{cube}}$  links.

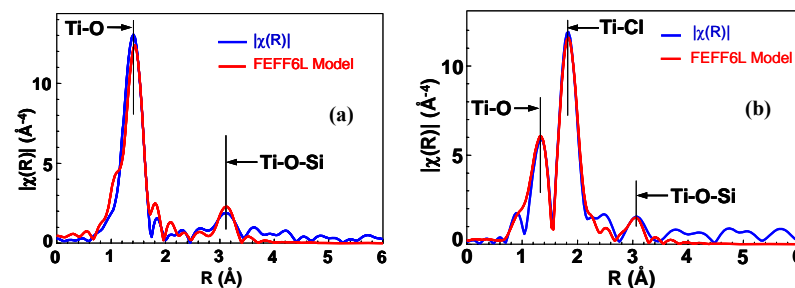


General approaches to synthesizing either “embedded” or “surface” catalysts have been developed. Irreversible cross linking of nanometer sized building blocks leads inherently to porous, high surface area matrices (100 – 700  $\text{m}^2/\text{g}$ ). The atomic dispersion with spatial isolation satisfies the requirements for the single-site catalysts thought to be needed to obtain high selectivities in selective oxidation reactions.<sup>1-4</sup>

The normal and inverse addition procedures yield “embedded” catalyst centers or “surface” catalyst centers. By choosing the addition technique, not only is the type of catalyst controlled, but also the potential for catalytic activity is varied.

**Catalyst Characterization.** The catalysts are fully characterized beginning with gravimetric analysis. This simple procedure provides insight into the average cross-linking around the metal center by tracking the weight loss of trimethyltin chloride. Gravimetric analysis provides an expectation and a starting point for EXAFS modeling by suggesting whether an “M-Cl” feature should be observed or only an “M-O” feature. The EXAFS data are analyzed with the IFEFFIT<sup>5</sup> suite of programs using theoretical phase and amplitude functions generated in FEFF.<sup>6</sup>

EXAFS of the embedded titanium catalyst is consistent with the gravimetric analyses and supports the claim of a fully embedded “ $\text{TiO}_4$ ” catalytic site (Figure 1a). Gravimetric analysis suggests a Ti-O coordination of 4 which is confirmed through modeling the EXAFS data. The identity of the surface titanosilicate is not as self evident as in the case of the embedded catalyst where the lack of a Ti-Cl feature is all that is needed to confirm its identity. Rather, the surface titanosilicate must have a Ti-Cl feature and the modeling must indicate that the number of chlorides around the titanium should be greater than that of oxygen. Preliminary analysis of the surface titanosilicate indicates that the Ti-O to Ti-Cl ratio is 2:2 confirming that the titanium is primarily on the surface of the support (Figure 1b).



**Figure 1.** EXAFS of (a) “embedded” and (b) “surface” titanosilicates.

Preliminary results of the catalytic activity toward dehydration/oxidative dehydrogenation of isopropanol with a 1 wt% titanium loading titanosilicates indicate both propene (dehydration) and acetone (oxidative dehydrogenation) formation with propene as the favored product. Further catalytic studies into the activity of the building block-based titanosilicates are currently ongoing.

### Conclusions

We describe here the general synthesis of a new class of heterogeneous catalysts for most high valent metals. The methodology described yield catalysts that contain atomically dispersed, site-isolated titanium(IV) catalytic centers. The titanosilicates have shown activity toward the dehydration of isopropanol to propene and oxidative dehydrogenation to acetone with propene as the favored product. Further research is ongoing to further optimize the titanosilicate catalysis.

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### References

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