# Design Strategies for the Molecular Level Synthesis of Supported Catalysts

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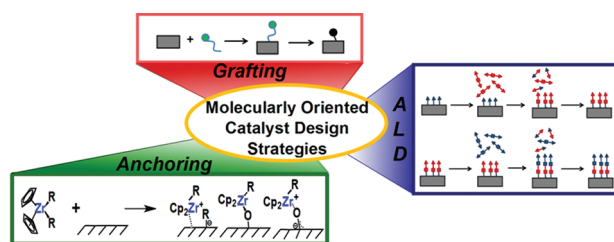
Supported catalysts, metal or oxide catalytic centers constructed on an underlying solid phase, are making an increasingly important contribution to heterogeneous catalysis. For example, in industry, supported catalysts are employed in selective oxidation, selective reduction, and polymerization reactions. Supported structures increase the thermal stability, dispersion, and surface area of the catalyst relative to the neat catalytic material. However, structural and mechanistic characterization of these catalysts presents a formidable challenge because traditional preparations typically afford complex mixtures of structures whose individual components cannot be isolated. As a result, the characterization of supported catalysts requires a combination of advanced spectroscopies for their characterization, unlike homogeneous catalysts, which have relatively uniform structures and can often be characterized using standard methods. Moreover, these advanced spectroscopic techniques only provide ensemble averages and therefore do not isolate the catalytic function of individual components within the mixture. New synthetic approaches are required to more controllably tailor supported catalyst structures.

In this Account, we review advances in supported catalyst synthesis and characterization developed in our laboratories at Northwestern University. We first present an overview of traditional synthetic methods with a focus on supported vanadium oxide catalysts. We next describe approaches for the design and synthesis of supported polymerization and hydrogenation catalysts, using anchoring techniques which provide molecular catalyst structures with exceptional activity and high percentages of catalytically significant sites. We then highlight similar approaches for preparing supported metal oxide catalysts using atomic layer deposition and organometallic grafting. Throughout this Account, we describe the use of incisive spectroscopic techniques, including high-resolution solid state NMR, UV−visible diffuse reflectance (DRS), UV−Raman, and X-ray absorption spectroscopies to characterize supported catalysts. We demonstrate that it is possible to tailor and isolate defined surface species using a molecularly oriented approach. We anticipate that advances in catalyst design and synthesis will lead to a better understanding of catalyst structure and function and, thus, to advances in existing catalytic processes and the development of new technologies.

1. Introduction

Heterogeneous catalysis is an essential industrial process technology. Over 90% of all commercial chemical processes make use of heterogeneous catalysts.[1] An efficient catalyst produces the desired products at high rates while minimizing undesired byproducts. An important class of heterogeneous catalysts uses metal or oxide centers supported on an underlying solid phase which can enhance heat and mass transfer, increase dispersion, suppress sintering, and, as a ligand/activator, alter the catalytic chemistry. Supported catalysts are employed on a large scale in applications including selective oxidation, selective reduction, and olefin polymerization.

The method of synthesizing supported oxide catalysts can be crucial in tuning activity and selectivity, with dispersion, particle size, and catalyst structure having a major influence. While many studies have provided structural information on catalyst surfaces, the link to the structures of *active catalytic species* remains tenuous, largely because the percentage of sites that are active is typically undefined and/or small.[2−4] Surface inhomogeneity obscures both fundamental and practical catalytic science, and better understanding of catalytic surface phenomena will require more controlled syntheses. Thus, the ability to design and tailor isolated, uniform supported catalytic species presents a true "grand challenge".

Traditional catalyst synthetic approaches use aqueous precursor solutions to deposit the active material onto the support. These approaches offer little control over surface species and their dispersion. An alternative technique, chemical vapor deposition (CVD), utilizes gaseous precursors and generally results in higher dispersions. In this Account, we summarize traditional catalyst synthesis techniques and then focus on recent molecular-level approaches to oxide-supported catalysts. Molecular-level syntheses provide tools for catalyst design and improved structural uniformity. Molecular control provides a platform for new supported catalyst technologies, as well as the potential to enhance existing processes on the basis of improved understanding.

2. Traditional Supported Oxide Catalyst Synthesis

2.1. Ion Exchange (IE) and Wet Impregnation (WI).
Supported catalysts are typically synthesized by solution ion exchange, impregnation, or deposition-precipitation.[5−8] The most common precursors are water-soluble metal salts. With ion exchange, an ionic precursor replaces charge-compensating ions on the support surface, excess solution and counterion byproducts are washed away, and the product is dried. The resulting material is then treated under high-temperature oxidizing or reducing conditions to generate the active catalyst. With impregnation, a soluble precursor is precipitated onto the support during solvent evaporation. When the solution volume equals the support pore volume, the technique is called incipient wetness impregnation (IWI). Subsequent deposition, drying, and high temperature activation generates the active catalytic component.

The nature of the catalyst precursor−support interaction critically determines catalyst loading.[5−8] Since the catalyst precursor is typically bound to the support electrostatically, the loading is sensitive to both surface and solution
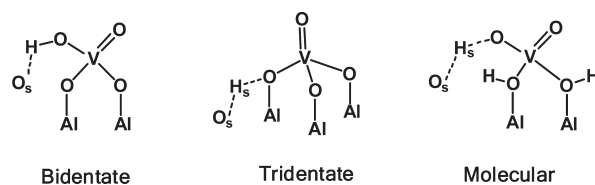
FIGURE 1. Various monomeric VO_x structures observed on low surface coverage vanadium oxide catalysts supported on alumina.

impurities. Addition of agents for precursor solubilizing or adjusting the pH and ionic strength can affect the precursor−support interaction and significantly influence catalyst structure. These adjustments can also change the nature of the support by altering acidic and basic surface sites and hydroxyl group density.[5−7] Furthermore, if the precursor−support interaction is weak, the catalyst dispersion can change during drying and calcination.[8] Consequently, it is frequently difficult to compare different literature catalysts because of subtle differences in the synthetic procedures.

2.2. Structures Prepared by Impregnation.
The inhomogeneity inherent in materials prepared by IWI is exemplified by well-studied vanadium oxide systems. Despite the fundamental and practical importance of these catalysts,[9−11] their active and selective sites are not well understood. Three classes of VO_x species are generally thought to be present on Al_2O_3 surfaces: monovanadate, polyvanadate, and crystalline V_2O_5.[9−11] Monomeric species that consist of a V center coordinated to four O atoms predominate at low V loading. Polymeric or cluster species form as the loading increases, until the entire support is eventually covered by a VO_x monolayer.[12−14] The exact structures of these clusters are unknown. Surfaces with V loadings exceeding monolayer coverage are dominated by V_2O_5 crystallites.[12] This dependence of VO_x surface structures on loading makes it difficult to isolate individual species for examination. At loadings below monolayer coverage, a mixture of monomers, dimers, and polymeric VO_x species is presumed,[12] and their differing contributions to various spectroscopic signatures complicates quantitative assignments.[14−16]

Even at very low loadings, where monomeric VO_x should predominate, mixtures of structures having differing mono-, bi-, and tridentate surface coordination were identified by resonance Raman spectroscopy and computational modeling (Figure 1).[17] Such mixtures are inherent to catalyst surfaces and greatly complicate any mechanistic discussion since they are expected to exhibit different reactivities and selectivities. Indeed, substantial reactivity differences are observed in H_2 temperature programmed reduction (H_2-TPR) experiments, with the bidentate surface structure

undergoing reduction at a significantly lower (~50 °C) temperature than the molecular or tridentate species.[18] The challenge of catalyst inhomogeneity and the limits it places on understanding catalytic chemistry has motivated efforts to produce more uniform structures.

2.3. Synthesis by Deposition-Precipitation (DP). Deposition-precipitation is a common supported catalyst preparation technique where the active catalyst precursor is deposited on the support by precipitation.[6,8] Precipitation is carried out on the dissolved catalyst precursor in a solution containing the suspended support such that bulk nucleation is prevented, and the precursor is deposited on the support. DP results in finely divided crystallites on the support and very high loading catalysts. Like WI and IE, the precursor–support interaction is decisive, and changes in pH, solubilizing agents, or complexing agents can significantly affect the resulting structures. The rates of nucleation and growth during precipitation determine the deposited crystallite size and are difficult to control, often resulting in nonuniform distributions of particle sizes and structures. Large crystallites result when nucleation and growth are both fast, while smaller particles are formed under rapid nucleation and slow growth. For rapid transport of the precursor to the surface, support dimensions must be small, <2 mm.[8] Alternatively, the support and the precursor can be precipitated together, with the active catalyst and support forming simultaneously. In this deposition-coprecipitation approach, simultaneous nucleation and growth of both catalyst and support significantly affect the resulting structure and properties.

2.4. Synthesis by CVD. CVD (chemical vapor deposition) is a common alternative to solution methods that eliminates some of the deficiencies in structural control discussed above.[6,19] In CVD, a gaseous precursor stream is chemisorbed onto the support. The absence of solvent facilitates precursor diffusion inside pores and precludes drying steps during which active phase redistribution may occur. CVD also offers better control of the initial support surface composition. A principal advantage of CVD is the ability to control coverage by adjusting the precursor supersaturation and hence nucleation rate and particle size.[6] CVD-synthesized catalysts generally show good dispersions and high catalytic activities compared to solution preparations; however, particle sizes are normally large and not necessarily uniform.

While the aforementioned synthetic methods are straightforward and produce catalysts with high surface areas, they do not provide ultimate control of site size, structure, active phase composition, or dispersion across the surface. Creating truly uniform catalyst surfaces requires more subtle methodology.

3. Molecular Anchoring for Supported Organometallic Catalysts

Synthetic strategies for the preparation of single-site heterogeneous catalyst are at the forefront of rational catalyst design. Bridging traditional homo- and heterogeneous catalysis, single-site heterogeneous catalysts have recently generated much academic and industrial interest.[20−26] Similar to enzyme active sites and traditional homogeneous catalysts with discrete metallo-active centers, single-site supported catalysts offer the potential of well-defined, uniform active sites, but with the separation and recyclability advantages of heterogeneous catalysts. Heterogenizing molecular catalysts also allows use in slurry reactors, offering excellent heat transfer, amenability to online catalyst addition or withdrawal, and ease of fabrication.[27−29]

Single-site supported catalysts are most commonly prepared by molecular-level anchoring, in which a molecular precursor undergoes reaction with the surface while maintaining most of the ligand environment of the parent molecule, and offering many attractions of heterogeneous systems.[30] Chemisorption of discrete organometallic complexes on oxide supports yields catalysts with well-defined active sites, greater thermal stability, and decreased reactor fouling versus the homogeneous analogues.[31] These catalysts exhibit very high activity for α-olefin polymerization[32−38] and hydrocarbon transformations.[38−42]

3.1. Representative Pathways to Single-Site Supported Catalysts. Understanding the reaction pathways of organometallic precursor anchoring enables tailored catalyst structure and reactivity. Operative pathways for ^{13}C enriched organogroup 4[43−46] and organoactinide[20,47−53] hydrocarbyl chemisorption have been characterized on various oxide surfaces by product analysis, isotopic labeling, and high-resolution solid-state NMR spectroscopy. Three distinct pathways have been identified (see Scheme 1 for Cp$_2$ZrR$_2$ complexes): (i) heterolytic M–C bond scission (A), (ii) M–C σ-bond protonolysis to form a covalent M–O$_s$ bond (B), and (iii) M–C σ-bond protonolysis to form an electrostatic M$^+$···O$_s^−$ bond (C). The support surface chemical properties govern the pathway and catalytic performance of the resulting active site. Heterolytic M–C bond scission is the primary pathway for highly Lewis acidic surfaces, such as MgCl$_2$ and dehydroxylated alumina. Here an alkide anion is transferred to the Lewis acid site to yield "cationic" organometallic

**SCHEME 1.** Chemisorption Pathways for Cp_2ZrR_2 Complexes[a]
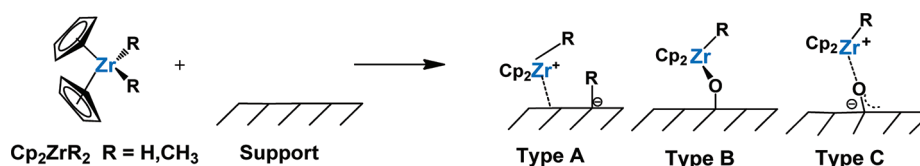
[a] The surface species formed depends on the nature of the support sites. Highly Lewis acidic sites yield Type A "cationic" adsorbate species, while weakly Brønsted acidic surfaces yield μ-oxo type surface species, Type B. Type C "cationic" organometallic species are formed on highly Brønsted acidic supports.

adsorbates (Type A).[20,47−53] For weakly Brønsted acidic surfaces such as partially dehydroxylated alumina, silica, and MgO, M−CH$_3$ protonolysis yields μ-oxo species (Type B).[20,47−53] In contrast to these pathways, chemisorption on highly Brønsted acidic sulfated oxide sites proceeds via M−C protonolysis, yielding electrophilic organometallic cations with the counteranionic charge dispersed over the electron-deficient oxide surface (Type C).[38,44−46]

Catalysts prepared by anchoring group 4 and actinide precursors are highly active for both olefin and arene hydrogenation and olefin polymerization, with activities exceeding those of the homogeneous analogs. Type B species have reduced activity versus Type A due to strong coordination by the oxo-conjugate base of the weak Brønsted site, thus saturating the metal coordination sphere and depressing electrophilicity. If the support has a diversity of acid sites, the resulting catalyst(s) will be a mixture of surface species (Types A−C) while a support dominated by a single type of surface site will generally afford uniform catalytic sites.[43] Therefore, surfaces can be tailored with specific reactivity by choosing supports with specific acid properties.

3.2. Mechanism Elucidation Using Single-Site Supported Catalysts. Several classes of supported single-site organozirconium hydrocarbyls have been synthesized via molecular-level anchoring and characterized using high resolution solid-state ^{13}C CPMAS NMR, active site poisoning experiments, and XAFS/XANES.[38,44,45] Highly electrophilic organozirconium species (Type C) formed on sulfated alumina exhibit unprecedented benzene hydrogenation activity and high olefin polymerization activity. Kinetic poisoning studies are used to assay the percentage of Zr sites active for benzene hydrogenation or olefin polymerization. Ideal "single-site" supported catalysts should have 100% of the sites active as in typical homogeneous systems yet retain the benefits of heterogenization.

Active site counting/poisoning experiments reveal that 97 ± 2% of $[\eta^5\text{-}C_5(CH_3)_5]Zr(CH_3)_3$/sulfated Al_2O_3 sites are active for benzene hydrogenation and 87 ± 3% for ethylene polymerization. Such high populations of active
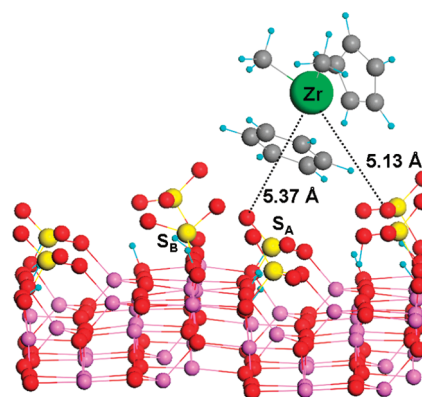
**FIGURE 2.** DFT computed energy-minimized structure of catalyst resting state $[\eta^5\text{-}C_5(CH_3)_5]Zr(CH_3)_2(\eta^6\text{-benzene})^+\cdots AIS^-$ species confirmed by XAFS.[54]

organometallic sites are, to our knowledge, unprecedented and also argue that the same sites are active for these very different transformations, or at least derive from a common intermediate. Because of the high percentage of active sites, these surfaces present a unique opportunity for detailed characterization of the actual structures of catalytically active species. In combined theory/experiment studies, the products of $(\eta^5\text{-}C_5H_5)_2ZrR_2$ (R= H, Me) and $[\eta^5\text{-}C_5(CH_3)_5]Zr(CH_3)_3$ chemisorption were characterized on Brønsted superacidic sulfated Al_2O_3.[54] For the $[\eta^5\text{-}C_5(CH_3)_5]Zr(CH_3)_3$ system with ∼100% active sites, the data indicate formation of organozirconium cations having largely electrostatic $[\eta^5\text{-}C_5(CH_3)_5]Zr(CH_3)_2^+\cdots AIS^-$ interactions with elongated $Zr\cdots O_{AIS}$ distances of ∼2.36 Å versus ∼1.95 Å for typical covalent Zr−O bonds (Figure 2). XAFS also indicates benzene capture by essentially every Zr site to form $[\eta^5\text{-}C_5(CH_3)_5]Zr(CH_3)_2(\eta^6\text{-benzene})^+\cdots AIS^-$ species, in agreement with computational results and the reaction kinetics. This work illustrates the unique "visualization" of active sites and reaction intermediates possible with these structurally uniform species.

4. Synthesis of Oxide Supported Catalysts by Atomic Layer Deposition

In recent years, atomic layer deposition (ALD) has proven effective for supported catalyst synthesis.[55−59] Originally

SCHEME 2. General Binary Reaction Sequence for Layer-by-Layer ALD Growth Processes
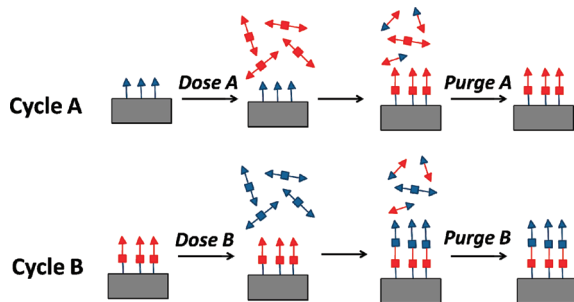
developed for thin film growth, ALD delivers uniform, conformal, thin films with atomic level precision on many substrates,[60,61] and is applicable to the synthesis of uniform catalyst structures on porous, high surface area supports. As with organometallic anchoring discussed above, ALD offers molecular-level control and relies on surface chemical bonds rather than electrostatic interactions. ALD couples sequential, self-limiting reactions that deposit precursors in a layer-by layer fashion (Scheme 2).[60−64] Two types of gaseous precursors are pulsed alternately, each reacting with the surface functional groups generated in the previous pulse. The support is first exposed to precursor A, generating a surface saturated with chemisorbed precursor molecules. When all available surface sites have reacted, further exposure to precursor results in no further deposition; the process is self-limiting. Unreacted precursor and any volatile byproducts are then removed by inert gas purging. The next step is exposure to precursor B, generating a new surface, followed by purging of unreacted precursor and gaseous byproducts (Scheme 2). Because surface functional groups are regenerated at the end of each cycle, many layers of catalytic material can be deposited. By repeating a binary reaction sequence in an ABAB... fashion, catalysts with desired loadings and surface structures can be synthesized. This precise layer-by-layer deposition suppresses catalyst aggregation, ensuring high dispersion. Hence, ALD addresses the typical inhomogeneity of heterogeneous catalysts and enhances the understanding of catalyst composition/structure/function relationships.

The self-limiting character of ALD enables controlled, uniform deposition on porous supports. Unlike CVD, the separation of reactant dosing steps limits uncontrolled growth and large aggregate formation. However, reaction temperatures must be fine-tuned for optimal growth; it must be sufficient for precursor vaporization, yet below the decomposition temperature to avoid uncontrolled growth

(CVD). ALD is limited by availability of suitable precursors that are volatile and reactive with the supports but thermally stable at growth temperatures. The reaction byproduct(s) must be unreactive and volatile. ALD can deposit a wide range of materials including oxides, nitrides, sulfides, and metals.[61] Current ALD research focuses on enlarging the scope of precursors and using the technique to create advanced catalysts, multilayer oxides, and supported metal nanoparticles.[65−71]

4.1. ALD Synthesis of Supported Vanadium Oxide Catalysts. There are several examples of supported oxide catalyst syntheses by ALD, including supported vanadium oxides.[55−58,72−76] Volatile vanadyl alkoxide precursors, $VO(OEt)_3$ or $VO(O^iPr)_3$, deposit vanadium in cycle A of Scheme 2, and H_2O or H_2O_2 regenerates the hydroxyl surface in cycle B. Compared with preparations by IWI, ALD-derived VO_x catalysts are better dispersed,[56,58] more selective, and exhibit comparable activity in propane[56,72] and *o*-xylene[55,57] oxidation.

Comparison of structural and catalytic differences between supported VO_x catalysts prepared by ALD and WI was performed in this laboratory for cyclohexane oxidative dehydrogenation (ODH).[76] Mechanistically, cyclohexane ODH provides more information on the catalytic oxidation reaction pathways via the formation of two different hydrocarbon products, cyclohexene and benzene, whereas propane or ethane yield only CO_x over-oxidation products. Thus, it is possible to evaluate the relative contributions from reaction pathways where benzene is produced during a single cyclohexane adsorption on the active site versus a sequential pathway involving a cyclohexene intermediate. At similar loadings, the activity of ALD-derived catalysts, quantified as turnover frequency (TOF), is significantly higher than catalysts prepared by WI (Figure 3). This is a direct consequence of the increased control of catalyst structure and dispersion via ALD.

4.2. ODH Kinetic Pathways on ALD-Derived Catalysts. Because of their high dispersion and activity, ALD-derived supported VO_x catalysts were used to investigate the reaction pathways in cyclohexane ODH. As the VO_x loading increases, TOFs increase and activation energies decrease, implying that polymeric VO_x surface structures are more active than the monomeric counterparts. However, as the VO_x loading increases, selectivity to cyclohexene falls dramatically. Numerical simulation of the reaction network yields Scheme 3 where formation of the deep oxidation products, benzene, and CO_x proceeds both by sequential and direct reaction pathways. At low catalyst loadings
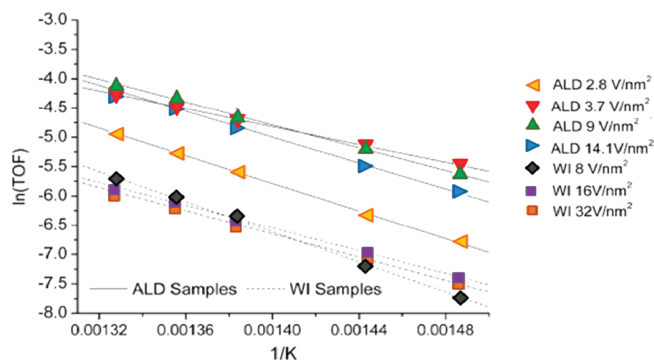
FIGURE 3. Dependence of the TOF for cyclohexane oxidative dehydrogenation on temperature for ALD-derived and wet impregnated VO_x catalysts. Reprinted with permission from ref 76. Copyright 2010 Elsevier.

SCHEME 3. Cyclohexane ODH Reaction Network[a]

Units: $(V\text{-sec})^{-1} \times 1000$
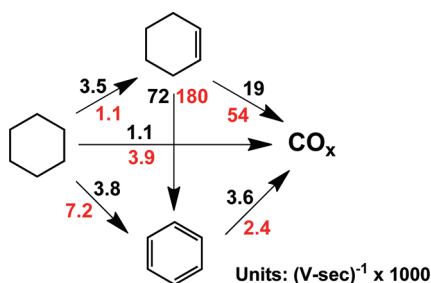
[a]Reaction rate coefficients are for VO_x coverages of 3.7 V/nm² (red) and 9.0 V/nm² (black). Reprinted with permission from ref 76. Copyright 2010 Elsevier.

(3.7 V/nm²), 56% of the cyclohexane follows the sequential reaction pathway and 33% is directly converted to benzene; however, at high catalyst loadings (9.0 V/nm²), over 70% of the reacted cyclohexane is directly converted to benzene. Although the overall reaction rate of 9.0 V/nm² is larger than that for lower loadings, the latter achieves 3× higher cyclohexene formation rates, arguing that cyclohexene is formed predominantly on monomeric VO_x surface species.

5. Synthesis of Supported Oxide Catalysts by Organometallic Grafting

Similar to catalyst syntheses using supported organometallic complexes and ALD reactions, organometallic grafting is a molecular-level technique for synthesizing supported oxides and is effective in depositing structured molecular complexes onto oxide supports. By definition, catalysts prepared using this technique have single sites with different chemical surroundings than the parent precursor.[30] In grafting, the metal coordination shell is partially modified during or after the deposition, usually via calcination or reduction. Organometallic grafting, like anchoring by organometallic immobilization and ALD, capitalizes on molecular precursor

uniformity. However, in contrast to organometallic immobilization, grafting removes the ligands in an additional step, similar to ALD but without precursor volatility restrictions; therefore, it is useful for synthesizing a wide variety of supported oxide catalysts.

In this laboratory, grafting was used to prepare discrete supported VO_x species using organovanadium precursors of preselected nuclearity.[18] Grafted onto θ-alumina surfaces were $VO(Mes)_3$, $[(Mes)_3V]_2(\mu\text{-O})$, and $[(\eta\text{-}C_5Me_5)V]_4(\mu\text{-}O_6)$ as shown in Scheme 4. UV−vis DRS spectroscopy, XAFS/XANES, UV−Raman spectroscopy, and H_2-TPR were used for structural elucidation of the grafted catalysts. Unlike supported VO_x catalysts prepared at low loadings by IWI that are a mixture of monomeric species with different surface coordinations, the supported catalysts prepared by organometallic grafting appear to have specific, tailored surface coordinations. Grafted catalysts are currently under study to correlate structures with spectroscopic characteristics as well as to develop a better mechanistic understanding of selective oxidation processes, especially ODH. Dimeric or higher nuclearity precursors should be valuable in understanding the catalytic role of V−O−Al and V−O−V structural features.

Organometallic grafting can also be employed to synthesize isolated catalytic sites of mixed oxides using a specific class of organometallic grafting termed the thermolytic molecular precursor (TMP) method.[77] This method utilizes organometallic precursors of the type $L_nM[OSi(O^tBu)_3]_m$ and $L_nM[O_2P(O^tBu)_2]_m$, (L_n = alkoxide, amide, alkyl ligands) that thermolytically release isobutene and water upon reaction with a hydroxylated oxide support of the type M/Si/O or M/P/O. TMP has been extensively employed to synthesize mixed-metal oxides including amorphous aluminosilicates with high acidity.[78] The TMP method has also been studied as a synthetic route to supported VO_x catalysts.[79−82] The resulting catalysts are highly dispersed and offer superior catalytic performance when compared with catalysts prepared by WI for the selective oxidation of methane and propane ODH.

6. Mobility of Supported Catalysts

Despite above examples of tailoring supported catalysts by molecular synthesis, questions remain about the mobility of oxide species on oxide surfaces.[83−85] The Tammann expression, $T_{Tam} \approx 0.5T_{bulk,melt}$, is used to describe the temperature at which supported oxide species become mobile, where $T_{bulk,melt}$ is the melting point of the bulk material and T_{Tam} is the Tammann temperature.[86] At the Tammann

SCHEME 4. Organometallic Grafting Reactions of Precursors $VO(Mes)_3$, $[(Mes)_3V]_2(\mu\text{-}O)$, and $[(\eta^5\text{-}C_5Me_5)V]_4(\mu\text{-}O_6)$ on $\theta\text{-}Al_2O_3{}^a$
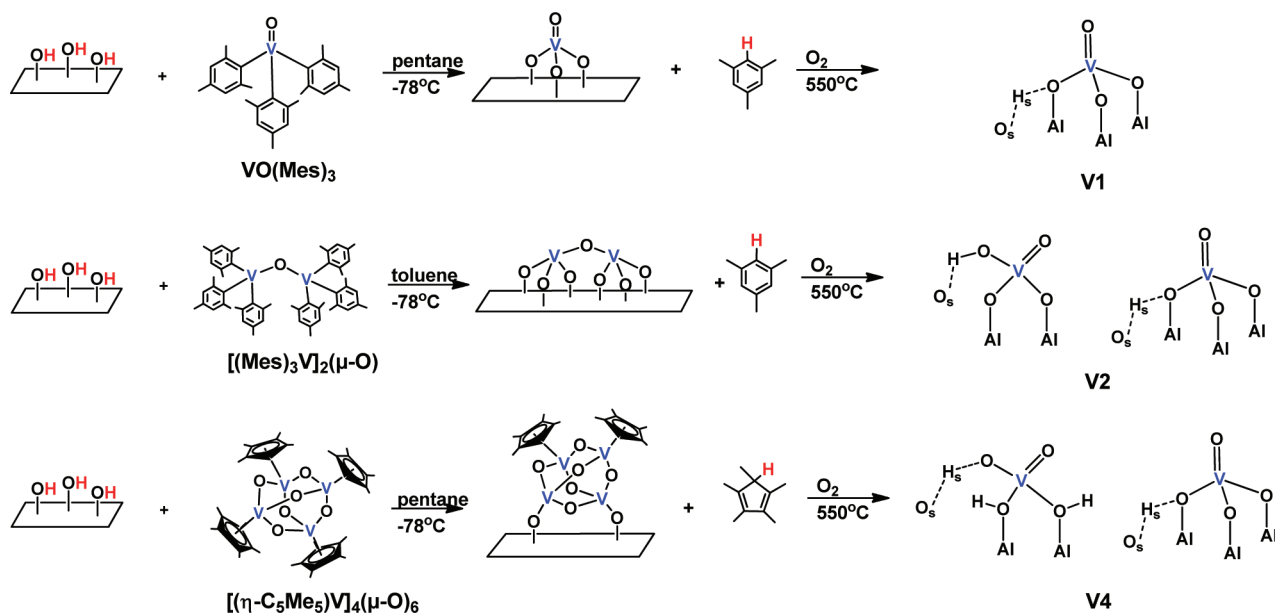
^{a}The supported vanadia catalysts **V1**, **V2**, and **V4** are characterized after calcination in oxygen.

temperature, it is presumed that the species will diffuse and transform to the thermodynamically stable form, regardless of the synthesis method. However, the relevance of Tammann temperatures to surface mobility is questionable for well-isolated species. Thus, the Tammann temperatures of bulk catalysts and oxide supports can differ substantially, as exemplified by the VO_x/Al_2O_3 system where T_{Tam} of bulk $V_2O_5 = 209\ °C$ and T_{Tam} of bulk $Al_2O_3 = 890\ °C$.[86] For low-loading VO_x/Al_2O_3 catalysts, preparation using different organometallic precursors produces markedly different structures and reactivities, even after treatment in O_2 at 550 °C,[18] well above the Tammann temperature of bulk V_2O_5. This implies that the bulk oxide Tammann temperature is not the only factor governing surface structure and that supported oxide structures can be strongly influenced by advanced molecular-level synthesis.

7. Conclusions and Prospects

In this Account, we emphasized the importance of achieving supported catalyst structural uniformity for reaction selectivity and for elucidating structure–function relationships. Traditional catalyst preparation techniques including ion exchange, impregnation, deposition-precipitation, and CVD typically afford mixtures of species, severely complicating any structure/mechanism deductions. In contrast, synthetic strategies based on molecular principles can yield more uniform surface species and aid mechanism determination in several classes of catalytic reactions. Anchoring is a

well-established synthetic route to single-site heterogeneous catalysts and affords structures and reactivities reminiscent of the homogeneous analogues. In some cases, remarkably high percentages of catalytically significant sites can be achieved, allowing precise structure determination and isolation of reaction intermediates. Atomic layer deposition and organometallic grafting make possible a level of control and flexibility that aids structure and mechanism elucidation. Compared with traditional catalyst preparation techniques, advanced molecular-level synthesis provides a pathway for rational catalyst design with broader implications for improving existing catalytic technologies, as well as the potential for developing new catalytic processes.

BIOGRAPHICAL INFORMATION

Staci L. Wegener was born in Bay City, Michigan. She received her B.S. from Saginaw Valley State University in 2006. She is currently a Chemistry Ph.D. student at Northwestern University working under the supervision of Tobin J. Marks and Peter C. Stair.

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FOOTNOTES

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