Design and synthesis of heterogeneous catalysts: the thermolytic molecular precursor approach

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Abstract

The use of the *thermolytic molecular precursor* (TMP) method for the generation of multicomponent oxide materials is reviewed with emphasis on the generation of catalysts and catalyst support materials. Various adaptations of the TMP method that allow manipulation of catalyst compositions are presented. Further, the generation of isolated catalytic centers via grafting techniques is summarized. The implications for syntheses of new catalysts and catalyst formulations are discussed, and specific examples that involve selective hydrocarbon oxidation catalysts are provided.
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1. Introduction

New analytical methods, high-level theoretical studies, and various mechanistic experiments are producing important information regarding factors that contribute to a catalyst's activity, selectivity, and stability [1–6]. The results from these studies are potentially quite valuable in leading us to new generations of catalysts, since they provide structure–reactivity correlations that can be used in catalyst design. Future advances in catalysis research will also be driven by the development of new synthetic methodologies, which allow the efficient and reliable construction of complex inorganic structures. These synthetic methods will provide access to catalytic materials that are currently unknown and to well-defined structures that can be used to test theories concerning the influence of structure on reactivity. Catalyst development clearly relies on synergistic relationships among research activities on several fronts, but advances in synthesis have lagged somewhat behind those occurring in characterization, theory, and mechanistic analysis. This situation contrasts with that in the field of electronic materials, where the development of new synthetic techniques has played a vital role in producing materials with improved properties [7–9].

Many synthetic challenges are presented by established structure–reactivity relationships and by well-recognized goals in catalysis research. This is particularly true for heterogeneous catalysts, since synthetic control over the structures of complex solids is still rather limited. One aspect of the challenge of synthesizing catalytic materials is that very often, structures for the most active and selective heterogeneous catalysts are metastable. This requires the use of low-temperature methods and often rather involved synthetic procedures [10–13]. In general, more practical synthetic methods are needed to achieve controlled, facile assembly of complex nanostructures [14–20]. The importance of nanostructural control is emphasized by the many nanoscaled structures that appear to markedly influence catalytic properties. These include supported monolayers, highly dispersed catalytic particles, catalyst–support interfaces, and framework mesoporosity [21,22]. Recent progress in the development of synthetic methods for creating nanostructures has been driven largely by the search for new electronic materials. Of relevance to catalysis, mesoporous materials have become available with the discovery of the surfactant-mediated growth of inorganic networks [22–26]. Other methods involving templating and formation of organic–inorganic interfaces have produced well-defined nanoparticles and nanowires [21,27–30].

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There is still a need for simple and versatile synthetic methods that allow manipulation of structure on an even smaller scale (atomic level), since for many of the best catalysts the spatial arrangement of metal atoms on a catalyst surface is crucial for defining reactivity. For example, the M–O–M′ heterolinkages of bimetallic oxides and catalyst–support interfaces are associated with reactivities that are not observed for the corresponding homolinkages M–O–M and M′–O–M′. This has led to considerable effort geared toward the production of well-dispersed (atomically homogeneous) mixed-element oxides. For the most part, these efforts have involved modifications of the sol–gel synthesis of oxides [10–12,31]; however, this approach is limited by the inherently different rates of hydrolysis for alkoxide precursors (e.g., $M(OR)_n$ and $M'(OR')_m$). For many catalysts, desirable properties appear to be associated with well-defined active sites containing one or perhaps a few metal centers (single sites) [32–37]. Thus, it is important to develop methods to achieve the controlled chemical modification of surfaces via the introduction of well-defined active sites. Most attempts to introduce inorganic structures of this type have centered on aqueous impregnation methods, which suffer from the tendency of many metal-based species to agglomerate on the surface of a support during dehydration. A very promising strategy for the production of well-defined and highly active sites on the surface of an oxide support involves grafting of an organometallic species, followed by activation of the resulting "site" via further chemical reactions [38,39]. This approach includes what may be described as "surface organometallic chemistry," which has been used by Basset and co-workers to prepare highly active catalysts for alkane metathesis and alkane hydrogenolysis [40–45].

Our research program in the synthesis of heterogeneous catalysts focuses on strategies that employ molecular design and molecular precursor chemistry. Much of this work has targeted the production of multicomponent oxides for which high dispersions of elements are expected to give desirable catalytic properties. For example, some materials of this type function as solid acids (e.g., ZrO_2–SiO_2 and Al_2O_3–SiO_2) [46–51]. In addition, a wide variety of complex metal oxides have been identified as selective partial oxidation catalysts [52–54]. For multicomponent catalysts of this kind, optimum performance should result from maximization of surface area, homogeneity, and active site distribution.

In synthesizing a variety of multicomponent oxide materials with tailored properties, we have employed a molecular building-block approach referred to as the *thermolytic molecular precursor* (TMP) method [55–83]. This molecular precursor approach employs metal complexes containing oxygen-rich ligands, such as those with the general formulas $L_nM[OSi(O^tBu)_3]_m$ [55–73,76–79] and $L_nM[O_2P(O^tBu)_2]_m$ [79–83], where L_n = alkoxide, amide, alkyl, etc. Such compounds function as excellent single-source precursors to carbon-free, homogeneous mixed-ele-

ment oxide materials of the types M/Si/O and M/P/O, respectively. The low-temperature (< 473 K) thermolytic conversion of these molecular species to three-dimensional networks occurs via elimination of isobutene and H_2O (after condensation of the resulting hydroxyl groups). When the thermolyses are performed in nonpolar solvents (e.g., toluene or *n*-octane), a solvent-containing gel is often obtained. The conventional air-drying of this gel provides a xerogel, and supercritical drying methods produce an aerogel. These drying methods provide materials with similar, very high surface areas and pore volumes.

Although the sol–gel process and the TMP method both represent low-temperature routes to metastable materials, the TMP method offers several advantages. First, the use of high-purity and well-defined species allows accurate control over the stoichiometry of the final material. Also, the preexistence of M–O–E groups in the molecular precursor maximizes the homogeneity of the final material and leads to a large number of such heterolinkages. The TMP method also offers benefits with respect to surface properties, since the use of nonpolar solvents minimizes pore collapse upon drying, thus providing high pore volumes and surface areas. Additionally, the use of nonaqueous media prevents M–O–E cleavage via hydrolytic means, a common occurrence in sol–gel processes that leads to inhomogeneity. Finally, the precursor complexes may serve as soluble molecular models for single-site catalysts involving a metal center on the surface of an oxide support. Other groups have developed so-called "nonhydrolytic" routes to oxide materials, including the condensation of metal alkoxides with metal acetates [84] or metal halides [85].

2. Thermolytic molecular precursor (TMP) route to oxide materials

Much of our early work on exploration of the TMP method focused on fundamental questions regarding the viability of this approach to mixed-element oxides and on investigation of the properties of the resulting materials. Key comparisons have been made to materials of the same composition that were prepared by more traditional aqueous or sol–gel procedures. Our initial interest centered on metal oxide–silica materials, for which homogeneity is thought to significantly influence properties. For example, such materials exhibit increased acidity and higher Brønsted acid site concentrations with increasing concentrations of M–O–Si heterolinkages. Another goal is to determine how the structural and chemical properties of the molecular precursor influence the properties (porosity, catalytic efficiency, surface acidity, etc.) of the ultimate materials.

The TMP method for materials synthesis works well for precursors of the type $M[OSi(O^tBu)_3]_4$ (M = Ti, Zr, Hf), which convert cleanly to carbon-free materials with the formula $MO_2 \cdot 4SiO_2$. These conversions occur under mild thermolytic conditions (373–473 K) in the solid state or by

heating solutions of the precursors [57,63]. For example, thermolysis of $Zr[OSi(O^tBu)_3]_4$ in toluene at 413 K results in elimination of 12 equivalents of isobutylene,

$$Zr[OSi(O^tBu)_3]_4 \overset{\overset{toluene}{413\,K}}{\rightarrow} ZrO_2 \cdot 4SiO_2 \\ + 12CH_2{=}CMe_2 + 6H_2O, \qquad (1)$$
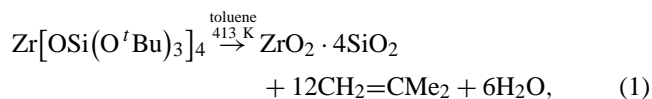
and formation of a transparent gel, which upon drying yields a high-surface-area xerogel ($520\ m^2\,g^{-1}$).

Solid state ^{29}Si MAS NMR spectra of these $ZrO_2 \cdot 4SiO_2$ xerogels, either uncalcined or after calcination at 873 K, show that the majority of the Si atoms are in Q^2 and Q^3 environments, attributed to the presence of $(ZrO)_2Si(OSi)_2$ and $ZrOSi(OSi)_3$ sites, respectively. These results suggest that these materials have a high degree of homogeneity [63]. Further evidence of the highly homogeneous nature of materials made via the TMP route is provided by an EDX HR-TEM study of a mesostructured $ZrO_2 \cdot 4SiO_2$ material, synthesized via solution thermolysis of $Zr[OSi(O^tBu)_3]_4$ in the presence of a structure directing block copolymer [66]. A constant 4:1 Si/Zr ratio was observed throughout the material using a 10-Å probe scanning at 35-Å intervals [66]. The presence of a large number of M–O–Si heterolinkages in these $ZrO_2 \cdot 4SiO_2$ xerogels would be expected to give rise to a highly acidic material [48]. Hammet acidity [86] measurements of these xerogels indicate that the Hammet acidity function (H_o) values are between -5.6 and -8.2, which is consistent with high acidity and homogeneity [63].
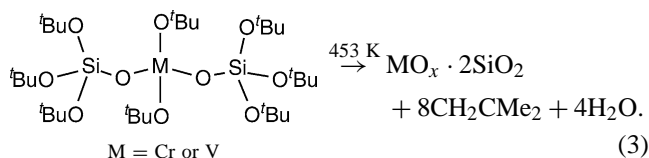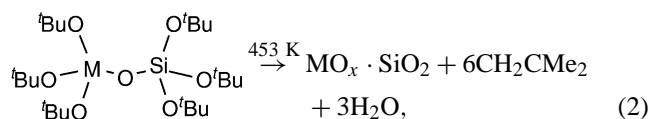
The thermal conversion of complexes containing M–$OSi(O^tBu)_3$ and M–$O_2P(O^tBu)_2$ moieties appears to be catalyzed by Brønsted acids [67,76]. In general, when M is electron poor and Lewis acidic, the thermal decompositions occur efficiently and at low temperatures. The addition of a catalytic amount of a Lewis or Brønsted acid ($AlCl_3$ or HCl) has been observed to accelerate elimination of isobutylene and the formation of a material [63,67,76]. For cases where conversion of a precursor to a material is slow or occurs at higher temperatures, the addition of such catalysts can effectively facilitate synthetic procedures.

In studies on use of the TMP method for generation of amorphous aluminosilicates, an important class of solid acid materials, the chemical nature of the precursor has a profound influence on the properties of the resultant solid. This was illustrated, for example, by the fact that $Al_2O_3 \cdot 2SiO_2$ materials derived from $Al[OSi(O^tBu)_3]_3(HO^iPr) \cdot \frac{1}{4}[Al(O^iPr)_3]_4$ and $[(O^iPr)_2AlOSi(O^tBu)_3]_2$ (both with Al/Si = 1) have quite different microstructures and surface acidities [70]. Thermolysis of a toluene solution of the former precursor provided a xerogel that, when compared to a similarly derived xerogel from the latter precursor, had a lower Brønsted acid site concentration (0.8 ± 0.2 vs 2.3 ± 0.2 sites nm^{-2}, by ^1H NMR spectroscopy after reaction of the samples with $Mg(CH_2C_6H_5)_2 \cdot 2THF$), a higher Lewis/Brønsted site ratio (1.6 vs 1.0, by NH_3 TPD), and a microstructure that more closely resembled that of mullite

(by PXRD and DSC). Apparently, the preexisteence of only Al–O–Si linkages in $[(O^iPr)_2AlOSi(O^tBu)_3]_2$ gives rise to more Brønsted acid sites, whereas the Al–O–Al linkages in the $[Al(O^iPr)_3]_4$ component of $Al[OSi(O^tBu)_3]_3(HO^iPr) \cdot \frac{1}{4}[Al(O^iPr)_3]_4$ provide a material with more mullite character and less Brønsted acidity. Such correlations between the nature of a precursor and the properties of a material derived from it should prove useful in the design and synthesis of tailored catalysts and support materials.

High-surface-area magnesia–silica xerogels ($245\ m^2\,g^{-1}$) and aerogels ($640\ m^2\,g^{-1}$) with the composition $MgO \cdot 2SiO_2$ were generated from the single-source molecular precursor $Mg[OSi(O^tBu)_3]_2$ using TMP methods [68]. Previous predictions and experimental evidence for high-SiO_2-content magnesia–silica materials suggested that the number of acid sites for the mixed oxide would be larger for a more homogeneous material [87]. In contrast, poorly dispersed magnesia–silica materials (containing large SiO_2 and MgO domains) were shown to have a higher basicity [88]. Thus, the acid–base properties of magnesia–silica materials appear to be directly correlated to the degree of homogeneity. The $MgO \cdot 2SiO_2$ xerogels made from $Mg[OSi(O^tBu)_3]_2$ were shown to have a high acid site concentration (from NH_3 TPD: 2.7 sites nm^{-2}) and a negligible basicity (from CO_2 TPD: 0.13 sites nm^{-2}), suggesting that these materials contain significant numbers of Mg–O–Si heterolinkages. Hence, use of the TMP route has generated high-surface-area magnesia–silica materials that exhibit unusually high acidities when compared to similar materials made via acid-catalyzed sol–gel routes and sulfation (0.3–2.4 sites nm^{-2}) [88]. In general, it seems that the TMP method is useful for generating homogeneously dispersed metal sites in an amorphous SiO_2 support matrix [57–73].

Other recent work has provided Cr(IV) and V(IV) complexes of the form $(^tBuO)_nM[OSi(O^tBu)_3]_{4-n}$ ($n = 2, 3$) that efficiently convert to carbon-free Cr/Si/O [69] and V/Si/O [71] materials, respectively, again via elimination of isobutylene and water:

$$\begin{array}{c} {}^tBuO \quad\quad O^tBu \\ \backslash \quad\quad / \\ {}^tBuO{-}M{-}O{-}Si{-}O^tBu \\ / \quad\quad\quad \backslash \\ {}^tBuO \quad\quad O^tBu \end{array} \overset{453\,K}{\rightarrow} \begin{array}{l} MO_x \cdot SiO_2 + 6CH_2CMe_2 \\ + 3H_2O, \end{array} \qquad (2)$$

$$\begin{array}{c} {}^tBuO \quad O^tBu \quad O^tBu \\ \backslash \quad\quad | \quad\quad / \\ {}^tBuO{-}Si{-}O{-}M{-}O{-}Si{-}O^tBu \\ / \quad\quad | \quad\quad \backslash \\ {}^tBuO \quad {}^tBuO \quad O^tBu \end{array} \overset{453\,K}{\rightarrow} \begin{array}{l} MO_x \cdot 2SiO_2 \\ + 8CH_2CMe_2 + 4H_2O. \end{array}$$

$$M = Cr\ or\ V \qquad (3)$$

Additional efforts provided a V(V) single-source molecular precursor, $OV[OSi(O^tBu)_3]_3$ [72,73]. The synthesis of multiple V/Si/O single-source precursors with different oxidation states and silicon contents provided an opportunity to study how the nature of the precursor influences the properties of the final material [71]. Vanadia–silica xerogels generated by thermolysis of $OV[OSi(O^tBu)_3]_3$ in n-octane exhibited phase separation and formation of

V_2O_5 crystallites at low temperatures (573 K in O_2). By comparison, V/Si/O xerogels derived from solution thermolyses of the V(IV) precursors $(^tBuO)_3VOSi(O^tBu)_3$ and $(^tBuO)_2V[OSi(O^tBu)_3]_2$ produced V_2O_5 much more slowly (673 K in O_2). This suggests that the initial materials derived from the V(IV) precursors are more homogeneous (by PXRD and TEM) [71].

Interestingly, a high-surface-area Cr/Si/O xerogel (~300 m^2 g^{-1}) derived from the solution thermolysis of $(^tBuO)_3CrOSi(O^tBu)_3$ exhibited higher activity (by a factor of 3) *and* selectivity (by 5%) for the oxidative dehydrogenation of propane than did a Cr/Si/O material with a similar (slightly higher) surface area and derived from the same precursor, but generated by a solid state thermolysis [69]. These results point to the fact that the specific conditions for the thermolyses also play an important role in determining the properties of the final material.

Molecular precursors of the type $M[O_2P(O^tBu)_2]_n$ have been used to obtain phosphates of Zn, Ti, and Al [79–83]. In all of these cases, thermal decomposition of the molecular precursor under mild heating led to the formation of homogeneous M/P/O materials. For example, $[Me_2AlO_2P(O^tBu)_2]_2$ and $[(O^iPr)_2AlO_2P(O^tBu)_2]_4$ were used to generate amorphous, high-surface-area $AlPO_4$ xerogels (up to 600 m^2 g^{-1}) and thin films [83,89].

The TMP approach may also be used with electron-rich metals, as illustrated by the conversion of $[CuOSi(O^tBu)_3]_4$ to Cu-silica materials [60]. Thermolyses under an atmosphere of argon gave Cu^0 nanoparticles embedded in silica. Heating under O_2 led to formation of Cu_2O and CuO, and at high temperature only CuO nanoparticles (10–30 nm) were detected. The mechanism by which this electron-rich complex decomposes is distinct from that of the electropositive metal examples discussed above, and the formation of significant amounts of $HOSi(O^tBu)_3$ and Cu^0 suggests that Cu–O homolysis may be involved. Using related tetrameric trialkylsiloxide Cu species, similar homolytic processes have been observed by Caulton and co-workers [90].

3. TMP-derived catalysts for the oxidative dehydrogenation (ODH) of propane

More recent efforts in our laboratories have focused on attempts to utilize aspects of synthetic control offered by the TMP method to produce catalysts that exhibit improved performance in heterogeneous processes. In this regard, we have addressed the development of catalysts for selective transformations of simple hydrocarbons that are readily available as inexpensive feedstocks [91–94]. A class of reactions that has attracted considerable attention involves the transformation of an alkane to a more valuable olefinic product [95–97]. One such process is the catalytic dehydrogenation of alkanes, but the endothermic nature of this process requires high temperatures at which cracking and the deposition of carbon present significant problems. Alter-
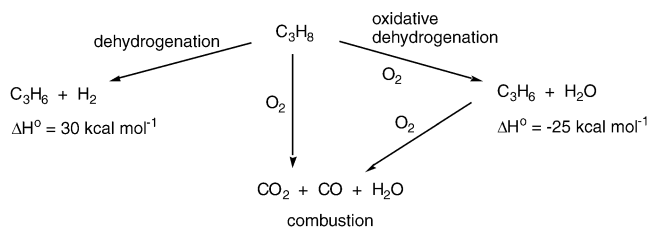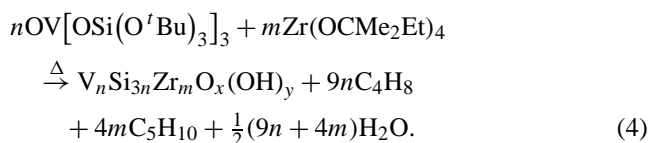
Scheme 1.

natively, the oxidative dehydrogenation (ODH) of alkanes is thermodynamically favored at lower temperatures and does not suffer from the detrimental effects of coking [95–97]. Given the widespread use of propylene in the production of polypropylene, acrylonitrile, and propylene oxide, propane ODH (Scheme 1) has attracted much attention as an alternative source of this industrially useful molecule [95–97]. However, this selective oxidation is difficult to achieve due to the tendency of propylene to overoxidize to CO and CO_2 under the reaction conditions. Recent reviews and reports on this subject have suggested that vanadium-based catalysts generally outperform other metal-containing catalysts for propane ODH [95–118]. Of the support materials that have been examined, some of the most promising are Al_2O_3, ZrO_2, and MgO.

From the results mentioned above, the TMP synthetic route offered the potential to produce catalysts with high surface areas and homogeneities relative to catalysts that were known for propane ODH. It was also hoped that use of this method might provide more controlled transformations to well-defined materials with high surface densities of the desired catalytic sites. A further discovery, which allows tuning of compositions for materials generated by the TMP method, is that the cothermolysis of different precursors in solution often results in homogeneous incorporation of each available building block into the final structure [72,84]. This allows versatility in targeting compositions over a wide range of catalyst formulations.

Using the molecular precursor $OV[OSi(O^tBu)_3]_3$ as a source of vanadium and the commercially available $Zr(OCMe_2Et)_4$ as a ZrO_2 source, a series of V/Si/Zr/O catalysts with vanadium contents from 2 to 34 wt% V_2O_5 were prepared via cothermolysis:

$$n OV[OSi(O^tBu)_3]_3 + m Zr(OCMe_2Et)_4$$
$$\xrightarrow{\Delta} V_nSi_{3n}Zr_mO_x(OH)_y + 9n C_4H_8$$
$$+ 4m C_5H_{10} + \tfrac{1}{2}(9n + 4m)H_2O. \qquad (4)$$

The surface areas of the catalysts prepared via the cothermolysis route were high, even after calcination at 773 K (from 300 to 465 m^2 g^{-1}). The performance of these materials as catalysts for propane ODH was evaluated by the method reported by Iglesia, Bell, and co-workers, which focuses on intrinsic selectivities (extrapolated to 0% conversion) that allow useful comparisons between catalysts [111,112]. The intrinsic selectivities for propylene for-

Table 1
Properties of some TMP-derived propane oxidative dehydrogenation catalysts

Catalyst	V_2O_5 (wt%)	Surface area ($m^2\,g^{-1}$)	Calcination temp. (K)	Intrinsic activity (mmol C_3H_6 (g cat)$^{-1}$ h^{-1})			Intrinsic selectivity (% C_3H_6)		
				673 K	723 K	773 K	673 K	723 K	773 K
V/Si/Zr/O[a]	5	428	773	9.1	n/a	45	78	n/a	78
	10	447	773	15	n/a	88	82	n/a	82
	14	466	773	28	n/a	100	90	n/a	90
	18	404	773	15	n/a	78	95	n/a	95
	23	268	773	7.6	n/a	46	96	n/a	96
V/Si/Zr/O[b]	18	121	773	0.3	n/a	0.9	80	n/a	80
V/Zr/O[c]	5	205	773	15.2	19.2	n/a	71	56	n/a
	10	294	773	36.9	70.7	n/a	85	65	n/a
	14	313	773	109	181	n/a	87	85	n/a
	18	284	773	69.4	162	n/a	93	90	n/a
	23	24	773	5.5	13.7	n/a	87	90	n/a
V/Zr/O[d]	10	122	773	18	n/a	n/a	80	n/a	n/a
V/Al/O[e]	6	190	823	4.0	5.9	12.1	82	77	75
	12	167	823	3.4	8.3	18.6	84	82	79
	18	151	823	1.9	10.4	27.6	80	78	73
	23	98	823	5.7	15.2	38.7	84	80	74
	27	133	823	7.2	20.8	49.0	81	73	68
V/Mg/O[f]	5	307	823	1.4	5.0	15.8	28	26	27
	10	299	823	8.3	21.3	60.2	56	50	50
	15	280	823	18.5	53.3	137	69	68	66
	20	256	823	18.2	45.1	124	72	70	69
	25	227	823	20.5	52.2	133	80	80	79

[a] Prepared via cothermolyses of OV[OSi(O^{t}Bu)$_3$ and Zr(OCMe$_2$Et)$_4$ [72].
[b] Prepared via NH$_4$VO$_3$-oxalic acid wet impregnation of a Zr/Si/O xerogel made via cothermolysis of Zr[OSi(O^{t}Bu)$_3$]$_4$ and Zr(OCMe$_2$Et)$_4$ [72].
[c] Prepared via cothermolyses of OV(O^{t}Bu)$_3$ and Zr(OCMe$_2$Et)$_4$ [74].
[d] Prepared via NH$_4$VO$_3$-oxalic acid wet impregnation of ZrO$_2$ [72].
[e] Prepared via cothermolyses of OV(O^{t}Bu)$_3$ and [Al(O^{t}Bu)$_3$]$_2$ [119].
[f] Prepared via OV(O^{t}Bu)$_3$ impregnation (in toluene) of MgO [75].

mation for the V/Si/Zr/O catalysts obtained via cothermolyses were as high as 95.5% at 673 K (for 23 wt% vanadia). The observed activities ranged from 28 mmol propylene produced (g cat)$^{-1}$ h^{-1} (673 K, 14% vanadia) to 100 mmol (g cat)$^{-1}$ h^{-1} (773 K, 14% vanadia). The presence of oligomeric tetrahedral vanadium sites appears to be a key component of the more active compositions (10–18% vanadia). The V/Si/Zr/O catalysts with 18 and 23% vanadia were as efficient as the most selective and active catalysts that had been reported for propane ODH [95–118]. Further comparisons showed that these catalysts were more active and selective, under the same ODH conditions, than materials of similar composition but prepared by conventional impregnation methods using NH$_4$VO$_3$-oxalic acid as the vanadium source. Table 1 provides a summary of some of the propane ODH data. This initial study on the use of TMP-derived materials as catalysts therefore suggested that this synthetic approach might be generally useful for the generation of catalysts with enhanced performance [72].
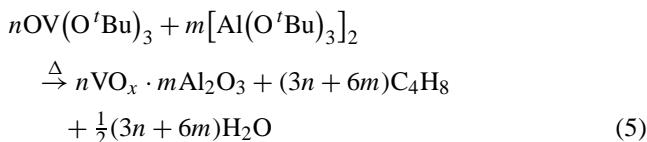
An attempt to further improve the performance of vanadia-based catalysts for propane ODH targeted silicon-free compositions, since the silica component is believed to give rise to Brønsted acid sites that could facilitate secondary reactions of the propylene product. Such V/Zr/O catalysts, containing vanadia supported on zirconia, were

readily obtained via thermolyses of solutions containing OV(O^{t}Bu)$_3$ and Zr(OCMe$_2$Et)$_4$ [74]. Upon calcination at 773 K, nanocrystals of ZrO$_2$ were produced and the vanadium appeared to be dispersed on the surface of the crystals as oligomeric VO$_x$ species in vanadium coordination environments similar to those in V$_2$O$_5$ (by PXRD and Raman, DRUV–vis, and ^{51}V NMR spectroscopies). The vanadia coating inhibits further crystallization of ZrO$_2$ and helps to maintain a high catalyst surface area. The best catalyst performance was observed for materials with 10–18% vanadia content, for which activities were as high as 180 mmol (g cat)$^{-1}$ h^{-1}, and intrinsic selectivities maximized at about 90% (see Table 1). The improved properties observed for V/Zr/O catalysts obtained by the TMP cothermolysis method may be at least partially attributed to higher surface areas and improved dispersions of VO$_x$ species relative to those in catalysts prepared by conventional means. The TMP route also appears to give a more controlled and complete conversion of vanadium species to catalytically active oligomeric VO$_x$ species.

Kinetic analyses of the propane ODH reactions at 606 K showed that the value of k_1 (the rate of propane ODH; L mol^{-1} s^{-1}) was three times greater for the TMP-derived catalysts than for V/Zr/O catalysts obtained by wet impregnation [111,112]. Additionally, catalysts derived from the

TMP method exhibited lower rates for the combustion of propane (k_2), as illustrated by lower k_2/k_1 ratios (0.02 vs 0.3 at ~ 4 VO_x nm^{-2}). However, the k_3 values (the rate constants for propylene combustion; $L\,mol^{-1}\,s^{-1}$) were similar for the two types of catalysts. The latter result is significant, in that dramatic improvements in propane ODH catalysis appear to hinge on development of catalysts with a much lower activity for propylene oxidation (low values of k_3) [111,112].

In a similar fashion, propane ODH catalysts with various V/Al/O compositions were generated by cothermolyses of $OV(O^tBu)_3$ and $[Al(O^tBu)_3]_2$ [119].

$$nOV\left(O^tBu\right)_3 + m\left[Al\left(O^tBu\right)_3\right]_2$$
$$\xrightarrow{\Delta} nVO_x \cdot mAl_2O_3 + (3n + 6m)C_4H_8$$
$$+ \tfrac{1}{2}(3n + 6m)H_2O \tag{5}$$

After calcination at 823 K, these catalysts had surface areas (from 98 to 190 $m^2\,g^{-1}$) that were lower than those for the corresponding V/Zr/O materials. For these catalysts, the intrinsic selectivities for propylene formation are good and very similar over a range of vanadium contents (up to 84% at 673 K, 82% at 723 K, and 79.5% at 773 K). These selectivities are similar to those observed for V/Al/O catalysts prepared via wet impregnation using NH_3VO_3/oxalic acid and Al_2O_3 (70–90% at 606 K [111]). The activities of the TMP-derived V/Al/O catalysts, on a per gram basis (up to 49.0 mmol $(g\,cat)^{-1}\,h^{-1}$ at 773 K), are moderate compared to those of the TMP-derived V/Zr/O systems (Table 1). Note that whereas the TMP-derived V/Al/O catalysts are less selective than their TMP-derived V/Zr/O counterparts (Table 1), the opposite is true for V/Al/O and V/Zr/O catalyst prepared by wet impregnation [111].

A further modified version of the TMP method involves the impregnation of a high-surface-area support. This was accomplished using nanocrystalline MgO, first synthesized by Klabunde and co-workers [120], as the support. This material was impregnated with vanadia by exposing it to $OV(O^tBu)_3$ in nonpolar media [75]. Calcination of $OV(O^tBu)_3$/MgO materials at 823 K led to catalysts with high surface areas (from 185 to 310 $m^2\,g^{-1}$). Based on catalytic and analytical data (PXRD, temperature-programmed reduction, and Raman, diffuse reflectance UV–vis (DRUV–vis), and ^{51}V NMR spectroscopy), it appears that the most active catalysts consist of nanocrystalline MgO particles covered by small $Mg_3(VO_4)_2$ domains. The formation of large $Mg_3(VO_4)_2$ domains is undesirable due to the loss of accessible vanadium species. At a reaction temperature of 773 K, catalysts with 15 and 25 wt% vanadia exhibited intrinsic selectivities of 66 and 79% and activities of 137 and 133 mmol $(g\,cat)^{-1}\,h^{-1}$, respectively (Table 1). The selectivities of these catalysts are equal to or better than the best V/Mg/O catalysts previously reported for propane ODH, and the observed activities are higher than literature values [106,110,116–118].

4. Molecular precursor route to isolated catalytic centers

A modification of the molecular precursor route described above may be used to introduce isolated catalytic sites onto the surface of an oxide support via simple chemical reactions. Advantages to this approach include the increased potential for molecular-level control over the structure of the catalytic site, the generation of site-isolated catalysts, and the ease with which the grafting reactions can be monitored to provide information about the nature of the grafted moiety. It is important to know several of the properties of the support prior to performing the grafting reaction. For example, the surface area of the support will determine the amount of precursor that can be introduced onto the surface. Knowledge of the porosity of the support is also critical since the precursor molecules (which can be rather large) must fit into any pores that are present to allow optimum coverage. Finally, the surface density of reactive surface sites (i.e., OH groups) can be used to estimate the potential for reaction of multiple surface sites with one molecular precursor. With respect to the latter issue, we have developed a simple method for determining the coverage of accessible hydroxyl groups on silica, involving reaction of $Mg(CH_2C_6H_5)_2 \cdot 2THF$ with the solid support, followed by quantification of the toluene that is evolved by ^1H NMR spectroscopy [70,79].

We have explored the molecular precursor route to isolated catalytic sites supported on various forms of silica. The first step in the grafting procedure involves chemical bonding of a $M[OSi(O^tBu)_3]_n$ precursor to the support via a protonolysis reaction, which results in elimination of HO^tBu and/or $HOSi(O^tBu)_3$. The progress of these reactions is easily monitored by solution ^1H NMR spectroscopy, and this provides insight into the nature of the grafted species. Both M–O–(surface) and Si–O–(surface) linkages may form in the grafting procedure, and quantification of the species released by these reactions provides information about the types of sites that are present and the approximate quantities of each. The as-synthesized catalyst can then be used for low-temperature reactions or calcined (< 473 K) to produce reactive, inorganic species of the form $MO_x \cdot nSiO_2$ or $MO_x \cdot (n - 1)SiO_2$ (with elimination of isobutylene from the remaining $OSi(O^tBu)_3$ ligands of the grafted precursor). The small amount of additional SiO_2 that is formed near the metal center may provide stability, hence reducing mobility and phase separation (Scheme 2).

5. Single-site Ti(IV) on SBA-15

The method outlined above was initially investigated for the introduction of isolated titanium sites onto silica support materials. Such materials are of interest as selective oxidation catalysts. For example, several years ago Shell developed a silica-supported titania catalyst for the epoxida-
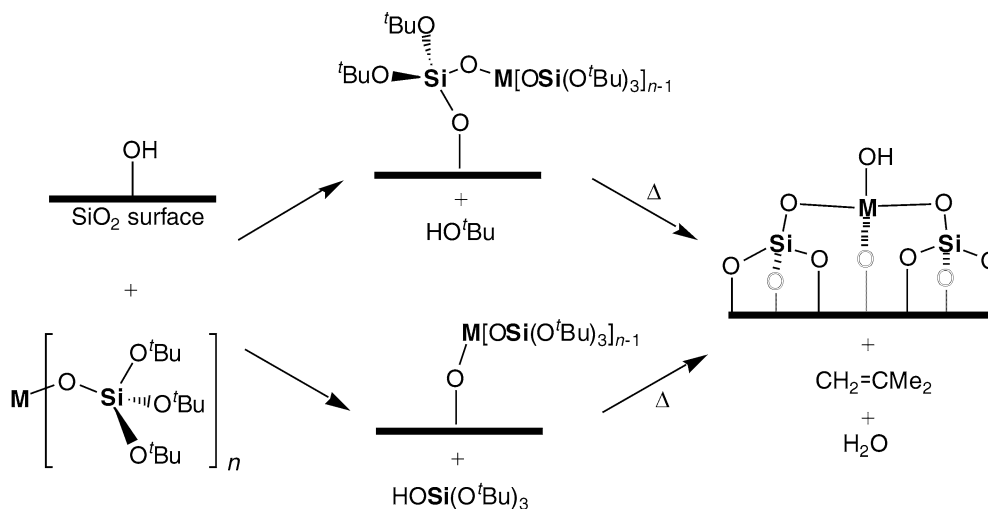
Scheme 2.

tion of propylene to propylene oxide [121–123]. Many other titania-substituted silica materials have been recently studied in the context of olefin epoxidation, including the molecular sieves TS1 and TS2, the zeolites Ti-β and Ti-ZSM, and mesoporous Ti-MCM41 materials with Ti in the walls or grafted onto the surface [124–135]. The active sites in such catalysts are believed to contain isolated, tetrahedrally coordinated titanium centers.

Our initial studies in this area involved the precursor Ti[OSi(O^{t}Bu)$_3$]$_4$, which serves as an excellent spectroscopic model for isolated, tetrahedral titanium sites due to its Ti[OSiO$_3$]$_4$ core. This complex was found to provide an efficient route to homogeneous TiO$_2 \cdot$ 4SiO$_2$ materials [57,63], and these were examined as catalysts for the epoxidation of cyclohexene [76]:

$$\text{(6)}$$

The catalytic reactions were carried out in toluene, with cumene hydroperoxide (CHP) as the oxidant.

A TiO$_2 \cdot$ 4SiO$_2$ aerogel obtained by the solution thermolysis of Ti[OSi(O^{t}Bu)$_3$]$_4$ was relatively active (2.82 mmol g^{-1} min^{-1}), giving a cyclohexene oxide yield of 48.8% after 2 h at 338 K. However, treatment of aerosil silica with Ti[OSi(O^{t}Bu)$_3$]$_4$ provided a material with 1.01 wt% Ti that, after calcination at 573 K, was more active (5.28 mmol g^{-1} min^{-1}) and selective for the oxidation of cyclohexene to cyclohexene oxide using CHP as the oxidant (94.4% yield after 2 h at 338 K). This new catalyst was more than twice as active as silica treated with Ti(O^{i}Pr)$_4$ (the Shell catalyst, 2.08 mmol g^{-1} min^{-1}) under our reaction conditions, even on a per titanium basis ($\sim$ 1500 mol product (mol Ti)$^{-1}$ h^{-1} vs $\sim$ 600 mol (mol Ti)$^{-1}$ h^{-1}). Thus, the OSi(O^{t}Bu)$_3$ ligands appear to exercise a beneficial effect on the structure of the supported titanium site, which likely involves OTi(OSi)$_3$ species with pseudotetrahedral Ti centers.

In attempts to optimize catalyst performance, we extended these studies to include additional types of precursors and supports with higher surface areas. Precursors with different Ti/Si ratios were examined to obtain information about the effects of the OSi(O^{t}Bu)$_3$ ligands on catalyst performance [77]. These investigations utilized Ti[OSi(O^{t}Bu)$_3$]$_4$ [57,63], (^{i}PrO)Ti[OSi(O^{t}Bu)$_3$]$_3$ [136], and (^{t}BuO)$_3$TiOSi(O^{t}Bu)$_3$ [137] complexes and three high-surface-area SiO$_2$ supports (aerosil, MCM-41 [138], and SBA-15 [139]). For comparison, Ti(O^{i}Pr)$_4$ was also used as a Ti source. During the grafting reaction both ^{t}BuOH and HOSi(O^{t}Bu)$_3$ were observed as reaction products, suggesting the presence of two different (but closely related) types of surface species, although elimination of HOSi(O^{t}Bu)$_3$ was the major pathway in all cases. The Ti centers derived from the siloxide-containing precursors appear to be in isolated TiO$_4$ environments, as indicated by use of DRUV–vis spectroscopy.

Precursors bearing fewer alkoxysiloxide ligands resulted in greater titanium incorporation. This presumably results from lower reactivities of the more sterically encumbered precursors with the surface –OH groups. However, the presence of more alkoxysiloxy ligands improves the catalytic activity by preventing the formation of oligomeric titania species that are known to exhibit low activities during epoxidation reactions [140]. These two competing factors point to the tris(siloxide) (^{i}PrO)Ti[OSi(O^{t}Bu)$_3$]$_3$ as the optimum precursor in this series [77]. For uncalcined catalysts derived from this precursor, the activities for cyclohexene epoxidation (338 K, toluene, CHP oxidant) over the first 10 min of reaction ranged from 3.8 (0.25% Ti) to 11.3 (1.64% Ti) mmol g^{-1} min^{-1}. When the activities are evaluated on a per titanium basis it is evident that as the titanium content increases the activity decreases (from $\sim$ 4400 mol (mol Ti)$^{-1}$ h^{-1} for 0.25% Ti to $\sim$ 2000 mol (mol Ti)$^{-1}$ h^{-1} for 1.64% Ti). Calcination of these catalysts at 573 K resulted in a loss of activity (by ca. 50%); however, the activities are still higher than those previously reported for

Ti/Si/O catalysts, including those prepared via other grafting methods [131,141–143]. The selectivity for cyclohexene oxide was between 90 and 100% for all of the catalysts made via grafting of the molecular precursors. The mesoporous supports (MCM-41 and SBA-15) provided catalysts with the best performance; however, there was little difference between the two. The high performance of the Ti/Si/O catalysts described above appears to result from the highly dispersed and site-isolated nature of the tetrahedral titanium centers that arise from the use of the molecular precursor approach.

6. Single-site iron(III) on SBA-15

Interest in site-isolated iron catalysts for the selective oxidation of hydrocarbons stems from promising results reported for the iron-containing zeolite FeZSM-5 (which may possess isolated iron sites [144–149]) and from the known abilities of various iron-based enzymes to carry out selective oxidations [150–154]. Thus, it is important to investigate the reactivities of well-defined iron sites and to evaluate the role of various structural parameters on catalytic activity and selectivity. In this context, it seemed possible to use a molecular precursor grafting methodology similar to that described above for the generation of well-defined surface iron sites.

The molecular precursor Fe[OSi(O^{t}Bu)$_3$]$_3$ · THF has been employed with SBA-15 for the preparation of isolated, inorganic Fe centers on a mesoporous support [78]. These investigations have provided catalytic materials that are active and selective for partial oxidations of hydrocarbons using hydrogen peroxide as the oxidant. In this case the grafting chemistry is quite simple, resulting in elimination of only HOSi(O^{t}Bu)$_3$. This suggests that the grafted iron centers retain one THF and two siloxide ligands. The presence of the THF ligand was confirmed by an exchange reaction whereby the Fe/SBA material was dosed with excess MeCN. The free THF released by this reaction corresponds to approximately 1 THF per iron center (by ^{1}H NMR spectroscopy). A number of other analytical and spectroscopic probes are also consistent with the following grafted structure:

$$(7)$$
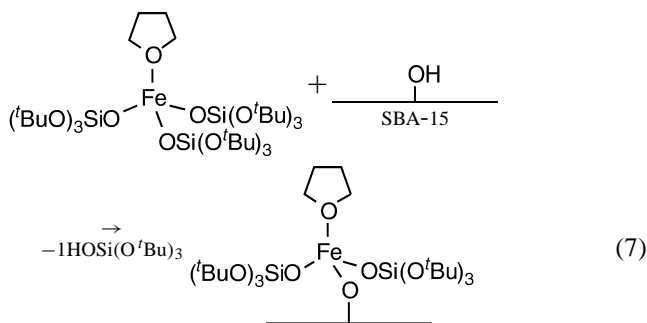
Calcination of the FeSBA-15 materials at 573 K resulted in loss of essentially all of the carbon and hydrogen, and

DRUV–vis spectra revealed charge-transfer bands that were very similar to those obtained for the uncalcined samples. Additionally, no bands attributable to octahedral iron(III) clusters were observed. Thus, calcination does not appear to form large iron oxide clusters. The majority of the iron sites maintain their isolated state with tetrahedral coordination geometry. Electron paramagnetic resonance studies also provided evidence for the presence of isolated iron(III) centers with a distorted tetrahedral geometry. Thus, this precursor method appears to provide a reliable route to well-defined, isolated, and stable iron centers. Several reports have described the preparation of Fe species supported on silica that utilize inorganic iron reagents such as FeCl$_3$ [155–157], FePO$_4$ [158], and Fe$_2$(SO$_4$)$_3$ · 7H$_2$O [159]; however, these procedures do not produce stable, isolated surface species due to the use of aqueous media and calcination conditions that lead to formation of iron oxide clusters.

Calcined FeSBA-15 materials (573 K, 2 h, O$_2$) were investigated as catalysts for the partial oxidation of various hydrocarbons using hydrogen peroxide as the oxidant. Leaching tests indicated that the observed catalytic reactions were indeed heterogeneous. Oxidation of benzene at 60 °C by a 0.50 wt% Fe catalyst resulted in the production of phenol with 100% selectivity after 96 h at 42% hydrogen peroxide conversion and 7.5% benzene conversion. No products were observed from formation of phenyl radicals, as has been observed previously for related catalysts [160]. The turnover frequency for this particular catalyst was 2.5×10^{-3} mol product (mol Fe)$^{-1}$ s^{-1}, which is comparable to those for other (less selective) iron-based heterogeneous systems [161,162]. The oxidation of toluene at 333 K using a FeSBA-15 catalyst (1.90 wt% iron) produced benzaldehyde (32%) and cresol (a mixture of *ortho* and *para* isomers totaling 68%). Interestingly, the activities of these catalysts (on a per-site basis) do not vary with iron loading. This is consistent with the presence of isolated and independent catalytic centers. Cyclooctene epoxidation proceeded with a very high selectivity for cyclooctene oxide (99%) with a turnover frequency of 6.2×10^{-4} mol product (mol Fe)$^{-1}$ s^{-1}. This selectivity exceeds that of Jacobson's recently reported and highly selective iron-based homogeneous catalyst that exhibited a selectivity for cyclooctene oxide production of 86% [163]. Overall, these catalysts operated with selectivities and activities that exceed or are comparable to other heterogeneous iron-based partial oxidation catalysts.

7. Summary and future

Several recent modifications of the TMP method have important implications for the use of this approach in synthesizing new catalysts and catalyst supports with improved properties. Among these is the finding that cothermolyses using mixtures of alkoxide precursors in a hydrophobic solvent yield dispersed metal oxide species within an ox-

ide "support." This allows considerable flexibility in tuning the catalyst composition. Examples of this approach include the cothermolyses of $OV(O^tBu)_3$ with $Zr[OCMe_2Et]_4$ or $[Al(O^tBu)_3]_2$, which result in the formation of high-surface-area V/Zr/O or V/Al/O xerogels, respectively. These materials exhibit excellent properties as catalysts for the oxidative dehydrogenation of propane. In addition, it has recently been possible to assemble molecular precursors containing more than two components. For example, $[(^tBuO)_3SiO]_2Al[\mu\text{-}O_2P(O^tBu)_2]_2Al(Me)OSi(O^tBu)_3$ is an efficient single-source precursor to silicoaluminophosphate (SAPO) materials and it is a structural model for microporous SAPOs [79]. Precursors of this type should offer further aspects of atomic-level control over the structures of catalytic sites and they should prove to be useful molecular models, especially for catalytic materials that contain multiple heteroelements. Additionally, the molecular precursors described here are convenient sources of isolated, inorganic catalyst sites supported on an oxide such as SiO_2. This is of particular interest given the importance of isolated sites in catalysis [32–37], and the need for control over the structures of such sites. It appears that additional components of the support, attached to the surface by way of oxygen-rich siloxide ligands (e.g., $OSi(O^tBu)_3$), may provide a stabilized environment that hinders ion mobility and prevents formation of M–O–M linkages.

The synthetic methods described in this report offer a number of potential advantages over more established routes to heterogeneous catalysts. The use of well-defined molecular precursors in the TMP method allows control over stoichiometry, nanostructure, homogeneity, and catalyst site structure, depending on various experimental parameters. The use of nonaqueous solvents in catalyst syntheses can be beneficial, in that water often has a strong influence over the structures that form. The precursors serve as molecular models for oxide supported catalytic sites, given their M–O–E heterolinkages and their oxygen-rich nature. It has been demonstrated that TMP methods can be used to produce catalytic materials that outperform related catalysts obtained by more traditional routes. Thus, we expect molecular precursor methods to contribute significantly to the development of new generations of catalysts and support materials.

Acknowledgments

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