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ORIGINAL PAPER

State of the Art and Perspectives in the "Molecular Approach" Towards Well-Defined Heterogeneous Catalysts

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Abstract Molecular understanding of heterogeneous catalysts is a key step towards their rational development since catalysis is a molecular phenomenon. Here we describe our efforts towards molecularly defined heterogeneous catalysts through the anchoring of molecular precursors on solid supports and our approaches towards bridging the gap between well-defined and industrial catalysts.

Keywords Catalysis · Molecular approach · Metal oxide · Metal nanoparticle · Grafting

1 Introduction

Catalysis is a key science and technology of the 21st century, and is particularly relevant to develop more efficient, sustainable and cleaner chemical processes. New catalytic processes will have to rely on a wide range of feedstocks, including those derived from biomass, coal and natural gas. Catalysis will also likely be a pillar of the energy domain for fuel cells and conversion of raw materials into liquid fuels. Traditionally catalysis is fragmented between homogeneous, heterogeneous and bio-catalysis, and efforts have been made to bring these disciplines together for many years. A unifying theme between these three fields is the "molecular approach," because catalysis is a molecular phenomenon where a substrate is converted to intermediates and products on an active site.

While heterogeneous catalysts have been at the heart of chemical processes for more than a century, homogeneous transition-metal based catalysis has revolutionized the field throughout the last sixty years with the discoveries of many efficient chemical processes, e.g. the highly selective low pressure and low temperature hydroformylation of alkenes, carbonylation of methanol, metallocene polymerization, asymmetric hydrogenation, cross-coupling, olefin/alkyne metathesis and ethylene oligomerization [1]. The molecular understanding of homogeneous catalyst is certainly responsible for the rapid development of highly efficient processes in petro-, bulk and fine chemical syntheses. It is thus not surprising that the catalysis community has recognized this power and tried to implement a "molecular approach" in heterogeneous catalysis [2–5]. Often cited as "Surface Organometallic Chemistry", this strategy literally constructs molecularly defined active sites at the surfaces of materials [6–11].

Controlling the surface functional group density (e.g. OH for metal oxides like silica or alumina) is the first step in using molecular approaches in heterogeneous catalysis. This control ensures site-isolation between reactive centers and also allows one to tune the chemical environment of a metal complex. The second step involves grafting a molecular transition-metal complex on the reactive surface sites. Generally, an organometallic reagent (L_nM-R) reacts with the surface OH groups in the grafting step to liberate a non-reactive and easily removable alkane byproduct in the grafting step. Molecular precursors containing a displaceable anionic ligand X (X = Cl, OR, NR_2, etc.) are also suitable substrates for this reaction (Scheme 1).

The surface species are characterized through establishing the stoichiometry of the reaction and advanced spectroscopic investigation. In some cases computational studies are necessary to gain deeper insight into the molecular structure of the catalyst on the surface by determining the reaction energies and spectroscopic

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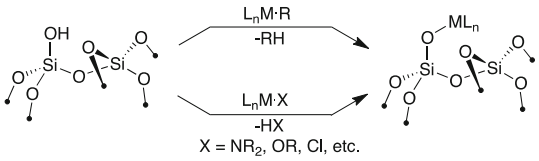
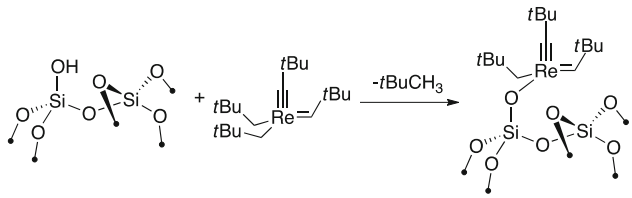


Scheme 1 Grafting organometallic or metalloinorganic complexes on silica



Scheme 2 Grafting an organometallic rhenium alkylidene on silica

signatures of intermediates. This combination of spectroscopic and theoretical data gives the coordination sphere of the surface complex, including any bonding with surface functionalities. Depending on the application, the surface complex can then be directly used as a well-defined "active site" if the proper ligands have been chosen, ultimately providing a method to draw quantitative structure—activity relationships. The grafted complex can also be used to generate isolated species with controlled surface density through post-treatment steps, or even small metal clusters/nanoparticles depending on the nature of the ligands, the support and the metal [3].

This field has benefited from the development of advanced spectroscopic techniques [12, 13], particularly in the realm of solid-state NMR [14, 15]. Detailed studies of molecular surface equivalents provide precursors, and in some cases mechanistic understanding to complement to spectroscopic characterization data. Computational chemistry has also become a necessary tool in the characterization and design of these molecularly defined heterogeneous catalysts [16].

Here, we will discuss the current state of the art of heterogeneous catalysts using the molecular approach focusing on examples from our research, as well as others closely related works in the field. The goal is not to be exhaustive, but to illustrate recent achievements, directions, and perspectives in the field. We will first describe the simplest systems, reacting organometallic complexes with partially dehydroxylated silica [17], and gradually introduce complexity throughout this perspective before ending with a few examples of studying industrially relevant catalysts using a molecular approach.

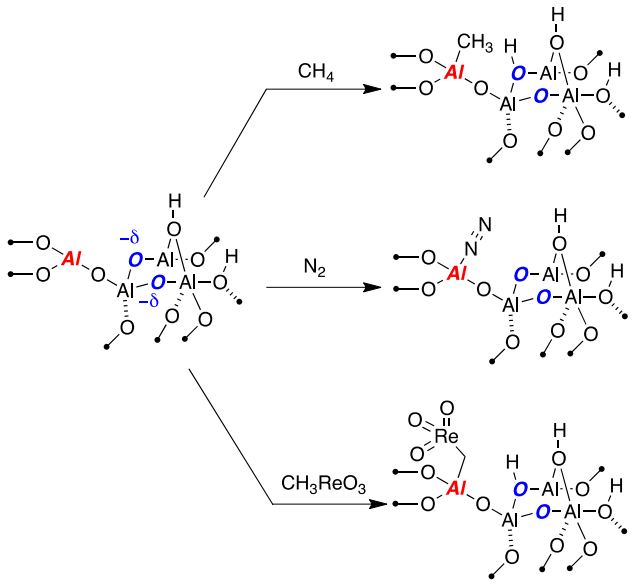
2 Well-Defined Metal Complexes Supported on Oxides

2.1 Silica-Supported Catalysts

Silica partially dehydroxylated at 700 °C contains 0.8 OH nm^{-2} and large surface areas (200–800 m^2 g^{-1}). These properties lead to site-isolated silica grafted organometallics that can be characterized by spectroscopic techniques, and for this reason silica is the support of choice to generate isolated metal sites. An illustrative example is the development of supported olefin metathesis catalysts, where extensive work has shown that alkylidenes are key reaction intermediates [18, 19]. We synthesized the first well-defined heterogeneous olefin metathesis catalyst based on Re, [(≡SiO)Re(≡CtBu)(=CHtBu)(CH_2tBu)], that was fully characterized by solid state NMR to establish the molecular structure (Scheme 2) [20]. This system showed unprecedented activity in alkene metathesis, even surpassing the best homogeneous catalysts known at the time [21]. The high activity was due to the serendipitous presence of the optimal ligand set: a strong σ-donor alkyl and a weak σ-donor siloxy ligand. This arrangement favors coordination of the incoming olefin *trans*-to the strong σ-donor that in turn destabilizes metallacyclobutane intermediates and favors cycloreversion [22, 23]. With this rule in hand, the isoelectronic silica supported Mo-imido complexes [(≡SiO)Mo(NAr)(=CHR)(Me_2Pyr)] were developed and showed improved stability and activity. [24, 25] It is noteworthy that isostructural MAP catalysts containing similar ligand arrangements (i.e. a strong σ-donor pyrrolide and a weak σ-donor aryloxide) [26–28] are among the best homogeneous catalysts available today. This illustrative example shows the interplay between homogeneous catalysis and heterogeneous catalysis, and the power of the molecular approach [29, 30].

2.2 Alumina-Supported Catalysts

Partially dehydroxylated alumina is a more complex support than silica. At 500 °C alumina contains 2 OH nm^{-2}, a high density of Lewis acid sites, and a small amount of defect sites (ca. 0.05 nm^{-2}). Defect sites have been identified as tricoordinated Al atom facing basic O atoms that result from the presence of chemisorbed H_2O on adjacent aluminums [31]. The tricoordinate aluminum defects coordinate N_2 [32, 33] and readily activate H_2 or CH_4 (Scheme 3) [34]. With early transition metal complexes such as $Zr(CH_2tBu)_4$, the alumina surface behaves as a bifunctional support, reacting through its OH and its Lewis acid sites to generate supported cationic zirconium-alkyl species, which are highly active towards the polymerization of ethylene [35]. $MeReO_3$, an organometallic reagent insensitive to protic media, reacts with alumina defects by C–H activation of the methyl group



Scheme 3 C-H activation of methane and CH_3ReO_3 on Al_2O_3 defect sites

to generate a μ^2-methylene species, which are highly active in alkene metathesis [36, 37].

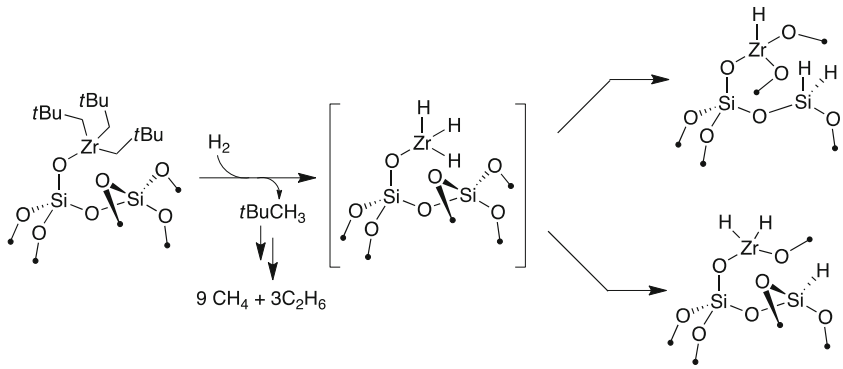
2.3 Stabilization of Highly Reactive Species

Surface species are typically more stable than their homogeneous equivalents and can lead to unprecedented reactivities. It has been shown in alkene metathesis by comparing the catalytic performances of isoelectronic and isostructural molecular and surface complexes [38]. The surface supported species $[(\equiv SiO)Mo(NAr)(=CHtBu)(CH_2tBu)_2]$ is more reactive and stable than the homogeneous equivalent because site-isolation shuts down bimolecular decomposition pathways. Another similar example is the reaction of $[(\equiv SiO)Ta(=CHtBu)(CH_2tBu)_2]$ with propane at 150 °C, which gives RCH_2tBu (R = H, Me, Et) along with metathesis products (ethane and butane) [39, 40]. Surface species of early transition-metals can also be converted to highly electron deficient or coordinatively unsaturated metal-hydrides, such as $[(\equiv SiO)_{4-x}ZrH_x]$ (x = 1 or 2, Scheme 4) or $(\equiv SiO)_2TaH_y$ (y = 1 or 3), due to the formation of additional M–O bonds by subsequent reactions of the grafted metal complex with adjacent siloxane bridges [3, 41]. These species catalyze the low temperature hydrogenolysis of alkanes [42, 43], the metathesis of alkanes [44–47], the cross-metathesis of methane and propane [48] and the non-oxidative coupling of methane at relatively low temperatures [49].

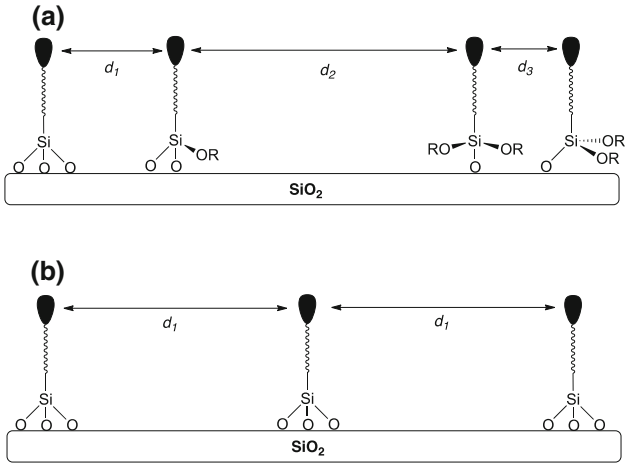
3 Supported Homogeneous Catalysts Through the Controlled Functionalization of Hybrid Materials

In view of the plethora of ligands in homogeneous catalysis, another effort has been directed at synthesizing so-called supported homogeneous catalysts. In these catalysts the organic ligand is attached to the surface of a material, typically an oxide like silica since it develops a large surface area. Typically in this area an organosilane precursor is contacted with a silica material to anchor the organic functionality to the surface of a material (Scheme 5a) [50, 51]. Though effective in some cases, this approach does not control the distribution of ligands or the number of bonds between the organic residue and the surface. Recent developments in material chemistry have found solutions to this problem by imbedding the organic ligand in the silica matrix at the synthesis stage in the presence of a surfactant [52, 53]. The surfactant leads not only to a structuration of the material (e.g. 2D hexagonal) [54], but also to the controlled incorporation and distribution of the organic fragment along the pore channel (Scheme 5b). The homogeneous distribution of the ligands with the silica matrix has been recently validated by EPR spectroscopy [55].

While this approach has been exploited very early in acid–base catalysis [56–59], it has only been recently applied to transition-metal complexes. In the latter case, it is necessary to avoid the reaction of the metal with the



Scheme 4 Formation of zirconium hydrides on silica



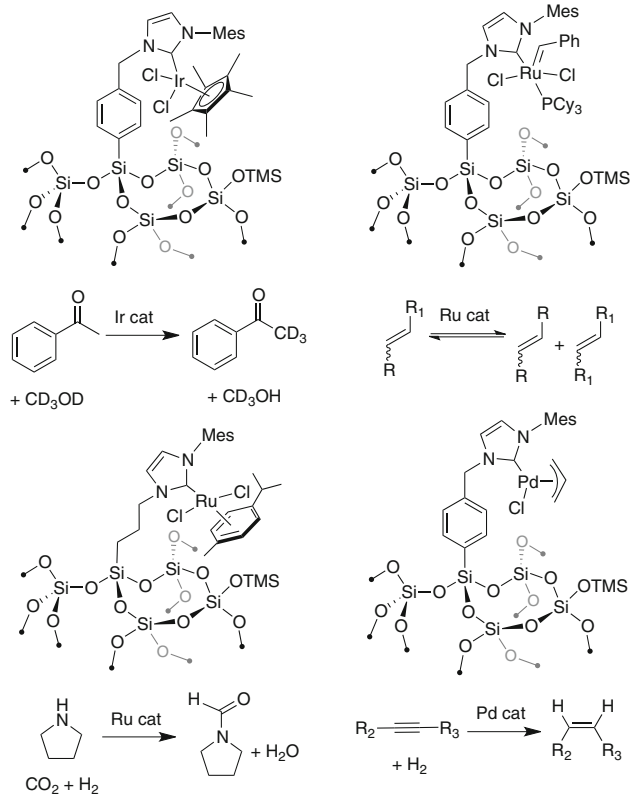
Scheme 5 **a** Surface species generated from grafting alkoxysilanes on silica; **b** Surface species from surfactant mediated material synthesis

oxide surface and to insure that the metal is strongly bound to a stable ligand. Passivation of the surface with trimethylsilyl groups overcomes the first challenge. *N*-heterocyclic carbenes (NHC) were the first successful results with application with a wide range of catalytic reactions: H/D exchange of unactivated C–H bonds [60], alkene metathesis [61, 62], CO_2 hydrogenation [63], and the semi-hydrogenation of alkynes (Scheme 6) [64].

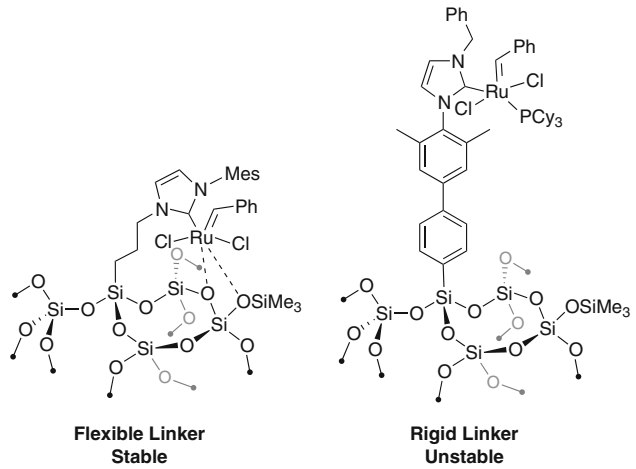
The tether can have a great influence on the catalytic performance of a surface tethered catalyst (Scheme 7). For instance, the Ru-NHC metathesis catalyst having a flexible propyl linker shown in Scheme 7 yields a catalyst without phosphine ligand, though surprisingly stable stability; in contrast to the rigid phenylmesityl equivalent. These results point to the beneficial role of the surface: the flexible linker allows interactions with the surface, as shown by DNP SENS, and stabilizes of the surface Ru-species [62].

4 Controlling the Composition, the Growth and the Interface of Supported Metal Particles

One of the important advantages of using organometallic precursors in place of metal salts as nanoparticles sources avoids unwanted halogen contaminants or adventitious salt residues. In fact, organometallics dispersed on a support readily decompose under mild conditions with only H_2 as reducing agent to afford metal nanoparticles [65]. For instance, small (<2 nm) and narrowly dispersed Ru and Os nanoparticles can be obtained by decomposition of silica wetted with Ru(cod)(cot) and Os(cod)(cot) under H_2 [66, 67]. Particle size and density is also controllable by grafting a molecular precursor prior to its decomposition under H_2 [68–70]. Finally, by choosing specific molecular precursors, it is

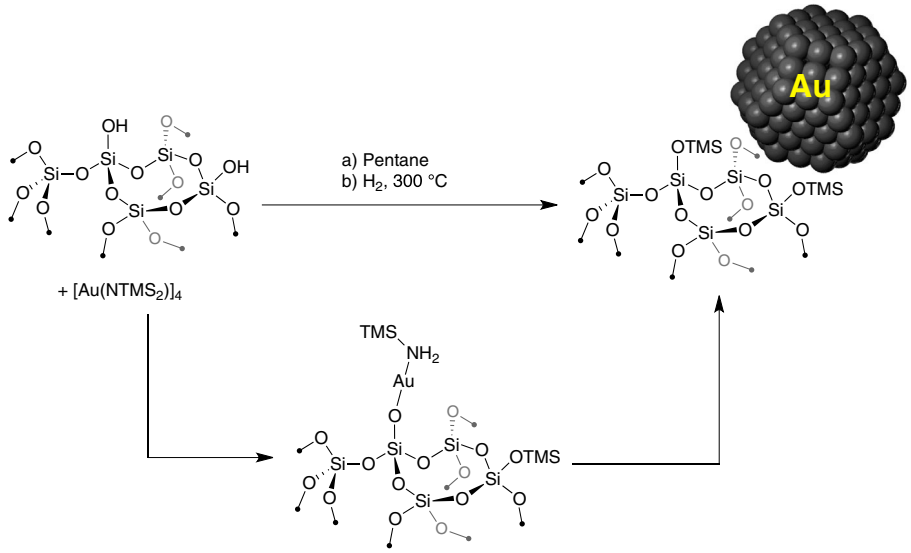


Scheme 6 Functionalized NHC-M complexes in hybrid materials



Scheme 7 Linker flexibility determines metal-surface interaction and stability for NHC-Ru metathesis catalysts

even possible to generate supported metallic nanoparticles while controlling the solid-particle interface. For instance, grafting of $[Au(N(SiMe_3)_2]_4$ and subsequent treatment under H_2 (Scheme 8) generates 1.8 nm gold nanoparticles supported on a passivated silica lacking OH groups, which greatly improved the performances in the aerobic epoxidation of stilbene [71].



Scheme 8 Formation of Au nanoparticles after grafting an metalloinorganic complex

5 Advances in Characterization Tools: Dynamic Nuclear Polarization–Surface Enhanced NMR Spectroscopy (DNP–SENS)

The molecular approach requires detailed characterization of surface species, which typically constitutes a very small fraction of the sample (<1–5 % in most cases). While NMR is the most powerful technique to assess structure of at a molecular level, particularly for molecules supported on amorphous supports, this method is inherently insensitive. As a consequence tedious labeling of the sample is often required in order to obtain NMR spectra in reasonable times (<24 h). Following the pioneering work of R. Griffin [72, 73], we have recently developed a technique coined DNP–SENS, Dynamic Nuclear Polarization Surface Enhanced NMR spectroscopy, that allows the selective NMR signal enhancement of surface species [74, 75]. This technique requires impregnation of a material with a minimum amount of a nitroxyl diradical solution (10–20 mM) and loading the sample into a pre-cooled (100 K) solid-state NMR spectrometer equipped with a high power single frequency microwave gyrotron, currently commercially available from Bruker. The microwave irradiation at low temperature results in the efficient polarization transfer of the electrons to protons, and CP-MAS from the protons to the desired nuclei results in signal enhancement (carbon-13, nitrogen-15 [76], silicon-29 [75], aluminium-27 [77]). The NMR signals can theoretically be enhanced by a factor of 660 ($\gamma_e/\gamma_H = 660$) corresponding to a decrease in acquisition time by ca. 440,000. In other words, an experiment that would take place in 300 days without SENS would take 1 min with a signal enhancement of 660.

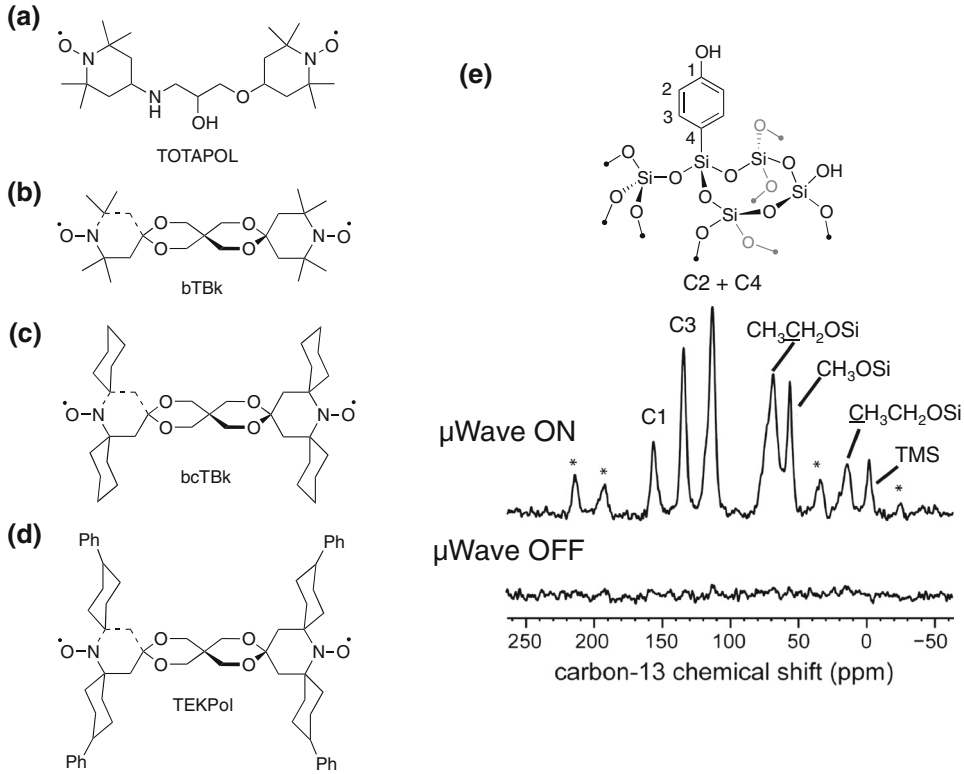
Our first experiments were performed with TOTAPOL [78] as the polarizing agent in water. We have shown that organic solvents such as toluene or tetrachloroethane work very well and give large enhancements with the family of bTbk radicals, ranging from 20 to 50 for parent bTbk [32] to more than 200 for TEKPol [79]. Originally discovered with simple hybrid organic–inorganic materials, this technique has been applied to alumina [77, 80], zeolites [81], and more recently to characterize well-defined metal complexes bound to the surface of hybrid materials [64, 82] (Scheme 9).

6 Bridging the Gap between Well-Defined Species and Classical Heterogeneous Catalysts

Industry relies extensively on supported catalysts for the production of polymers. This can be found in the Philipps and Ziegler–Natta olefin polymerization catalysts, which provide range of materials used in everyday life. While catalysis very likely takes place at a single-metal center, the aforementioned catalysts are in fact quite complex, and the structure of their active sites are not known, though Surface Organometallic Chemistry has provided some information concerning the interaction of metallocene complexes with oxide surfaces [83–87].

The classical Ziegler–Natta catalysts, [$TiCl_4.MgCl_2.L$], where L = EtOH, THF, or other alcohols/ethers, have been studied in detail by X-ray Absorption Spectroscopy [88, 89]. NMR spectroscopy combined with computational modeling has revealed that the THF ligand in [$TiCl_4.MgCl_2.THF$] is not innocent, and generates an alkoxy surface species as the result of its ring opening (Scheme 10a) [90]. While similar alkoxy species are formed with other L such as ethanol, it is not clear what the importance/relevance of such surface species to the final catalytic active sites.

In the case of Phillips catalyst, silica-supported Cr oxide species, the ideal oxidation state of the active species and



Scheme 9 **a–d** Nitroxyl radicals used for SENS; **e** SENS spectrum of a hybrid-silica material containing phenol groups in the mesopores with microwaves on (*top spectrum*) and microwaves off (*bottom spectrum*)

the formation of the first Cr–C bond remain controversial [91–94]. Recent efforts from our laboratory have shown that dinuclear Cr(III) silicates are highly active in ethylene polymerization while the Cr(II) analogues are much less active, suggesting that Cr(III) is probably the active polymerization oxidation state (Scheme 10b). Notably, similar observations have been made for homogeneous chromium polymerization catalysis [95, 96]. In addition, we have shown that the formation of the active species results from the heterolytic C–H activation of ethylene on a Cr–O bonds, which opens a new paradigm in polymerization catalysis and may shed light on the initiation mechanism of the classical Phillips catalyst [97].

Another well-know "single-site" industrial catalyst is the silica supported $TiCl_4$ propene epoxidation catalyst [98]. Combining a detailed reaction analysis, advanced NMR spectroscopy, and computational chemistry has revealed that the primary $\equiv SiOTiCl_3$ surface species readily reorganizes upon thermal treatment at high temperature by reaction with adjacent siloxane bridges and adjacent $\equiv SiOTiCl_3$ to generate stable $(\equiv SiO)_2TiCl_2$ and $TiCl_4$ (Scheme 10c) [99].

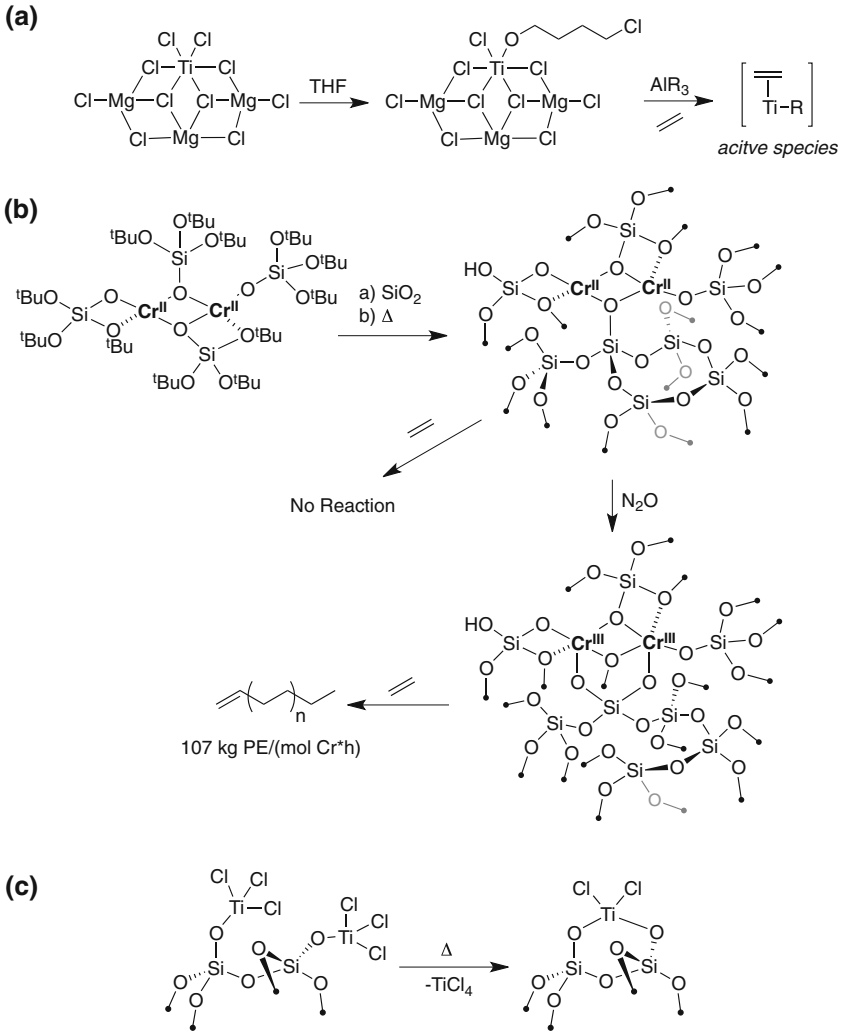
With the advancement of spectroscopic techniques and computational chemistry, it is now possible to study complex systems, even the aforementioned industrial catalysts, to provide new molecular views on existing systems.

7 Conclusions and Perspectives

With our current level of understanding of the surface chemistry of oxides, in particular silica and alumina, we can predictively design and prepare highly active and selective supported catalysts with molecular level definition. Molecular approaches can also help to directly address structure—activity relationships in industrial catalysts, with the goal of addressing one of the major challenges in industrial catalysis: developing more robust/stable catalysts.

The 'simple' grafting strategy is one step closer to using surfaces in a similar way ligands are used in homogeneous catalysis. Not discussed here are the opportunities on other supports. For example, mixed metal oxides have benefited from molecular approaches in non-hydrolytic sol–gel of mixed metal oxides [100] and the thermolysis of molecular precursors [101]. Though these methods have already shown interesting features, in particular the control of material composition and the discrete arrangement of atoms within mixed metal oxides, very little has been done in understanding the structures and the reactivities of these surfaces.

Hybrid organic–inorganic materials, silica-based materials with pendant ligand in the pores, offer intriguing material compositions that can directly functionalized as catalysts. Similar to this approach, a large effort is currently focusing on metal organic frameworks and related materials as a source of well-defined chemical environments for



Scheme 10 Transferring the molecular approach to industrial heterogeneous catalysts

catalysis [102]. The realm of silica-based materials is not only limited to SBA type structures. In particular periodic mesoporous silicates are a promising platform of materials that have high levels of structural order, good thermal stability, and large pore volume [103, 104].

The above materials are considered as model supports and catalysts. One of the largest classes of industrially relevant catalysts is supported nanoparticles for which a clear need for more molecular level investigations persists. The use of well-defined molecular precursors has already shown some promise with the control of size and distribution of particles as well as the interface between the metallic nanoparticles and the support. However, the need to reach smaller nanoparticles with a narrower particle size distribution has recently led to colloidal approaches [105–107]. Combining material chemistry of oxide and colloidal chemistry can also open new opportunities [108]. Material chemistry has shown the possibility to control the shape and the texture of oxide materials, and to incorporate metal nanoparticles within the pore or the wall of the material [109, 110]. This could provide several advantages, such as reducing the possibility for sintering or the preparation of bifunctional systems.

Molecular approaches, whether discussing surface science or surface chemistry, is clearly an essential tool in rational design. The molecular approach will continue to blossom as the advances in spectroscopy, material and molecular chemistry continue, and will likely be key to the development of optimal catalysts.

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