

Bridging the Gap between Industrial and Well-Defined Supported Catalysts

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Bridging the Gap between Industrial and Well-Defined Supported Catalysts

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Abstract

Many industrial catalysts contain isolated metal sites on the surface of oxide supports. While such catalysts have been used in a broad range of processes for more than 40 years, there is often a very limited understanding about the structure of the catalytically active sites. This review discusses how Surface Organometallic Chemistry (SOMC) engineers surface sites with well-defined structures and provides insight about the nature of active sites in industrial catalysts, focusing in particular on olefin production and conversion processes.

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1. Introduction

Chemical industry relies on heterogeneous catalysts because they are usually robust and can be integrated in continuous processes.^[1] Heterogeneous catalysts can be divided into several categories: supported metal nanoparticles, bulk metals, metal oxides or sulphides, zeolites, and dispersed metal sites on high surface area supports. Dispersed metal sites correspond to isolated metal sites with non-zero formal oxidation states bound to the surface of an oxide; they are associated with important catalytic processes such as the homologation of olefins *via* metathesis (Lummus OCT process),^[2-3] the epoxidation of propylene (SMPO process),^[4-5] the polymerization of olefins with Ziegler-Natta,^[6-7] Phillips,^[8-9] and supported metallocene and post-metallocene catalysts,^[10-12] as well as alkane dehydrogenation (Catofin process).^[13] Most of these catalysts involve organometallic reaction intermediates. However, the initial state and structure of the active sites are ill-defined and often unknown, leading to speculation about putative reaction intermediates. The development of these catalysts has thus remained mostly empirical. In contrast, the progress in molecular organometallic chemistry has led to the development of numerous homogeneous catalysts and successful processes which are more amenable to structure–activity relationship and rational developments.^[14-16] This review will discuss well-defined metal sites supported on oxide surfaces that are active in some of the key reactions mentioned above. These studies show that more precise control over surface structures can lead to more active and selective catalysts, enable rational development of *well-defined* or *single-site supported heterogeneous catalysts*,^[17-19] and can even provide information about the corresponding ill-defined industrial catalysts.

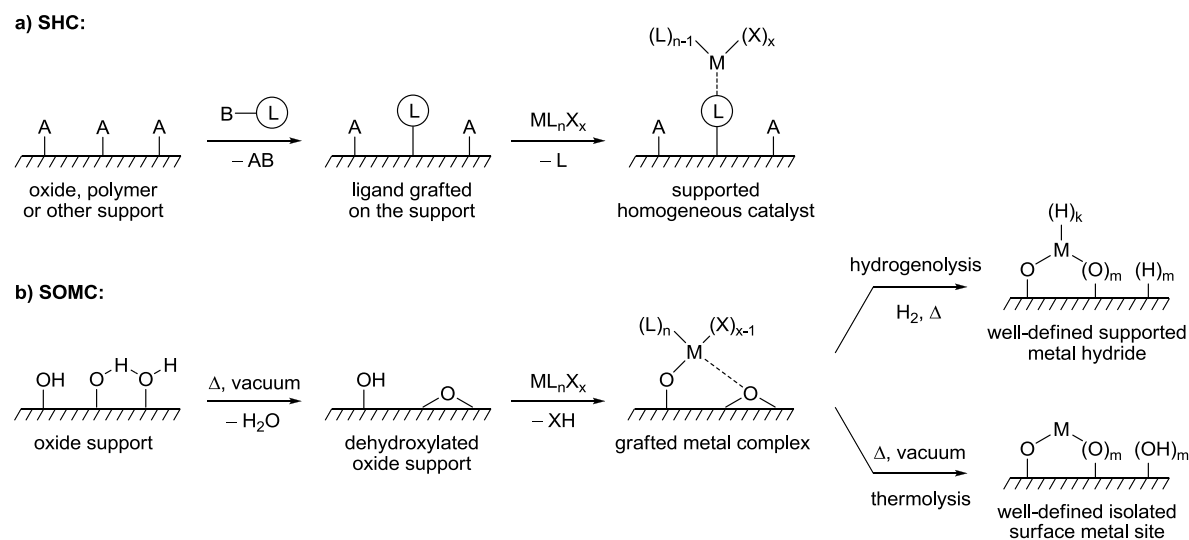
2. Well-Defined Supported Catalysts: Approaches and Concepts

Well-defined supported catalysts prepared from molecular complexes and oxides have long been considered ideal heterogeneous catalysts.^[20-32] Indeed, they combine the advantages of structural understanding of molecular homogeneous catalysts and more efficient processes, intrinsic to heterogeneous catalysis. The most common approaches to well-defined supported catalysts are referred to as: i) Supported Homogeneous Catalysis (SHC)^[33-41] and ii) Surface Organometallic Chemistry (SOMC).^[12, 42-51] Alternatively, homogeneous catalysts can also be immobilized *via* non-covalent methods (encapsulation and physisorption *via* electrostatic interactions, such as van der Waals or hydrogen bonding, ion pairing, ...).^[17, 19, 52-53]

With SHC, an organic ligand is first incorporated in a material, and the metal sites are subsequently bound to this ligand, generating species as close as possible to the structure of the respective homogeneous catalyst (Scheme 1a). The SHC approach often yields materials much less active than their homogeneous counterparts possibly due to the hindered access to active sites encapsulated in the support matrix, inhomogeneous distribution of surface sites, and uncontrolled interactions of the metal sites with the support. Structure-directing agents provide materials with improved structuration and localization of the organic moieties in the inorganic matrix;^[54] other alternatives include periodic mesoporous silicas,^[55-58] metal organic^[59-60] or covalent organic frameworks.^[61] However, these approaches are costly, time-consuming and rarely provide materials with improved catalytic performances.^[62] Similarly, encapsulation strategies have not yielded highly active systems, mainly suffering from the incompatibility of the molecular precursors with the conditions employed for the synthesis of the inorganic matrix.^[63] Finally, catalysts immobilized *via* adsorption and electrostatic interactions, with the

exception of few particular cases, often lack stability due to weak interaction of the molecular complex and the support leading to leaching under reaction conditions.^[52-53]

In SOMC, the surface functionalities of a support, usually a high surface area oxide, allow anchoring a metal site directly at the surface of the material (the oxygen surface sites act as anionic X-type ligands). This approach controls the site density as a function of the OH density on the surface, and incorporate neutral (L) or anionic (X) ancillary ligands to modulate the reactivity of the metal sites (Scheme 1b). The choice of tailored ligands allows generating isolated surface species without ancillary organic ligands after post-treatment at higher temperatures under reactive or inert gas. For instance, surface complexes with perhydrocarbyl ligands generate hydrides under H_2 ,^[45, 64-65] while Thermolytic Molecular Precursor approach (TMP)^[66-67] uses ligands undergoing clean and controllable thermolysis (*e.g.* $-OSi(OtBu)_3$) to produce isolated metal sites often structurally similar to those proposed as active sites in the corresponding industrial heterogeneous catalysts.



Scheme 1. Key concepts in preparation of well-defined supported catalysts: a) Supported Homogeneous Catalysis (SHC), b) Surface Organometallic Chemistry (SOMC).

The objective of this review is to describe the relationship between industrial catalysts and the corresponding well-defined catalysts prepared *via* SOMC. We restrict the discussion to supported single-site or well-defined catalysts involving organometallic intermediates used for the production, homologation and polymerization of olefins, with only a short section on supported metallocenes, as many reviews have appeared on this subject.^[10-12] Epoxidation^[5, 37] and denitrification^[68] with supported single-site catalysts have also been reviewed recently and will not be discussed here. The review is divided in five sections according to the application of single-site catalysts: alkane dehydrogenation (Section 3), alkene oligomerization (Section 4), direct homologation of ethylene to propylene (Section 5), alkene polymerization (Section 6) and metathesis (Section 7). In each section the industrial catalysts will be discussed briefly before describing the current state of the art for well-defined systems. When possible, we relate the chemistry of well-defined sites to the corresponding industrial systems.

3. Alkane Dehydrogenation

3.1. Industrial Context and Background

The production of light alkenes, primarily ethylene and propylene, is a key industrial process. Steam or fluid catalytic cracking produces a variety of aliphatics with up to 8% and 20% of ethylene and propylene, respectively.^[13, 69-72] However, a recent focus on natural and shale gas resources, comprised primarily of C₁–C₃ alkanes, has spurred interest in alternative olefin production processes. One such approach is the direct alkane dehydrogenation, a highly endothermic chemical transformation requiring high temperature to reach reasonable conversion ($\Delta_r H^\circ_{298} = 137 \text{ kJ mol}^{-1}$ and 124 kJ mol^{-1} for ethane and propane, respectively). Industrially relevant conversions require temperatures between 550 and 750 °C.

Propane dehydrogenation (PDH) technologies utilize two major classes of catalysts: Pt-Sn/Al₂O₃ (the Oleflex process) and CrO₃/Al₂O₃ (CB&I Lummus Catofin process).^[13, 69-73] Although the precise nature of the catalytically relevant sites in the latter catalyst is unknown, low coordinated Cr^(III) sites were proposed to be the active sites.^[74-75]

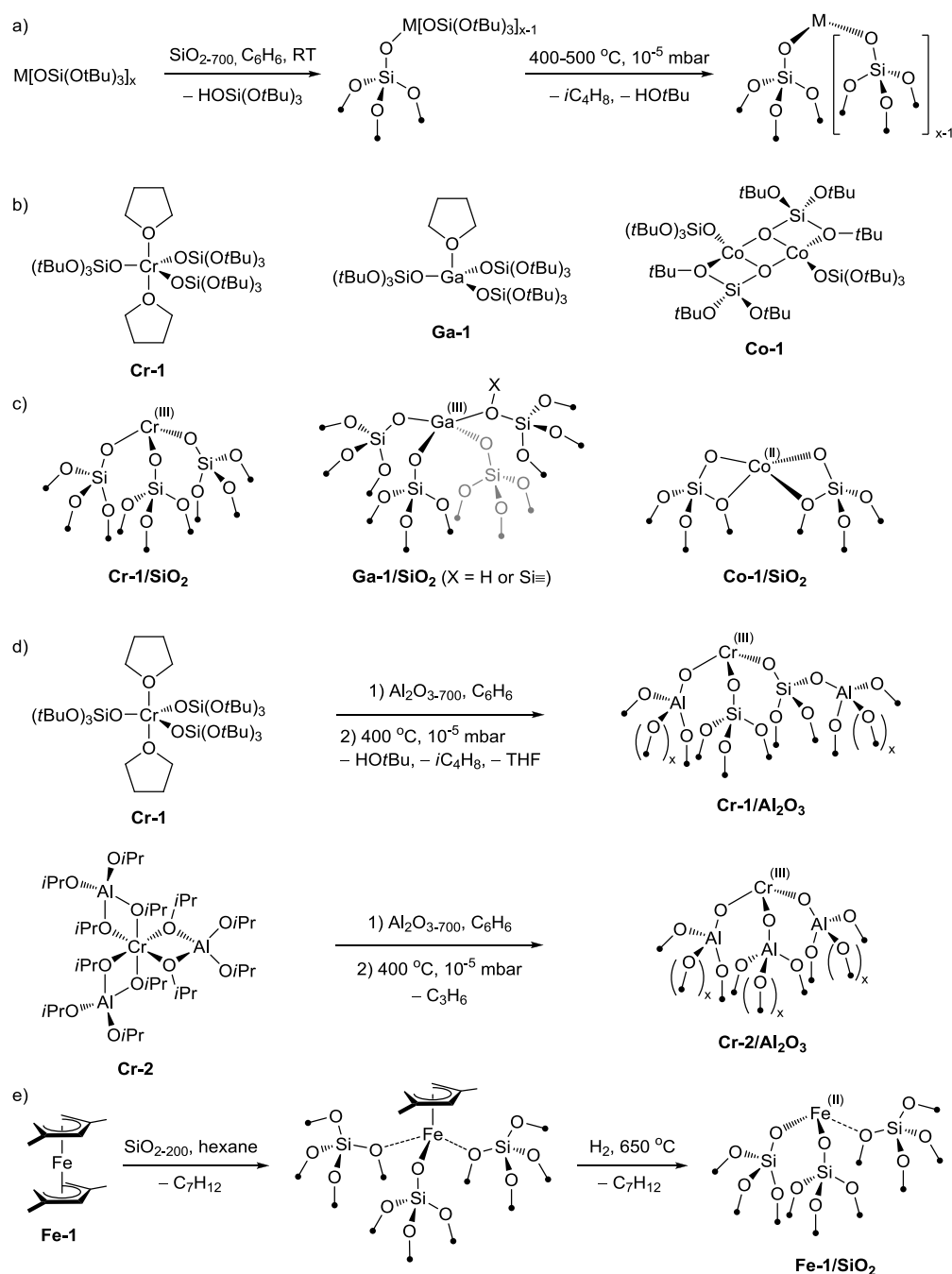
Another, more thermodynamically favorable, approach is the oxidative dehydrogenation of alkanes, which converts formed H₂ with O₂ to water.^[76-83] Although favorable, this reaction is often associated with low selectivity due to over-oxidation unless the process is carried out at low conversions. The most common catalysts are based on supported V_xO_y species, which produce a variety of surface sites ranging from monomeric VO_x species to crystalline V₂O₅ domains depending on the surface coverage.^[78-80, 82] Extensive redistribution of sites and redox events occur during catalysis making identification of active sites challenging. Despite the thermodynamic advantages of oxidative dehydrogenation, the low yield has so far prevented its implementation as a replacement for the highly energy intensive non-oxidative dehydrogenation technologies.

The active sites of these key petrochemical processes are proposed to be isolated metal sites. The following sections will describe heterogeneous dehydrogenation catalysts (both oxidative and non-oxidative) based on supported isolated metal sites generated *via* SOMC,^[42-43, 45-46] whose activity will be compared to the related systems prepared using classical methods. The alternative approach based on supported homogeneous catalysts^[84-86] has been recently reviewed and will not be discussed.^[87]

3.2. Non-Oxidative Dehydrogenation

A two-step process combining SOMC and the Thermolytic Molecular Precursor approach (Scheme 2a)^[66] has been used to generate isolated Cr^(III) sites using Cr(OSi(O*t*Bu)₃)₃(THF)₂ (**Cr-1**) as a molecular precursor and silica and alumina partially dehydroxylated at 700 °C (SiO₂₋₇₀₀ and Al₂O₃₋₇₀₀) as supports, yielding **Cr-1/SiO₂** and **Cr-**

1/Al₂O₃, respectively (Scheme 2).^[88-89] A chromium aluminate material free of surface Si sites, **Cr-2/Al₂O₃**, has also been prepared *via* grafting of Cr(κ^2 -Al(O*i*Pr)₄)₃ (**Cr-2**) on Al₂O₃₋₇₀₀ followed by a thermal treatment at 400 °C (Scheme 2d).^[89] Similarly, monomeric Ga^(III)^[90] and Co^(II)^[91] sites supported on silica have also been prepared using this approach (Scheme 2). The presence of monomeric sites was established through a variety of spectroscopic techniques including a Wavelet transform analysis of the EXAFS data. In all these examples the molecular precursors retain their oxidation state when generating the corresponding surface sites. Isolated Fe sites have also been prepared by SOMC through the reaction of Fe(*o*Cp)₂ (**Fe-1**; *o*Cp = 2,4-dimethylpentadienyl) with silica partially dehydroxylated at 200 °C (SiO₂₋₂₀₀) yielding (\equiv SiO)Fe(*o*Cp)(\equiv SiOSi \equiv)₂.^[92] Its thermal treatment at 650 °C under H₂ gives **Fe-1/SiO₂**, a material with Fe^(II)/SiO₂ surface sites (Scheme 2e).



Scheme 2. a) Preparation of isolated metal sites on silica using TMP approach. b) Siloxide molecular precursors and c) the corresponding silica-supported single sites. d) Preparation of isolated Cr^(III) sites on alumina using siloxide and aluminate molecular precursors. e) Preparation of Fe^(II) single sites on silica using Fe(*o*Cp)₂.

The catalytic performances in PDH of the isolated metal sites generated *via* SOMC are summarized in Table 1 and can be compared to those of the catalysts prepared using classical methods.^[93-96] Propane conversions for these SOMC catalysts are reported below

equilibrium conversion (3–10% conversion) and display significantly higher specific activities ($\text{mol}_{\text{C}_3\text{H}_6} \text{mol}_{\text{M}}^{-1} \text{h}^{-1}$) than for the corresponding systems – Ga(III) and Co(II) – prepared by electrostatic adsorption methods. Note however, that catalysts prepared by electrostatic adsorption methods show increased selectivity and in some cases, higher specific activity at longer reaction time, suggesting structural change of the active sites. The isolated sites prepared utilizing SOMC exhibit greater overall selectivity and activity despite similar reported structures, which is likely due to a more uniform distribution of active sites.

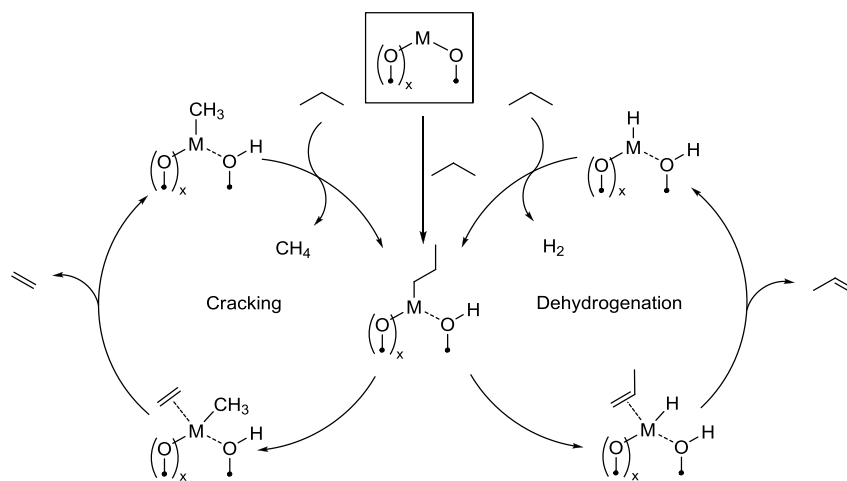
Table 1. Preparation, reaction conditions, selectivity and activity of well-defined isolated metal sites for propane dehydrogenation. “I” and “F” stand for initial and final, respectively; “el. ads.” stands for electrostatic adsorption.

Surface sites	Preparation	wt% metal	Temp.	Conv.	Select.	TOF (h^{-1})	Time	WHSV (h^{-1})	Ref.
$\text{Cr}^{(\text{III})}/\text{SiO}_2$	grafting Cr-1 , thermolysis	1.51	550 °C	I – 10% F – 3%	I – 86% F – 72%	I – 19 F – 5	2 h	3.1	[88]
$\text{Cr}^{(\text{III})}/\text{SiO}_2/\text{Al}_2\text{O}_3$	grafting Cr-1 on Al_2O_3 , thermolysis	0.21	550 °C	I – 5% F – 3%	I – 72% F – 70%	I – 51 F – 28	2 h	3.1	[89]
$\text{Cr}^{(\text{III})}/\text{Al}_2\text{O}_3$	grafting Cr-2 on Al_2O_3 , thermolysis	0.18	550 °C	I – 4% F – 3%	I – 72% F – 66%	I – 60 F – 34	2 h	3.1	[89]
$\text{Ga}^{(\text{III})}/\text{SiO}_2$	grafting Ga-1 , thermolysis	1.45	550 °C	I – 9% F – 7%	I – 94% F – 93%	I – 20 F – 14	20 h	2.1	[90]
			500 °C	– –	I – 95% F – 96%	I – 0.75 F – 0.55	6 h	0.30	[94]
	el. ads. $\text{Ga}(\text{NO}_3)_3$, calcined at 550 °C	2.64	550 °C	– –	I – 91% F – 93%	I – 1.5 F – 1.1	6 h	0.30	[94]
			600 °C	– –	I – 86% F – 89%	I – 2.2 F – 1.7	6 h	0.30	[94]
			550 °C	26%	97%	3.9	6 h	0.037	[94]
$\text{Co}^{(\text{II})}/\text{SiO}_2$	grafting Co-1 , thermolysis	1.67	550 °C	I – 10% F – 4%	I – 73%* F – 67%*	I – 13 F – 5.0	14 h	2.0	[91]
$\text{Co}^{(\text{II})}/\text{SiO}_2$	el. ads. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, calcined at 300 °C	2.1	550 °C	I – 4.0% F – 10%	I – 91%* F – 95%*	I – 0.66 F – 1.8	20 h	0.18	[96]
			650 °C	I – 60% F – 35%	I – 86%* F – 95%*	I – 16 F – 8.3	20 h	0.18	[96]
$\text{Fe}^{(\text{II})}/\text{SiO}_2$	grafting Fe-1 , H_2 treatment at	1.11	650 °C	I – 4.9% F – 6.3%	I – 99%* F – 99%*	I – 1.1 F – 1.4	18 h	0.18	[92]

650 °C									
Zn ^(II) /SiO ₂	el. ads. Zn(NO ₃) ₂ , calcined at 300 °C	3.9	550 °C	–	I – 95%*	I – 0.77	12 h	0.18	[93]
				–	F – 95%*	F – 0.39			
			650 °C	–	>95%*	2.3	0.5 h	0.18	[93]

* Reported selectivity after subtraction of background cracking reactions.

Mechanistic considerations for the aforementioned dehydrogenation catalysts have converged to a similar non-redox mechanism (Scheme 3).^[88-89, 91, 93, 96] The rate-limiting step involves heterolytic C–H bond activation across an M–O bond, resulting in formation of an M–propyl species. Subsequent β -hydride elimination forms propylene. After release of propylene, hydrogen elimination from the resulting M(–H)···OH intermediate completes the catalytic cycle for PDH. This mechanism has been supported computationally for Zn^(II), Co^(II) and Cr^(III)/SiO₂ using cluster models^[88, 93, 96] and, for Cr^(III)/Al₂O₃, using a periodic alumina model.^[89] Calculations performed for Cr^(III)/SiO₂ also suggest that β -alkyl elimination of an M–propyl intermediate can lead to ethylene and methane, the cracking products.^[88]

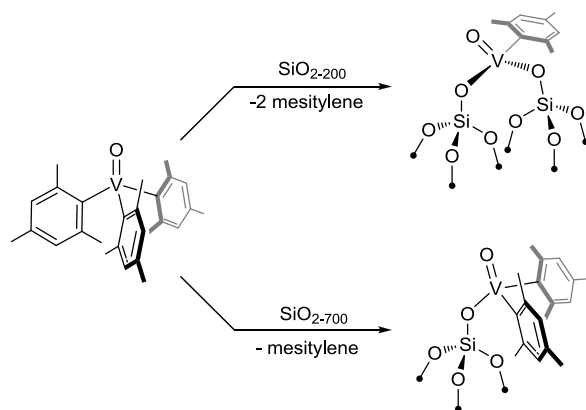


Scheme 3. Non-redox mechanism proposed for propane dehydrogenation and formation of cracked products over isolated metal sites.

Hydrogenation of propene, the microscopic reverse of dehydrogenation, has also been studied to gain mechanistic insight to the PDH reaction over isolated metal sites.^{[89, 91,}

^{93-94, 96]} Para-Hydrogen Induced Polarization (PHIP) experiments for Cr and Co have indicated that *p*-H₂ could be incorporated into propene in a pairwise fashion, consistent with hydrogenation and dehydrogenation involving heterolytic H–H and C–H splitting on an M–O site.^[89, 91] The low yield of product incorporating *p*-H₂ (<5%) has been attributed to significant relaxation of para-hydrogen by the investigated paramagnetic metal centers.

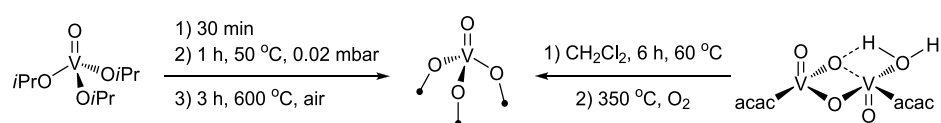
Isolated vanadyl sites have also been generated on the surface of oxide-supports through grafting of molecular complexes.^[97-100] The generation of well-defined vanadyl sites for non-oxidative dehydrogenation of propane was achieved on SiO₂₋₇₀₀ and SiO₂₋₂₀₀ via grafting of V(=O)(Mes)₃ (Mes = 2,4,6-trimethylphenyl) (Scheme 4).^[99] Using silica at different degrees of dehydroxylation results in mono- and bis-grafted sites. Both surface species were active in propane dehydrogenation with initial conversions of 17% for the mono-grafted complex and 16% for the bis-grafted at a WHSV of 0.11 h⁻¹. Over the duration of 7 days the conversions decreased to 9% and 12% for the mono- and bis-grafted species, respectively. The selectivity for propylene remained constant over the duration of the experiments at *ca.* 83 and 90%.



Scheme 4. Preparation of mono- and bis-grafted isolated vanadium oxo sites on SiO₂₋₂₀₀ and SiO₂₋₇₀₀.

3.3. Oxidative Dehydrogenation

Supported vanadium oxides are promising catalysts for oxidative dehydrogenation (ODH).^[80] There is still an uncertainty regarding the structure of the vanadium active sites in ODH due to the complexity of surface sites in supported V_2O_5 systems. As a result, the number of well-defined heterogeneous V-based systems is limited. In attempts to generate isolated active sites, the molecular precursors $V(=O)(OiPr)_3$ and $V_2O_4(acac)_2(H_2O)$ have been grafted on the surface of dehydroxylated SiO_2 (Scheme 5).^[97-98]



Scheme 5. Preparation of VO_x/SiO_2 using $V(=O)(OiPr)_3$ and $V_2O_4(acac)_2(H_2O)$.

The catalytic performance of VO_x/SiO_2 prepared using $V(=O)(OiPr)_3$ for ODH under flow conditions at 490 °C exhibits a propylene selectivity of 78% at propane conversions of 3%, while at higher conversions (6%) propylene selectivity drops to 68%. A material with a similar vanadium loading (3 wt%) prepared by incipient wetness impregnation of SiO_2 using the same molecular precursor shows comparable activity and selectivity under similar reaction conditions with both materials having a specific activity of *ca.* 54 h^{-1} .^[98] Spectroscopic investigations indicate no oligomeric vanadium sites on the surface. However, other reports using $V_2O_4(acac)_2(H_2O)$ with lower loading (1 wt%) observed specific activities for ODH of *ca.* 160 at 525 °C. At propane conversions in the range of 5–12% propylene selectivity remains at 65%.^[97] Materials with similar and higher loadings prepared by incipient wetness impregnation, using NH_4VO_3 , indicated a decrease in specific activity with increasing metal loading. These results suggest that a fraction of surface sites are inactive for oxidative dehydrogenation even at sub-monolayer coverage.^[97]

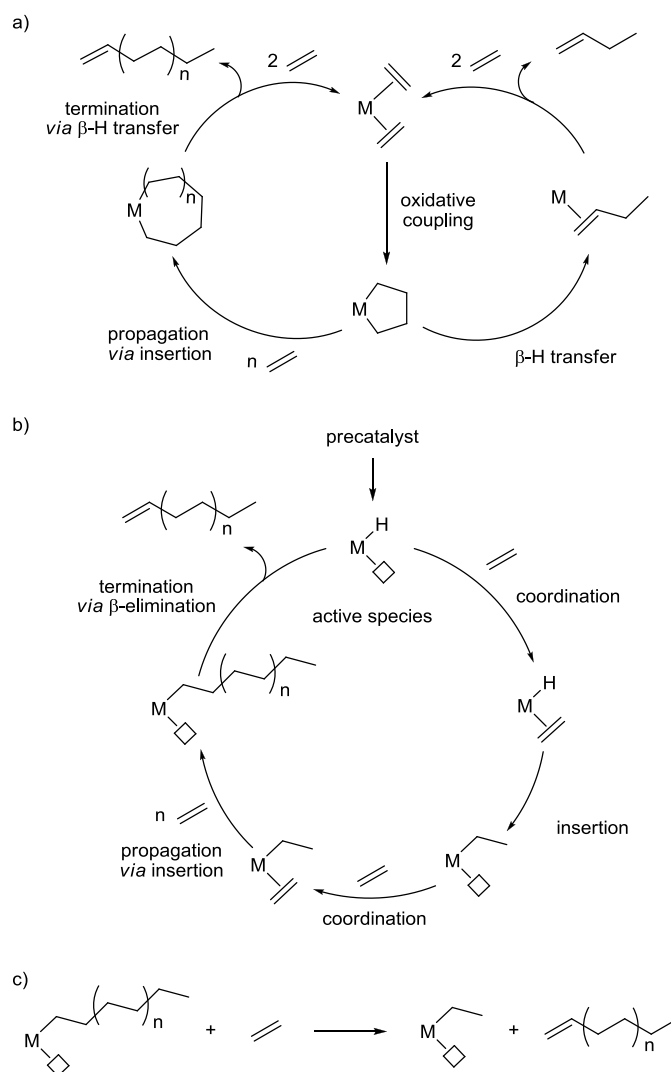
4. Alkene Oligomerization

4.1. Industrial and Mechanistic Background

4.1.1. General Considerations and Context

Oligomerization of olefins, typically ethylene, propene or butenes, yields dimers, trimers, etc., with a relatively small number of repeating monomer units ($2 \leq n < 100$, often 2–10). Such oligomers have a broad range of applications^[14, 101-103] and their structure – linear *vs.* branched – and the chain length of oligomers depend on the monomer, the catalyst, the oligomerization mechanism and operating conditions (temperature, pressure, monomer-to-catalyst ratio and concentration).^[104] Molecular oligomerization catalysts involve metallacycle intermediates that produce 1-butene, 1-hexene or 1-octene (Scheme 6a), or metal hydride intermediates that insert olefins to form a Schulz-Flory distribution of oligomers (Scheme 6b).^[105] The former mechanism typically employs early transition-metals, *e.g.* Ti, Zr, Ta and Cr, while the latter is mainly based on late transition metals (Ni, Fe, Co, ...).^[101] In both cases, a cocatalyst, typically aluminum alkyl reagent such as methylaluminoxane (MAO), is necessary to generate the active species.

While numerous molecular oligomerization catalysts have been reported, there are only few well-defined supported systems. Common strategies to generate the active sites use *in situ* activation of well-defined supported complexes or utilize molecular catalysts along with supported cocatalysts. Alternative strategies, not discussed here, use immobilized ligands, ionic liquids or supported ionic liquids.^[106-114]



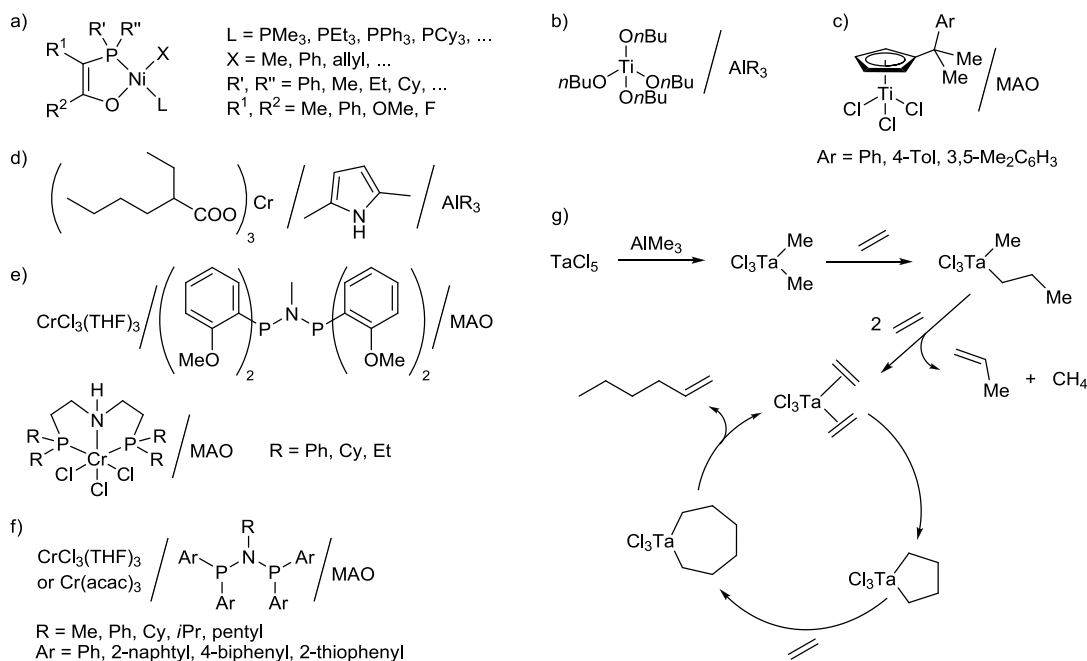
Scheme 6. Simplified a) metallacycle and b) coordination–migratory insertion mechanisms of olefin oligomerization; c) termination *via* a chain transfer to monomer.

4.1.2. Selected Homogeneous Systems

The Shell Higher Olefin Process (SHOP process) developed in 1968 provides a mixture of even-numbered α -olefins with a Schulz-Flory distribution from ethylene and a $\text{Ni}^{\text{(II)}}$ phosphine complexes (80–120 °C, 70–140 bar).^[101, 115] SHOP-catalysts typically contain a P,O- or a P,N-ligand and monodentate L and X ligands, where X is an organyl (Scheme 7a).^[116] For Ni-based catalysts, it is generally accepted that the oligomerization takes place *via* multiple insertions of the olefin into a Ni–C bond (Scheme 6b), while chain termination proceeds by β -H elimination regenerating the nickel-hydride and releasing an

α -olefin.^[117] Termination *via* a chain transfer step has also been proposed (Scheme 6c).^[101]

The relative rate of insertion *vs.* β -H elimination/transfer controls the distribution of the olefin chain length leading to Schultz-Flory distribution of olefins, whose average molecular weight depends on the operating conditions.^[117]



Scheme 7. Some of the well-known homogeneous olefin oligomerization systems: a) SHOP catalyst for ethylene oligomerization; b) Alphabutol ethylene dimerization catalyst; c) Ti catalyst for ethylene trimerization based on a modified Cp ligand; d) Phillips ethylene trimerization system; e) BP and Sasol ethylene trimerization systems; f) Sasol ethylene tetramerization system; g) Mechanism for TaCl₅-mediated ethylene trimerization.

In 1980s, IFP and SABIC developed the Alphabutol process for selective ethylene dimerization that now accounts for ca. 25% of world's production of 1-butene (Scheme 7b).^[102, 118-119] This process employs Ti(OnBu)₄ homogeneous catalyst activated by trialkylaluminum and reaches 93% selectivity in 1-butene at 80–85% ethylene conversion (50–60 °C, 20–30 atm). The main by-products are C₆ and higher alkenes that arise from coupling of 1-butene with ethylene or two 1-butenes. The generally accepted mechanism includes a Ti^(II)/Ti^(IV) cycle operating *via* a metallacycle intermediate (Scheme 6a).^[120]

Alternatively, a coordination/insertion mechanism with a very high rate of the chain transfer was proposed.^[105] Recent work on well-characterized single-site titanium complexes suggests that a metallacycle mechanism is more likely.^[121] With tailored ligands, *e.g.* $(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{Ar})\text{TiCl}_3$ (Ar = Ph, 4-Tol, 3,5-Me₂C₆H₃, Scheme 7c), Ti catalysts can also become selective towards trimerization of ethylene to 1-hexene with high productivity and selectivity (1070 g_{hexenes} mmol_{Ti}⁻¹ h⁻¹ with selectivity to 1-hexene >80 wt%) when activated with MAO.^[122-123] While the metallacycle mechanism was proposed for this system, no titanacycloheptane intermediates have been spectroscopically characterized so far.

The selective trimerization of ethylene to 1-hexene using homogeneous Cr catalysts was discovered by Union Carbide^[124] and commercialized by Chevron Phillips (Phillips trimerization system, Scheme 7d).^[125] For these systems, a metallacycle mechanism is accepted and supported by theoretical investigations.^[126-128] However, the nature of the active sites is still very much debated, implying several possible redox couples such as Cr^(I)/Cr^(III) or Cr^(II)/Cr^(IV).^[105, 129] Very active and selective homogeneous Cr trimerization catalysts based on PNP ligands (Scheme 7e) were developed by BP^[130] and Sasol^[125, 131] (up to 10⁶ g_{hexenes} g_{Cr}⁻¹ h⁻¹ and >90% 1-hexene selectivities). Specific PNP ligands allow for the control of C₆/C₈ product distribution leading to high 1-octene selectivity, up to 70% (Scheme 7f).^[132-133]

TaCl₅ activated with AlMe₃ or ZnMe₂ catalyzes the selective trimerization of ethylene to 1-hexene (Scheme 7g).^[134-136] Similar results were obtained by the *in situ* reduction of TaCl₅ with 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (BTCD) or its 2-methyl derivative (MBTCD) to give Ta^(III) species that in turn provided metallacyclopentane intermediates characterized by NMR.^[136] Dimethyltantalacyclopentane intermediates were detected using CpTa(=CHCMe₃)Cl₂ alkylidene catalyst that presumably enters the catalytic

cycle by [2+2] cycloaddition of propene followed by a rearrangement of the initially formed tantalacylcobutane complex.^[137] A related intermediate was proposed for the propylene oligomerization on Ti⁽⁰⁾ and Zr⁽⁰⁾ butadiene complexes.^[138]

4.2. Supported Ni Oligomerization Catalysts

4.2.1. Supported Ni Ions

Supported NiO catalyzes ethylene dimerization at room temperature.^[139-154] Studies on NiO/Al₂O₃-SiO₂ suggest that isolated Ni^(II) sites with neighboring Al³⁺ sites,^[155] or Ni^(II) assisted by Brønsted acidic sites are active.^[140] However, a linear dependence of ethylene conversion rates on the Ni^(I) concentration suggests that Ni^(I) sites may also be involved.^[156-157] NiSO₄ dispersed on oxides also yields ill-defined ethylene oligomerization heterogeneous catalysts. The oxidation state of Ni in these systems is unknown.^[148, 158-162] The activities of NiO- and NiSO₄-based catalysts lie in the range of 0.3–3.3 g_{olig} g_{cat}⁻¹ h⁻¹ (Table 2).

Table 2. Catalytic performance of heterogeneous Ni-based catalysts in the oligomerization of ethylene and proposed oxidation state of the active sites.

Catalyst	Ni (wt%)	Reactor	T (°C)	P (bar)	Activity, g _{olig} g _{cat} ⁻¹ h ⁻¹	C ₄ (wt%)	Active sites	Ref.
NiO/Al ₂ O ₃ -SiO ₂	3.6	Batch	150	28	3.2	85.4	Ni ^(II) and Al ^(III)	[160]
NiO/Al ₂ O ₃ -SiO ₂	4.0	Flow	40	20.7	0.325	50	Ni ^(II) and Al ^(III)	[154]
NiO/B ₂ O ₃ -Al ₂ O ₃	3.0	Flow	200	10	0.33	73.8	n.d. ^a	[145]
NiO-ZrO ₂ /WO ₃	18.0	Batch	20	0.4 ^b	0.4	100	n.d.	[149]
NiSO ₄ /Al ₂ O ₃	6.4	Batch	20	0.4 ^b	1.4	100	Ni ^(I) and acid site	[158]
NiSO ₄ /Al ₂ O ₃ -ZrO ₂	3.1	Batch	20	0.4 ^b	3.3	100	n.d.	[163]
NiO-ZrO ₂ /SO ₄ ²⁻	18	Batch	20	0.4 ^b	0.7	100	n.d.	[153]
NiO-TiO ₂ /SO ₄ ²⁻	36.5	Batch	20	0.4 ^b	0.9	100	n.d.	[152]
Ni-Y	5.6	Flow	60	28	0.3	67	n.d.	[164]
Ni-NaY	5.6	Flow	70	41	0.4	67.3	n.d.	[165]
Ni-Beta	1.7	Flow	120	26	1.6	72.3	Ni ^(II)	[166]
Ni-MCM-41	2	Batch	150	35	150	45	Ni ^(I) and dehydrat. Ni ^(II)	[167]

Ni-MCM-48	0.5	Batch	150	35	113	42	n.d.	[168]
Ni-SBA-15	5	Flow	120	30	1.0	n.d.	n.d.	[169]

^a n.d. – not determined; ^b initial pressure.

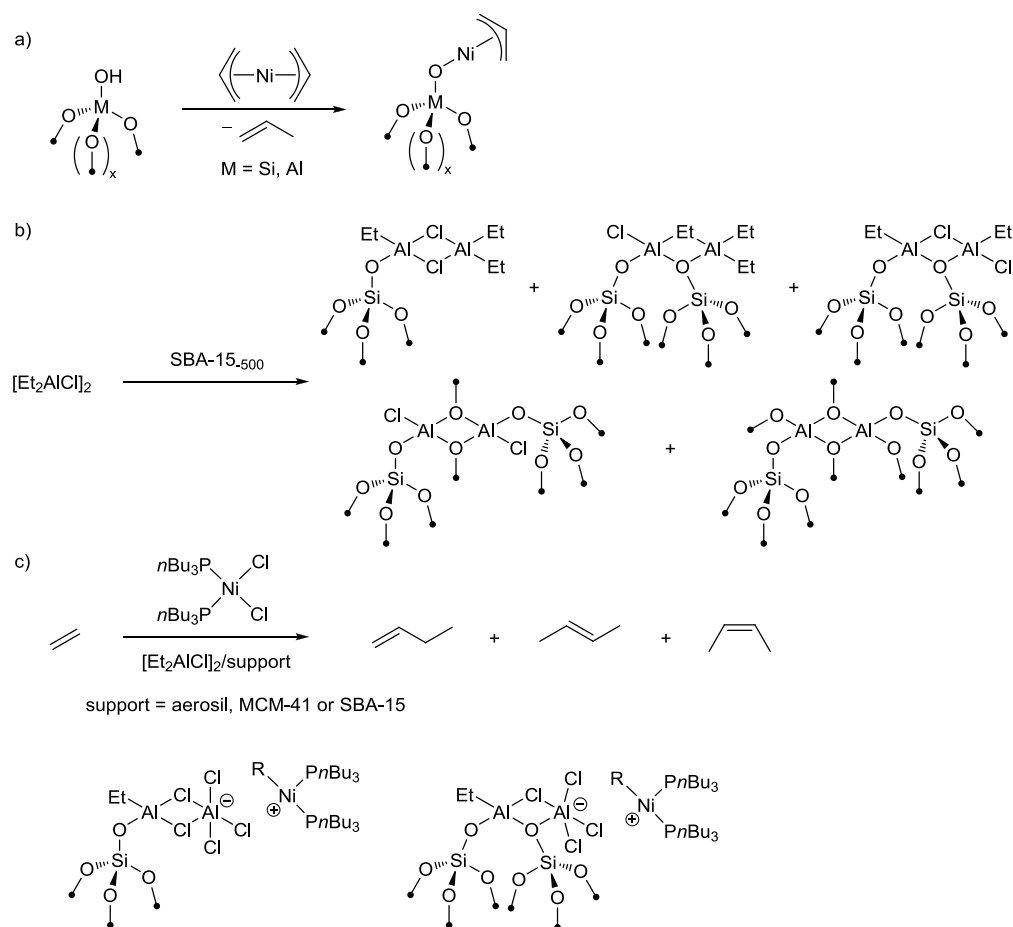
Ni-exchanged zeolites (faujasite X and Y) have activity similar to that of NiO/SiO₂ (Table 2).^[170] However, these catalysts rapidly deactivate forming polymeric waxes that block access to the pores in these materials.^[171] Materials with larger pores, such as dealuminated Y zeolites, are more active than NiO catalysts and have greater stability than zeolites with small pores.^[172] While XANES studies on nickel-modified zeolites showed retention of the Ni^(II) oxidation state under catalytic conditions,^[166, 173] reduction to Ni^(I) under thermal activation was demonstrated in certain cases by EPR spectroscopy and IR with adsorbed CO, suggesting that low-valent nickel ions could be responsible for the olefin oligomerization.^[156, 169, 174-179] Ni^(I) species with one, two or four phosphine ligands were prepared by reducing well-dispersed Ni^(II) species on silica.^[180-181] Only unsaturated sites with one or two PEt₃ ligands are active in ethylene and propylene oligomerization forming dimers with selectivities up to 95%.^[180-181] A metallacyclopentane mechanism was proposed for Ni^(I) sites.^[180-181] Recent reports described metal organic frameworks as heterogeneous catalysts for Ni-catalyzed ethylene dimerization. Such systems serve as models of Ni surface sites.^[182-185]

4.2.2. Well-Defined Supported Ni Oligomerization Catalysts

Many attempts were made to immobilize molecular Ni oligomerization catalysts on inorganic supports,^[186-191] though the resulting surface species are often poorly characterized and lack activity, selectivity or stability. The first well-defined heterogeneous olefin oligomerization systems were developed in the 1970s, via grafting Ni(η^3 -allyl)₂ molecular precursor on silica and silica-alumina.^[192-193] The structures of the resulting surface complexes (Scheme 8a) were proposed based on quantification of propylene

evolved during grafting and more recently confirmed with elemental analysis, IR and ssNMR spectroscopies.^[194] While the silica-supported catalyst is only active in the presence of MeAlCl₂, the corresponding silica-alumina-supported system catalyzes propylene oligomerization without any additives.^[192-193] The activity strongly depends on the Si/Al ratio and is the highest at 70 wt% of Al₂O₃, indicating the necessity of both strong Brønsted and Lewis acidity of a support.

An alternative approach to immobilized catalysts consists in activating a homogeneous catalyst by a solid cocatalyst obtained by treating silica with organoaluminum reagents. Early attempts to prepare SHOP-type heterogeneous Ni catalysts using (SiO)_nAlMe_{3-n} as a support gave materials with activity similar to and selectivity approaching that of the respective homogeneous catalysts.^[195] Recent studies have shown that the reaction of diethylaluminum chloride (DEAC) with various silicas (aerosil, MCM-41, SBA-15) yields several alkyl-aluminum surface sites with structures shown in Scheme 8b. Using high-field and ultrafast magic angle spinning NMR complemented by DFT calculations points to the presence of mainly dinuclear Al species with bridging chlorides.^[196-197] Contacting this material with (*n*Bu₃P)₂NiCl₂ generates active ethylene dimerization catalysts with TOFs up to 498,000 mol_{C₂H₄} mol_{Ni}⁻¹ h⁻¹ when MCM-41 is used as a support (Scheme 8c).^[197] Reacting (*n*Bu₃P)₂NiCl₂ with SBA-15-supported triethylaluminum (TEA), which also contains dimeric species, provides a catalyst inactive in ethylene oligomerization, suggesting that chlorine-bridging Al sites are likely important in the activation process, possibly because of the formation of metal–ion pairs that cannot form tight methyl bridged bimetallic Ni,Al species.^[198]



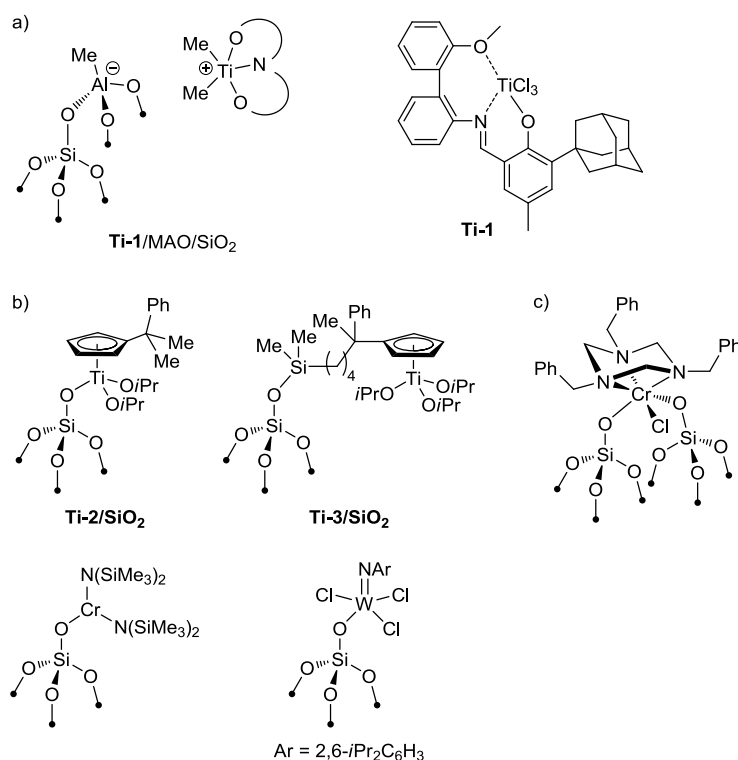
Scheme 8. a) Grafting of $\text{Ni}(\eta^3\text{-allyl})_2$ on silica. b) Possible surface species generated upon reaction of Et_2AlCl and SBA-15₅₀₀. c) Activation of homogeneous nickel catalyst for ethylene dimerization with Et_2AlCl grafted on silica supports, and the possible structures of the active site.

4.3. Supported Group 4–6 Oligomerization Catalysts

Oligomerization catalysts based on group 4–6 metals typically require an organoaluminum cocatalyst and hence can be either grafted on a modified support or activated after immobilization. **Ti-1** ethylene trimerization catalyst has been immobilized onto silica-supported MAO (Scheme 9a).^[199–200] The activity of **Ti-1**/MAO/SiO₂ was lower than that of the corresponding MAO-activated homogeneous catalyst. However, **Ti-1**/MAO/SiO₂ is more stable than its homogeneous analogs, possibly because of the suppressed bimolecular deactivation of Ti species due to site isolation. Moreover, while the

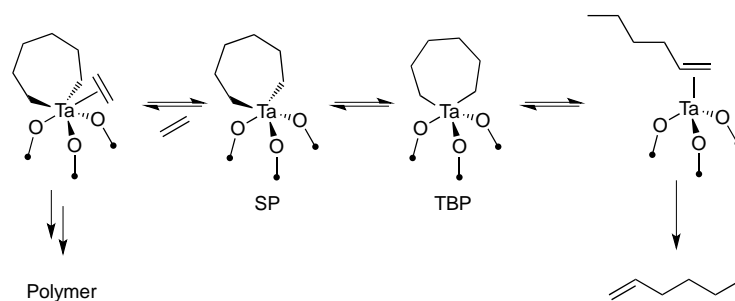
homogeneous system switches from selective trimerization to polymerization in the presence of aluminum alkyls, the corresponding heterogeneous catalyst retains its trimerization selectivity.^[199] Cationic Ti dimethyl complexes were proposed as the active species.^[199-200] Similarly, starting from MAO-modified SBA-15, the reaction of a mixture of $\text{Cr}(\text{acac})_3$ and *N*-isopropyl-*bis*(diphenylphosphino)amine yields an ethylene tetramerization catalyst with selectivity to 1-octene up to 70% and TOF of *ca.* $6.88 \cdot 10^6 \text{ h}^{-1}$. Note that the aforementioned mixture of the ligand and $\text{Cr}(\text{acac})_3$ in solution exhibits 3 times higher activity with similar selectivity.^[201]

Alternatively, a well-defined surface complex **Ti-2/SiO₂** (Scheme 9b), prepared by grafting of titanium precursor $(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{Ph})\text{Ti}(\text{OiPr})_3$ (**Ti-2**) on silica^[202] and further activated with MAO, provides a selective ethylene trimerization catalyst, that displays catalytic performance comparable to the corresponding homogeneous catalyst, but leaches under the reaction conditions. In contrast, **Ti-3/SiO₂** prepared *via* SHC approach (Scheme 9b) is inactive in ethylene trimerization. $\text{Cr}[\text{N}(\text{SiMe}_3)_2]_3$ supported on silica (Scheme 9b) activated with isobutylaluminum yields a highly active ($3170 \text{ g mmol}_{\text{Cr}}^{-1} \text{ h}^{-1}$) and selective ethylene trimerization catalyst, while the molecular complex $\text{Cr}[\text{N}(\text{SiMe}_3)_2]_3$ is almost inactive under the same conditions ($4 \text{ g mmol}_{\text{Cr}}^{-1} \text{ h}^{-1}$).^[203] Subsequent treatment of these supported catalysts with 1,2-dimethoxyethane (DME) increases the selectivity to 1-hexene up to 80%. Grafting $\text{W}(=\text{NAr})\text{Cl}_4(\text{THF})$ ($\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) on silica (Scheme 9b) and other supports followed by an activation with MAO yields heterogeneous ethylene dimerization catalysts demonstrating activities comparable to those of the molecular complex. Significantly higher activity is found when the complex is grafted on polymethylaluminum.^[204]



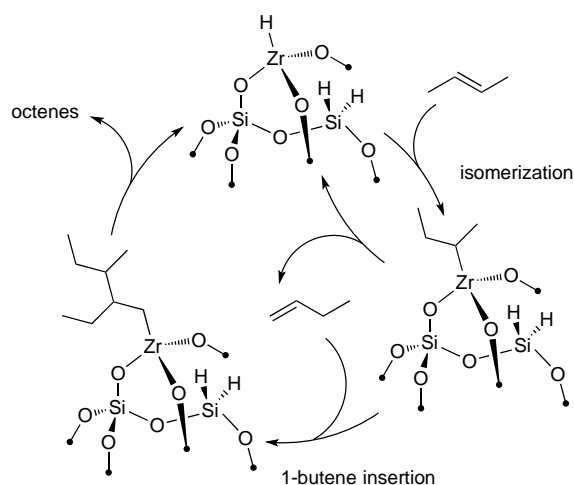
Scheme 9. a) Ethylene trimerization catalyst **Ti-1** supported on MAO-modified silica. b) Silica-supported Ti, Cr, and W ethylene oligomerization catalyst precursors. c) Proposed active site structure for Phillips catalyst modified with TAC ligand.

Another approach is to modulate the reactivity of supported polymerization catalysts thereby transforming them into oligomerization catalysts. Treatment of the reduced Phillips polymerization catalyst, containing mostly Cr^(II) sites (see Section 6.1.1.2), with 1,3,5-tribenzylhexahydro-1,3,5-triazine (TAC) provides a material three times more active than its homogeneous analogue CrCl₃(TAC) and selective towards 1-hexene (up to 91%) at low pressures when activated with Al*i*Bu₃.^[205-206] While the homogeneous CrCl₃(TAC) complex produces 1-hexene immediately, heterogeneous catalyst shows induction behavior, indicating a transformation of the active site. EXAFS analysis of the as-synthesized material reveals that it contains Cr^(III) sites, supposedly coordinated by two oxygen ligands from the silica lattice and one chloride ligand abstracted from the chlorinated solvent during the synthesis (Scheme 9c).^[207]



Scheme 11. Intermediates in the reaction of $(\equiv\text{SiO})_3\text{Ta}$ with ethylene leading to polyethylene and 1-hexene.

Tantalum and zirconium hydrides supported on silica-alumina convert 2-butenes mostly into dimers, Zr catalyst being more active and selective (5300 TON *vs.* 4400 for Zr and Ta, respectively).^[214] Minor amounts (<5% for Zr and 20% for Ta) of pentenes, hexenes and heptenes (products of metathesis) were observed as byproducts. The proposed dimerization mechanism involves isomerization of 2-butenes to 1-butene *via* insertion/ β -elimination, followed by 1-butene insertion into Zr–sBu bond. β -Elimination of the resulting C₈ alkyl closes the catalytic cycle. (Scheme 12).^[214]



Scheme 12. Proposed mechanism for 2-butene dimerization on zirconium hydride surface species.

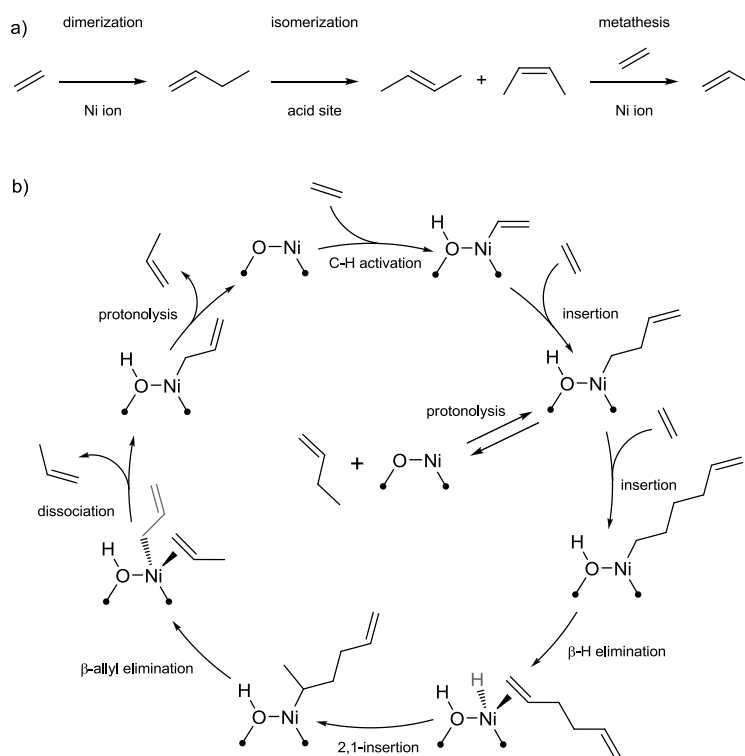
Discussion above shows that while homogeneous catalysts for olefin oligomerization are understood better than their heterogeneous analogs, some immobilized catalysts show better performance.

5. Direct Homologation of Ethylene to Propylene

The direct conversion of ethylene to propylene (ETP reaction) was observed in the early 1970s when contacting $\text{Mo}(\text{CO})_6$ supported on alumina with ethylene at 165 °C in a static reactor.^[215] Under these conditions ethylene conversion to propylene reaches 19% with minor amounts of butenes as the only side products. The ETP process was later reported on reduced silica-supported molybdena $\text{MoO}_3/\text{SiO}_2$.^[216] This catalyst features a long (*ca.* 90 min) induction period at 200 °C unless H_2 is added.^[217] Magnesia-supported $\text{Fe}_3(\text{CO})_{12}$ after decarbonilation also catalyzes the ETP reaction as well converting ethylene to propylene at 170 °C with 70% selectivity, albeit with a very low conversion (1%).^[218] Other products were methane, 1-butene, *cis*- and *trans*-2-butenes. Little is known about the nature of the active site(s) on these Fe and Mo-based catalysts and the actual mechanism of ethylene to propylene conversion; proposed reaction intermediates include metallocarbenes.^[218]

In the past decade the ETP conversion was also reported on Ni-based mesoporous materials such as MCM-41^[179, 219-220] or its aluminum-doped analog.^[221-222] Ni ions loaded into MCM-41 *via* an ion-exchange method afforded 55% ethylene conversion at 400 °C in a flow reactor with selectivity to propylene and butenes of 54 and 35%, respectively.^[222] The necessity to co-feed steam to ethylene is a limitation of this system that can compromise the long-term stability of MCM-41. However, incorporating aluminum into Ni-MCM-41 material not only increases the catalytic activity but also eliminates the requirement of co-feeding steam.^[222] The optimal Si/Al ratio was 60; higher amounts of Al lead to lower ethylene conversion and propene selectivity. Spectroscopic evidence points to the formation of a 2:1 nickel phyllosilicate phase containing 5- and 6-membered Si–O rings with tri- and tetra-coordinated $\text{Ni}^{(\text{II})}$ sites in these Ni-MCM-41 catalysts.^[223] The proposed mechanism for ETP on Ni sites includes three steps: i) ethylene dimerization to 1-butene,

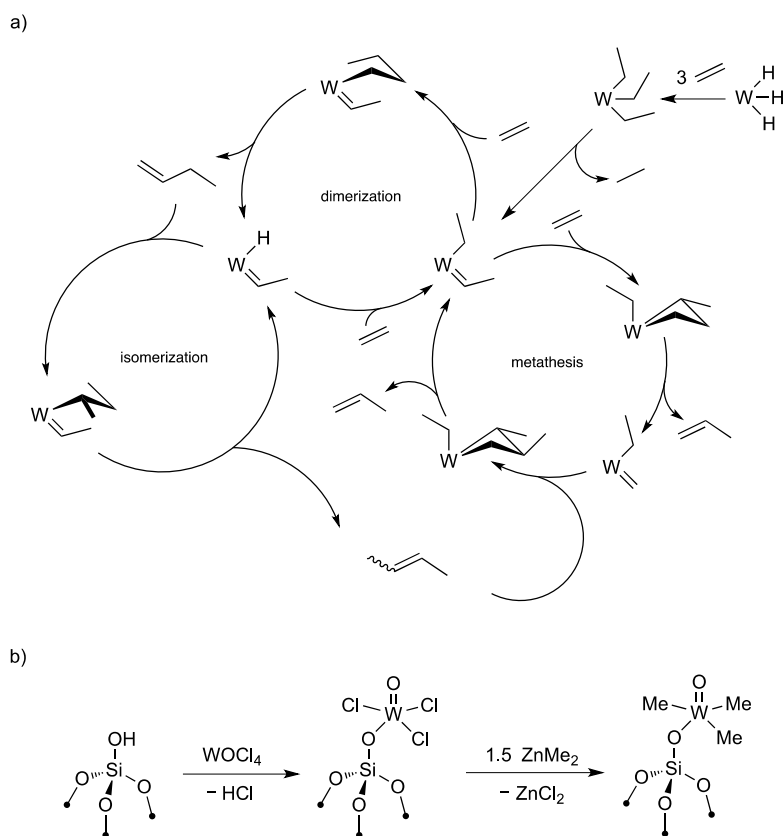
well-known for nickel sites,^[171] ii) isomerization of 1-butene to a mixture of 2-butenes, where both acidic sites of MCM-41 and nickel sites might be catalytically relevant, and iii) an olefin metathesis step between ethylene and 2-butenes on Ni sites giving propene^[219] (Scheme 13a). However, there is currently no unequivocal evidence that nickel can catalyze olefin metathesis. An alternative mechanism includes C–H activation of ethylene over a Ni–O bond followed by an insertion of two ethylene molecules into a Ni–vinyl bond, chain isomerization *via* β -H elimination/2,1-insertion, and β -allyl elimination to form one molecule of propene; the second C₃H₆ molecule is formed by the protonolysis of a Ni–allyl bond by a Si-(μ -OH)-Ni proton (Scheme 13b). This mechanism implies that propene is formally not a secondary product derived from butene.



Scheme 13. a) Postulated mechanism for the ETP reaction on Ni-MCM-41; b) Proposed alternative mechanism for the ETP on Ni active sites.

A recent and probably the best understood catalyst for ETP is the alumina-supported tungsten hydride (see also Section 7.3.2.3). $\text{WH}_3/\text{Al}_2\text{O}_{3-500}$ converts ethylene to propylene

at 150 °C in a continuous-flow reactor with a remarkable selectivity of 95%, reaching TON of 1120 after 120 h on stream. The selectivity in butenes remains below 4.5%, while higher olefins are present only in trace amounts (<0.5%).^[224] The proposed reaction mechanism involves a tandem of ethylene dimerization into 1-butene, isomerization of 1-butene into 2-butenes, and ethylene/2-butenes cross-metathesis (Scheme 14a). The catalyst deactivates forming long-chain alkyl intermediates due to the multiple ethylene insertion into W-alkyl bonds.^[225] More recently another W-based ETP catalyst was prepared from ZnMe₂ and silica-supported WOCl₄, which yields (≡SiO)W(=O)(CH₃)₃ catalyst precursor (Scheme 14b).^[226] The results in a static reactor at 150 °C suggest that this catalyst has higher activity and selectivity compared to other silica-supported organometallic complexes. Similarly to WH₃/Al₂O₃₋₅₀₀ described above, the proposed mechanism involves formation of W carbene-hydride active species.^[226]



Scheme 14. a) Proposed mechanism for the ETP reaction on $\text{WH}_3/\text{Al}_2\text{O}_3$. b) Synthesis of $(\equiv\text{SiO})\text{W}(=\text{O})\text{Me}_3$ surface species.

6. Alkene Polymerization

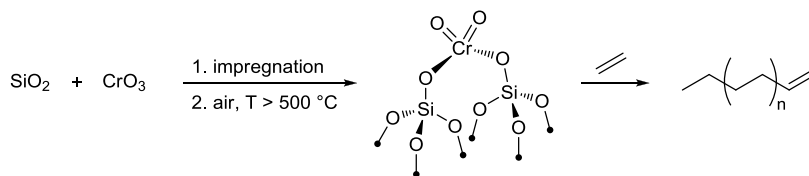
6.1. Supported Cr Polymerization Catalysts

6.1.1. Industrial and Mechanistic Background

6.1.1.1. Phillips and Union Carbide Catalysts

In 1951 Hogan and Banks at Phillips Petroleum discovered that Cr oxides supported on silica ($\text{CrO}_3/\text{SiO}_2$) are active in the polymerization of ethylene.^[227-228] The associated process produces a large proportion of world's high-density polyethylene (HDPE).^[8, 229-230] The Phillips catalyst is typically prepared by introducing a Cr precursor, usually CrO_3 or $\text{Cr}(\text{OAc})_3$, to silica and calcining at temperatures above $500\text{ }^\circ\text{C}$. The calcined material is active in ethylene polymerization in the absence of a cocatalyst or activator, though an induction period is observed under reaction conditions (Scheme 15). Although the Phillips

catalyst does not require a cocatalyst, AlEt_3 or BEt_3 enhance activity, shorten the induction period,^[231-234] tend to broaden the molecular weight distribution, and increase the amount of branching in the polymer.^[231-232, 235-236]



Scheme 15. Ethylene polymerization on the Phillips catalyst.

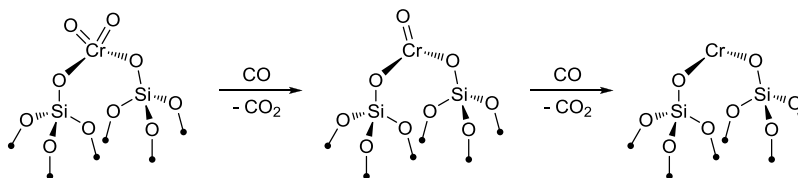
The support has a profound effect on the kinetics of polymerization and the polymer properties.^[8, 229] CrO_3 on silica-titania ($\text{CrO}_3/\text{SiTiO}_x$) has a shorter induction period and higher polymerization rates than $\text{CrO}_3/\text{SiO}_2$. The polymer has a broader molecular weight distribution and higher long-chain branch levels than the polymer produced with $\text{CrO}_3/\text{SiO}_2$.^[234, 236-239] $\text{CrO}_3/\text{Al}_2\text{O}_3$ is less active than $\text{CrO}_3/\text{SiO}_2$ in ethylene polymerization, but $\text{CrO}_3/\text{Al}_2\text{O}_3$ can produce ultra-high molecular weight polymer. Chromium sites supported on aluminum phosphate (AlPO_4) react with ethylene without an induction period but deactivate rapidly.^[240] Compared to $\text{CrO}_3/\text{SiO}_2$, $\text{CrO}_3/\text{AlPO}_4$ gives polymer with a broader molecular weight distribution.^[241]

Another well-known chromium-based heterogeneous polymerization catalyst is $\text{Cp}_2\text{Cr}/\text{SiO}_2$ developed by Union Carbide.^[242-243] Similarly to the Phillips catalyst, it displays high activity in ethylene polymerization at low temperature and pressure and does not require a cocatalyst. The nature of the active species remains unknown.^[244-245] Noteworthy, this is likely the first example of an industrial catalyst prepared *via* SOMC.

6.1.1.2. Active Sites in the Phillips Catalyst

The catalytic induction period implies that the high valent Cr sites are converted to an active species in the presence of ethylene. Many studies focused on the characterization of active sites in the Phillips catalyst.^[9, 246] The initial $\text{CrO}_3/\text{SiO}_2$ contains predominantly

Cr^(VI) dioxo surface complexes ($\equiv\text{SiO}$)₂Cr(=O)₂ (Scheme 16),^[247-250] although small amounts of EPR active Cr sites are also present.^[251-253] In the presence of ethylene, the Cr^(VI) dioxo is reduced to Cr^(II) sites as the major surface species,^[254-255] and a small amount of Cr^(III) sites.^[250, 256-257] Reduction of the metal sites can be also carried out by the reaction with CO.^[258-263] The reduced Cr sites are more readily activated, indicating that some of the sites generated by CO reduction are active. Detailed studies showed that this reduced material contains mostly Cr^(II) sites.^[258] However, <10% of the Cr sites are active in catalysis, this being a major challenge in determining the true active site structures in these catalysts.^[228, 264-265]



Scheme 16. Stepwise reduction of Cr^(VI) to Cr^(IV) and Cr^(II).

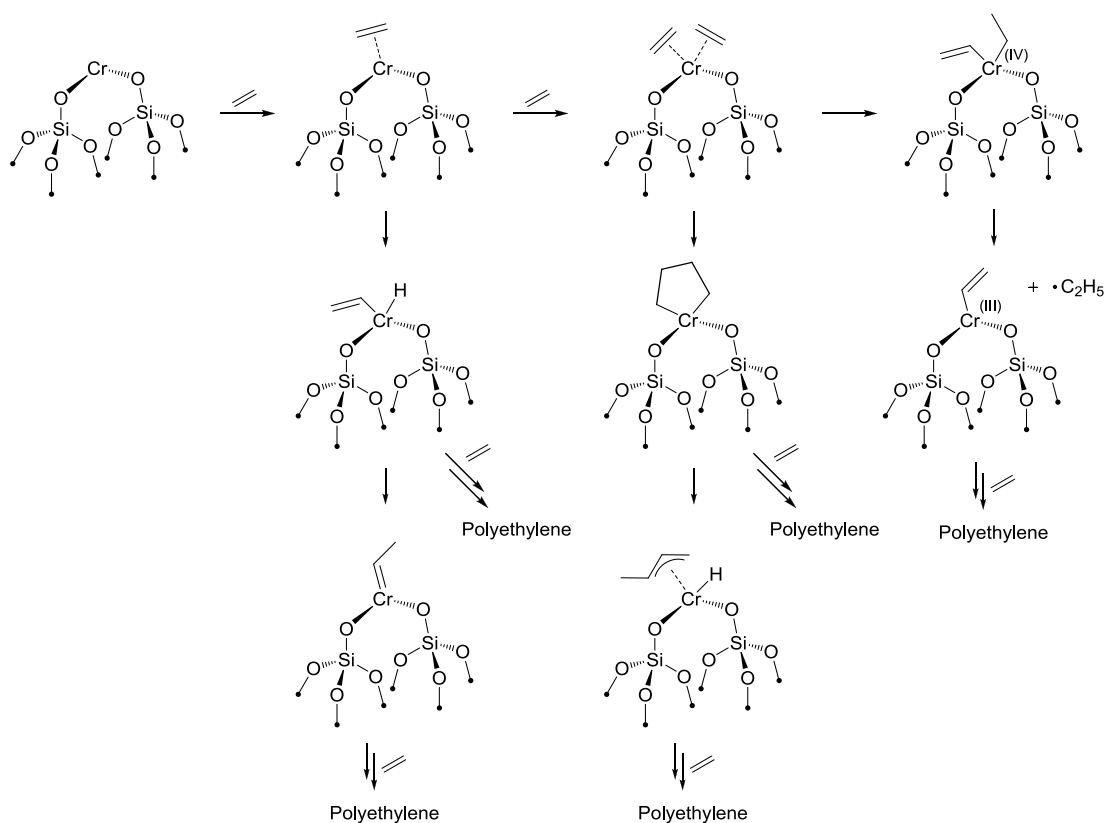
Recent spectroscopic studies on CrO₃/SiO₂ monoliths are consistent with the data discussed above; in the presence of ethylene the Cr^(VI) dioxo reacts in a stepwise manner to form a Cr^(IV) monoxo, and then an isolated Cr^(II) site shown in Scheme 16.^[266-267] However, the Cr^(II) sites further evolve to Cr^(III) at longer reaction times.^[267-268] The formation of Cr^(III) active sites is consistent with earlier reports showing that Cr^(III) salts supported on silica,^[269] or well-defined Cr^(III) silicates discussed below,^[270-271] are active polymerization catalysts.

6.1.1.3. Chain Growth in the Phillips Catalyst

The Phillips catalyst is unique because the first Cr–C bond is not present in the precatalyst and does not originate from an alkylating cocatalyst. In the presence of ethylene, the reduced Cr^(II) site was proposed to form Cr^(IV) alkyls that could coordinate and insert ethylene (Scheme 17).^[260-263] For example, coordination of ethylene to ($\equiv\text{SiO}$)₂Cr

forms $(\equiv\text{SiO})_2\text{Cr}(\text{C}_2\text{H}_4)$ that can activate a C–H bond in ethylene to form the $\text{Cr}^{(\text{IV})}$ vinyl-hydride $(\equiv\text{SiO})_2\text{Cr}(\text{H})(\text{vinyl})$ that can initiate polymerization by insertion of ethylene in either the Cr–vinyl or the Cr–H bond.^[272] It could also isomerize to $\text{Cr}^{(\text{IV})}$ alkylidene $(\equiv\text{SiO})_2\text{Cr}(\text{=CHMe})$ which could propagate polymer growth through a Green-Rooney mechanism.^[259, 273-280] Another possibility is the oxidative coupling of ethylene on a $\text{Cr}^{(\text{II})}$ site to form a $\text{Cr}^{(\text{IV})}$ metallacyclopentane (Scheme 17)^[262, 281] that can grow a polymer by ring expansion^[282] or by β -H elimination to form a $\text{Cr}^{(\text{IV})}$ allyl-hydride $(\equiv\text{SiO})_2\text{Cr}(\text{H})(\eta^3\text{-allyl})$ that is able to insert ethylene and start polymer growth.^[280] However, computational studies on cluster models for $(\equiv\text{SiO})_2\text{Cr}$ show that polymerization on $\text{Cr}^{(\text{IV})}$ centers, *via e.g.* metallacyclic or Rooney-Green mechanisms, is not viable, because chain propagation is disfavored due to a weak affinity of $\text{Cr}^{(\text{IV})}$ for ethylene coordination and high activation barriers associated with ethylene insertion.^[283-285]

As mentioned above, the $\text{Cr}^{(\text{II})}$ sites of the Phillips catalyst evolve to $\text{Cr}^{(\text{III})}$ sites. The conversion of $\text{Cr}^{(\text{II})}$ to $\text{Cr}^{(\text{III})}$ has been proposed to take place *via* a radical mechanism based on DFT calculations using small cluster models,^[286] where $(\equiv\text{SiO})_2\text{Cr}(\text{C}_2\text{H}_4)_2$ is converted into a $\text{Cr}^{(\text{IV})}$ ethyl-vinyl species $(\equiv\text{SiO})_2\text{Cr}(\text{C}_2\text{H}_5)(\text{vinyl})$ involving an endoergic spin crossing from the quintet to triplet state ($\Delta G = 13.7 \text{ kcal mol}^{-1}$) followed by a concerted H-atom transfer through an overall large energy span of $+36.0 \text{ kcal mol}^{-1}$ (Scheme 17). It has been proposed that the reversible binding of two siloxane bridges to Cr promotes the conversion of this intermediate into a $\text{Cr}^{(\text{III})}$ vinyl species with the concomitant loss of an ethyl radical with an activation barrier of $11.3 \text{ kcal mol}^{-1}$. Without prior coordination of two siloxane bridges, the overall free energy barrier for Cr–C bond homolysis was calculated to be a very large value of $50.0 \text{ kcal mol}^{-1}$.



Scheme 17. Proposed intermediates in ethylene polymerization starting from Cr^(II) sites and involving oxidation to Cr^(IV) sites.

Several computational studies on active site cluster models for the Phillips catalyst showed that chain propagation is energetically favorable for monoalkyl Cr^(III) sites in contrast to Cr^(IV) sites. These studies showed that ethylene insertion into the Cr–C bond of monoalkyl Cr^(III) sites is associated with activation barriers of *ca.* 13–18 kcal mol⁻¹, which allows the fast propagation observed experimentally for the Phillips catalyst.^[283-285]

6.1.2. Well-Defined Cr Sites on Oxides

6.1.2.1. Preamble

The discussion above shows that several Cr^(II) initiation mechanisms are possible, and that high-energy pathways to form Cr^(III) sites may also be viable. Resolution of these mechanistic scenarios would be aided by a model system containing a high quantity of

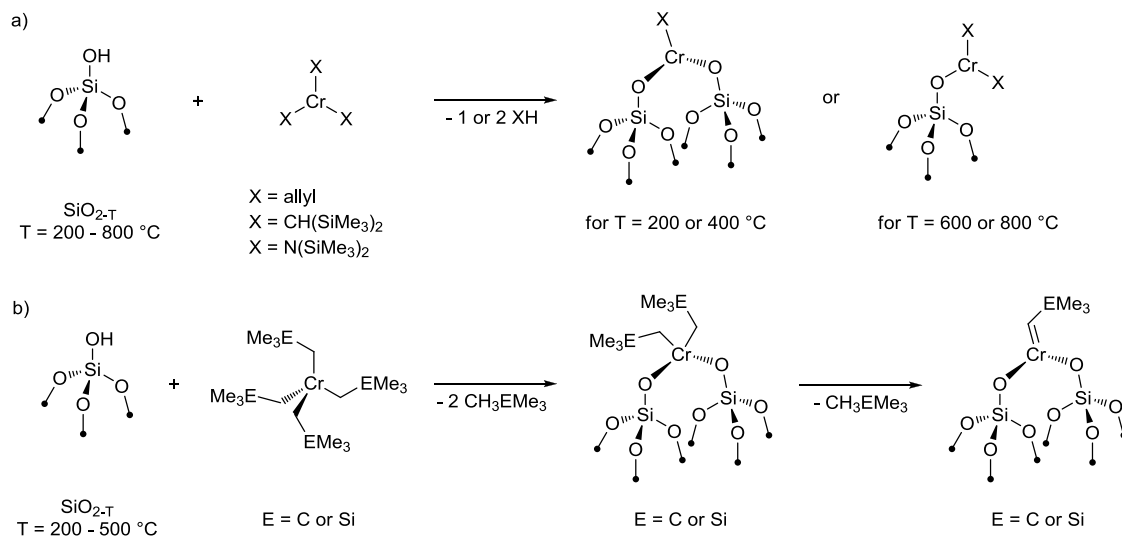
active sites, which could be studied in more detail. The use of CrO_2Cl_2 or related chromates with silica were investigated in order to obtain well-defined $\text{Cr}^{(\text{VI})}$ dioxo surface species.^[287-292] Contacting the $\text{Cr}^{(\text{VI})}$ containing materials with ethylene forms active species and shows similar behavior as observed in the Phillips catalyst.^[288, 290]

$\text{Cr}^{(\text{II})}$ and $\text{Cr}^{(\text{III})}$ salts supported on dehydroxylated silica without exposure to air nor to high temperature calcination steps were investigated.^[269] Optical spectroscopy of these materials confirmed that the $\text{Cr}^{(\text{II})}$ or $\text{Cr}^{(\text{III})}$ oxidation state was conserved in the grafting step. Exposing these materials to ethylene and monitoring the pressure drop showed that $\text{Cr}^{(\text{II})}$ containing materials were inactive, and that $\text{Cr}^{(\text{III})}$ containing materials were active, in the polymerization of ethylene. These results are probably the first studies suggesting that $\text{Cr}^{(\text{III})}$ sites are active in ethylene polymerization.^[269]

6.1.2.2. Well-Defined Organometallic Cr Sites on Silica

The reaction of organochromium complexes with dehydroxylated silica forms well-defined Cr sites that have been proposed as models of the Phillips catalyst active sites. The well-defined catalysts shown in Scheme 18 contain a Cr–C bond and polymerize ethylene. For example, $\text{Cr}(\text{allyl})_3$ reacts with silica to form $(\equiv\text{SiO})_2\text{Cr}(\text{allyl})$ or $(\equiv\text{SiO})\text{Cr}(\text{allyl})_2$ depending on the calcination temperature of the silica support (Scheme 18a).^[20, 23-24, 293-294] In the presence of ethylene, these materials produce high-molecular weight polyethylene as well as a distribution of ethylene oligomers if the support is treated at higher calcination temperatures. $\text{Cr}(\text{CH}(\text{SiMe}_3)_2)_3$ and $\text{Cr}(\text{N}(\text{SiMe}_3)_2)_3$ react with silica to form $(\equiv\text{SiO})_n\text{Cr}(\text{CH}(\text{SiMe}_3)_2)_{3-n}$ and $(\equiv\text{SiO})_n\text{Cr}(\text{N}(\text{SiMe}_3)_2)_{3-n}$ ($n = 1$ or 2), respectively (Scheme 18a).^[295-297] $(\equiv\text{SiO})\text{Cr}(\text{CH}(\text{SiMe}_3)_2)_2$ polymerizes ethylene to produce HDPE with a broad molecular weight distribution ($\text{Đ} = 20.0$) at 100 °C and 1.4 MPa ethylene partial pressure without activator. In contrast, $(\equiv\text{SiO})\text{Cr}(\text{N}(\text{SiMe}_3)_2)_2$ is active in ethylene polymerization

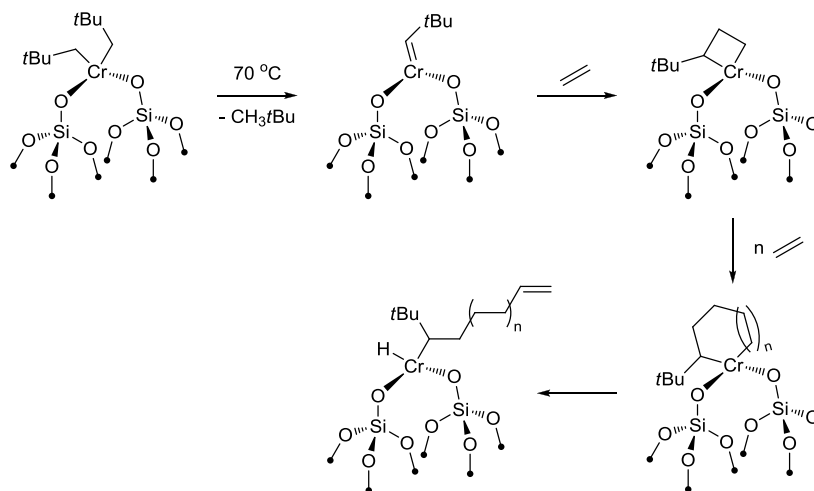
only in the presence of isobutyl-modified methylalumoxane or isobutylalumoxane as cocatalyst yielding polymer with lower molecular weights and broader molecular weight distributions ($\bar{M}_w = 49.3$) than $(\equiv\text{SiO})\text{Cr}(\text{CH}(\text{SiMe}_3)_2)_2$.



Scheme 18. a) Reaction of homoleptic CrX_3 ($X = \text{allyl}, \text{CH}(\text{SiMe}_3)_2, \text{N}(\text{SiMe}_3)_2$) with silica calcined between 200 and 800 °C. b) Grafting of $\text{Cr}(\text{CH}_2\text{EMe}_3)_4$ ($E = \text{C or Si}$) on silica and its evolution to surface alkylidene.

$\text{Cr}(\text{CH}_2\text{EMe}_3)_4$ ($E = \text{C or Si}$) reacts with partially dehydroxylated silica to generate $(\equiv\text{SiO})_2\text{Cr}(\text{CH}_2\text{EMe}_3)_2$ (Scheme 18b). Heating $(\equiv\text{SiO})_2\text{Cr}(\text{CH}_2\text{EMe}_3)_2$ to 70 °C or 150 °C results in the elimination of 1 equiv of the corresponding alkane per Cr, suggesting the formation of $(\equiv\text{SiO})_2\text{Cr}(\text{=CHEMe}_3)$ through α -H abstraction.^[278-279, 298-301] The putative $(\equiv\text{SiO})_2\text{Cr}(\text{=CHEMe}_3)$ species is proposed to react with ethylene to form oligomers and polymers (Scheme 19). The polymerization of ethylene on $(\equiv\text{SiO})_2\text{Cr}(\text{=CH}t\text{Bu})$ was proposed to take place *via* [2+2] cycloaddition to form a chromacyclobutane that can insert ethylene to form expanded metallacycles. An expanded metallacycle can then undergo β -hydride elimination to form a Cr alkyl-hydride surface species that propagates polymer growth.^[299] This result is consistent with kinetic isotope experiments giving $k(\text{C}_2\text{H}_4)/k(\text{C}_2\text{D}_4) = 1.29 \pm 0.05$;^[299] a small kinetic isotope effect that is inconsistent with

rate-limiting 1,3-hydrogen migration that is expected in a Green-Rooney propagation mechanism. This result is also consistent with the presence of some oligomers present under polymerization conditions. However, recent computational studies have indicated that the reaction of alkylidene with ethylene and the subsequent ethylene polymerization is not favored.^[285-286]

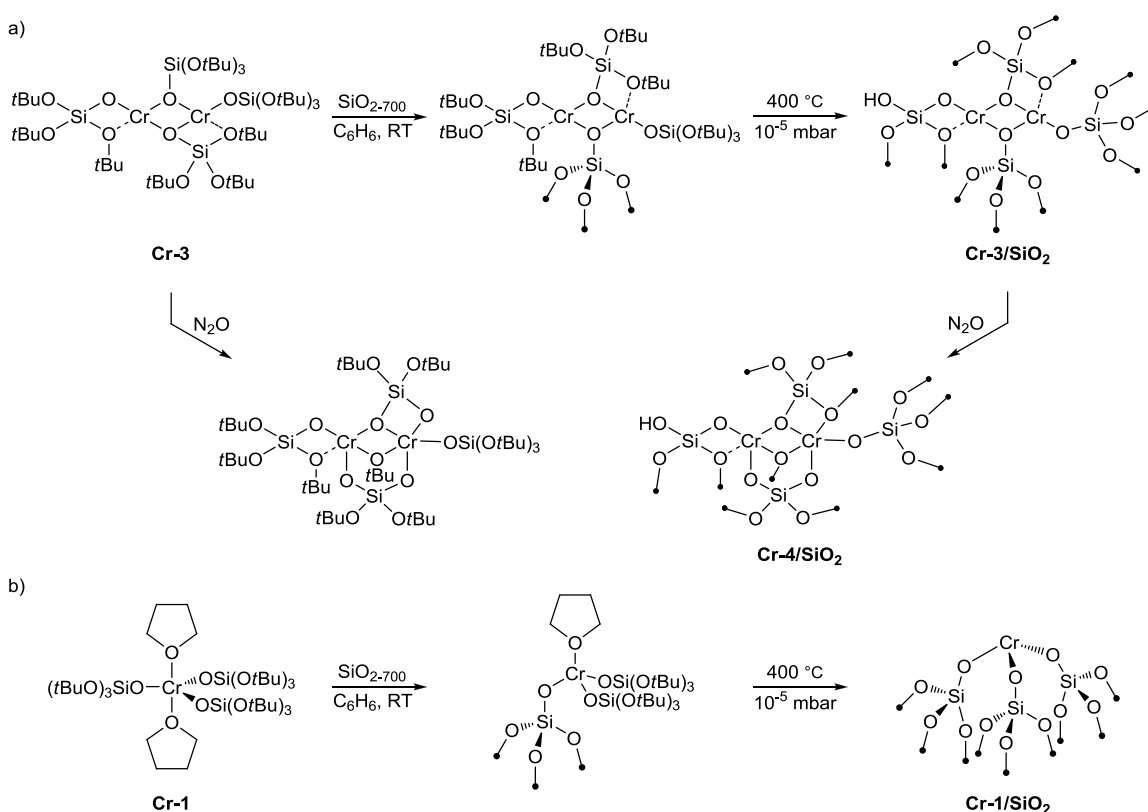


Scheme 19. Proposed mechanism of ethylene polymerization on putative $\text{Cr}^{\text{(IV)}}$ alkylidene supported on silica.

6.1.2.3. Well-Defined Cr Silicates

The examples discussed above show that $\text{Cr}^{\text{(III)}}$ or $\text{Cr}^{\text{(IV)}}$ sites containing Cr–C bonds can initiate ethylene polymerization. However, the Phillips catalyst does not contain a preformed Cr–C bond. Cr sites containing only Cr–O bonds would be a better model of the Phillips catalyst. Using SOMC combined with the TMP approach^[66-67] (see Schemes 1b and 2), dinuclear $\text{Cr}^{\text{(II)}}$ silicate **Cr-3/SiO₂** free of any organic ligands (Scheme 20a) can be obtained from grafting of of $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2]_2$ (**Cr-3**) on partially dehydroxylated silica followed by thermal treatment under vacuum.^[270] Treating **Cr-3/SiO₂** with N_2O , which is known to activate the CO-reduced Phillips catalyst,^[302] forms the $\text{Cr}^{\text{(III)}}$ dimer **Cr-4/SiO₂**. The structures of surface sites are confirmed by XAS,^[270] in particular through comparison with the corresponding molecular analogs.

Cr-3/SiO₂ has hardly any ethylene polymerization activity (1.6 kg_{PE} mol_{Cr}⁻¹ h⁻¹) by comparison with **Cr-4/SiO₂** containing exclusively Cr^(III) sites (19 kg_{PE} mol_{Cr}⁻¹ h⁻¹ at 300 mbar ethylene pressure, 107 kg_{PE} mol_{Cr}⁻¹ h⁻¹ at 6 bar ethylene pressure). **Cr-3/SiO₂** contains a small fraction of Cr^(III), which could explain its activity and points to the inactivity of Cr^(II) sites. Worthy of note, polymerization with **Cr-4/SiO₂** takes place without an induction period in contrast to the Phillips catalyst, while the broad molecular weight distribution ($\bar{M} = 9.4$) and few branches resemble what is observed for Phillips catalyst.



Scheme 20. a) Grafting, thermal treatment and N₂O oxidation of [Cr(OSi(O*t*Bu)₃)₂]₂ (**Cr-3**). b) Grafting and thermal treatment of Cr(OSi(O*t*Bu)₃)₃(THF)₂ (**Cr-1**).

Mononuclear Cr^(III) silicates (**Cr-1/SiO₂**, Scheme 20b), prepared by grafting Cr(OSi(O*t*Bu)₃)₃(THF)₂^[303] (**Cr-1**) onto silica followed by thermolysis under vacuum,^[271] also polymerize ethylene with activity similar to **Cr-4/SiO₂** (15 kg_{PE} mol_{Cr}⁻¹ h⁻¹ at 300 mbar ethylene pressure, 104 kg_{PE} mol_{Cr}⁻¹ h⁻¹ at 6 bar ethylene pressure) and generates a polymer with similar properties.

CO adsorption studies combined with DFT calculations using cluster models indicated the presence of two different Cr^(III) sites on the surface of **Cr-1/SiO₂**, the second being identified as four-coordinate Cr^(III) species ($\equiv\text{SiO}$)₃Cr($\equiv\text{SiOSi}\equiv$) arising from additional siloxane bridge coordination.^[271] This is in agreement with poisoning experiments that showed *ca.* 60% of Cr sites in **Cr-4/SiO₂** and **Cr-1/SiO₂** can initiate polymerization, suggesting that four-coordinate sites are inactive.^[271]

Overall, both **Cr-4/SiO₂** and **Cr-1/SiO₂** polymerize ethylene without an induction period. The polymers produced by **Cr-4/SiO₂** and **Cr-1/SiO₂** contain unsaturated end-groups from ¹H NMR analysis, and in both cases, rather broad polydispersities are obtained. The broad molecular weight distribution is surprising because of the expected “single-site” behavior of well-defined catalysts, which should produce polymers with $\text{Đ} \leq 2$. Overall, these results show that well-defined Cr^(III) silicates lacking a preformed Cr–C bond are active in polymerization of ethylene to form HDPE, and that Cr^(II) silicates are much less active in polymerization.

Initiation and Polymerization Mechanism. XANES shows that the oxidation state of Cr^(III) in **Cr-4/SiO₂** and **Cr-1/SiO₂** is conserved after ethylene polymerization.^[270, 271] A mechanism consistent with conservation of Cr^(III) during catalysis is the heterolytic activation of a C–H bond of ethylene across a Cr–O bond. Heterolytic activation of C–H and H–H bonds is common on oxides.^[88-89, 91-92, 96, 304-308] For example, Al₂O₃ surface sites in dehydroxylated alumina activate the C–H bond of methane at low temperatures.^[305-306] A proposed catalytic cycle is shown in Figure 1a. Coordination of ethylene to a Cr^(III) site results in heterolytic activation of a C–H bond to form a Cr^(III) vinyl species. Cr–vinyl inserts ethylene, and polymer continues to grow by a Cossee-Arlman mechanism. Chain termination is the microreverse of C–H activation. This mechanism was studied by DFT calculations using cluster model of a ($\equiv\text{SiO}$)₃Cr^(III) site shown in Figure 1c.^[271] The rate

limiting activation of an ethylene C–H bond across the Cr–O bond has a calculated energy barrier of 36.6 kcal mol⁻¹ with a transition state typical for σ -bond metathesis (Figure 1d).^[309] Alternatively, initiation and chain growth can take place *via* ethylene insertion into the Cr–O bond through the formation of oxachromacycle followed by insertion in the Cr–C bond (Figure 1b).^[310] Chain termination can occur *via* H-abstraction. Both mechanisms are possible, the latter being particularly favored on strained sites, while both are competitive on less strained sites (*vide infra*). Other mechanisms involving the formation of Cr^(V) metallacyclopentane or vinyl-hydride (Figure 1e) from (\equiv SiO)₃Cr sites, with mechanisms similar to these proposed for Cr^(II) (Scheme 17) are unlikely. The transition states and products could not be located from Cr^(V) vinyl-hydride species, indicating that these reactions have high activation energies and form thermodynamically unstable products. This result is consistent with the disfavored 2-electron oxidation of Cr^(III) to Cr^(V).^[311]

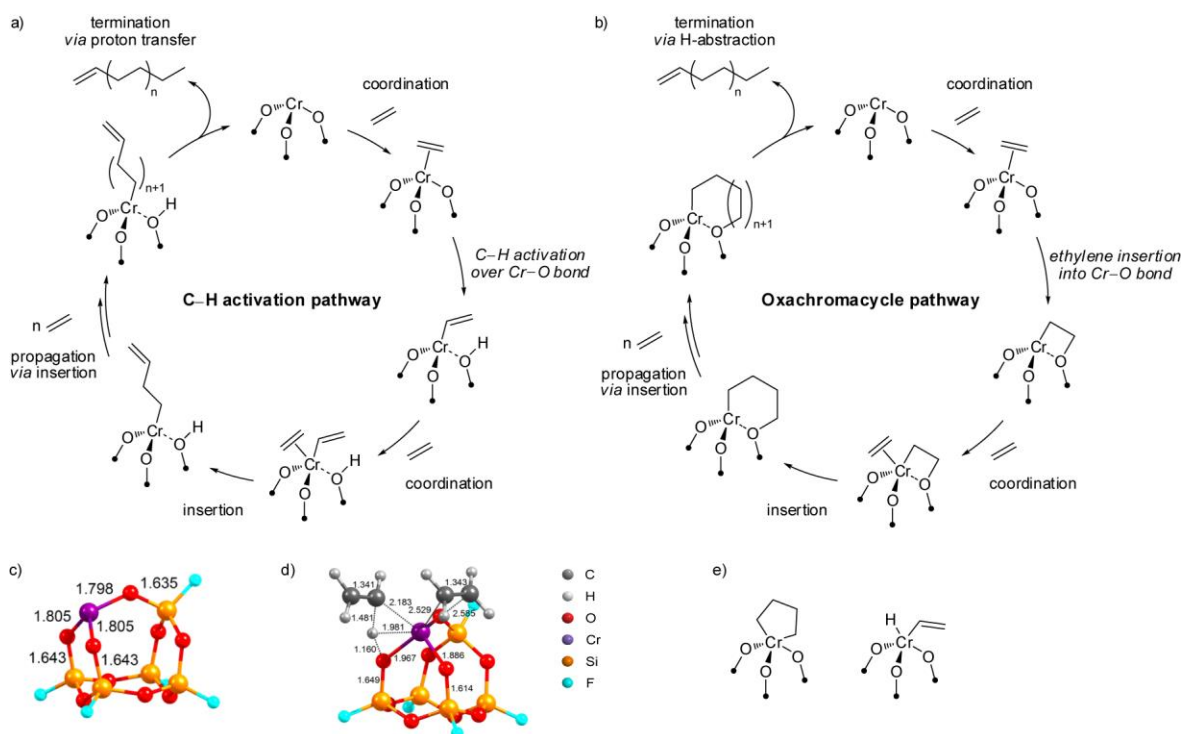
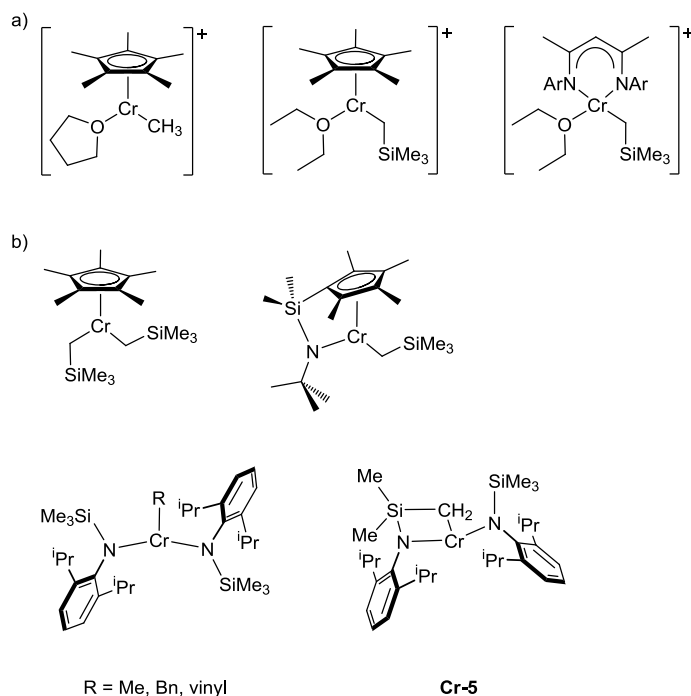


Figure 1. a) C–H activation and b) oxachromacycle mechanisms of ethylene polymerization on isolated (\equiv SiO)₃Cr^(III) sites. c) Cluster model of an isolated (\equiv SiO)₃Cr^(III)

site used in DFT calculations (distances given in Å). d) C–H activation transition state. e) Schematic structures of Cr^(V) chromacyclopentane and vinyl-hydride species.

The proposed neutral Cr^(III) alkyl species (vinyl or oxachromacycle) could be considered unusual for ethylene polymerization because cationic Cr^(III) complexes are more common polymerization catalysts in solution. For example Cp^{*}CrMe(THF)⁺ and (nacnac)Cr(CH₂SiMe₃)(THF)⁺ are very active homogeneous catalysts for the polymerization of ethylene to make HDPE with high molecular weight and narrow dispersity (Scheme 21a).^{Theopold, 1998 #245} In addition, neutral Cr^(III) alkyl complexes are also competent to initiate ethylene polymerization in the absence of cocatalyst (Scheme 21b).^[312-315] For instance, neutral Cr^(III)–R species (R = methyl, benzyl, and vinyl) containing bulky amide ligands catalyze the polymerization of ethylene.^[316] These catalysts produce a broad molecular weight distribution ($\mathcal{D} = 38.4$) of ultra-high molecular weight polyethylene (UHMW-PE) together with C₈–C₁₄ oligomers. The oligomers were attributed to the formation of cyclometallated species **Cr-5** that is less selective for polymerization.



Scheme 21. Structures of a) cationic^[245, 313, 317-320] and b) neutral^[312-316] Cr complexes for the polymerization of ethylene.

Heterogeneity of Sites. Silica is amorphous, which would probably form a distribution of sites on the surface. Indeed, the polymer dispersity measurements range from 9.4 to 13.1 for polymerizations catalyzed by **Cr-4/SiO₂** and **Cr-1/SiO₂**. These values are far larger than the expected value of 2 for a single-site catalyst, indicating that **Cr-4/SiO₂** and **Cr-1/SiO₂** have multi-site behavior. While cluster models are typically used to calculate energy profiles and to evaluate reaction mechanisms, it is not ideal for an amorphous support resulting from high temperature treatment. Recently, models for amorphous silica surfaces have been developed, whose OH density are close to experimental findings for silica treated at high temperature,^[321] *i.e.* 1.1 OH nm⁻² for the model *vs.* 0.8 ± 0.1 OH nm⁻² for SiO₂₋₇₀₀ as determined experimentally. This model, which contains five different types of isolated ≡SiOH, can be used to generate five types of (≡SiO)₃Cr^(III) — by substitution of (≡SiO)₃SiOH with (≡SiO)₃Cr sites — (models **I-V**),^[310] two of which are shown in Figure 2 (**IV** and **V**). These five models with a total of 15 Cr–O

bonds display a broad range of Cr–O distances (1.79–1.90 Å) and Si–O–Cr bond angles (109.8–158.0°), illustrating the variation in local structure at chromium on the amorphous silica surface.

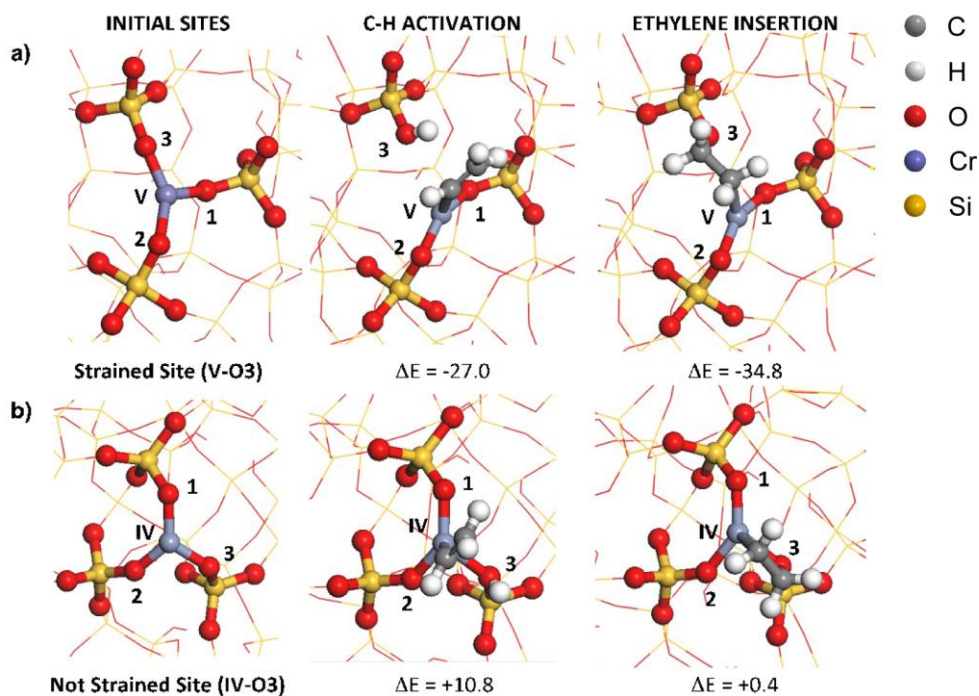


Figure 2. Representative models of $(\equiv\text{SiO})_3\text{Cr}^{\text{(III)}}$ sites on amorphous silica (left), and the corresponding intermediates after ethylene C–H bond activation across Cr–O(3) bond (center) and ethylene insertion into Cr–O(3) bond (right). a) Strained site (model V). b) Not strained site (model IV). The energies are given in kcal mol^{-1} and are with respect to the free system (bare model + ethylene).

These five different sites display a broad range of reactivity towards ethylene.^[310] For instance, coordination of ethylene is a favorable process with energies ranging from -18.4 to $-8.6 \text{ kcal mol}^{-1}$ illustrating the influence of the local coordination environment at $\text{Cr}^{\text{(III)}}$ on binding energy. Similarly, the C–H bond activation step to form $\text{Cr}^{\text{(III)}}$ vinyl species displays barriers ranging from $+25.5$ to $+41.3 \text{ kcal mol}^{-1}$ with respect to the corresponding Cr ethylene complexes and shows an even larger span of reaction energies varying from -54.3 to $+10.8 \text{ kcal mol}^{-1}$. The most exoergic reaction energies (-54 and $-27 \text{ kcal mol}^{-1}$) are associated with C–H activation across the Cr–O(2) or Cr–O(3) bonds in

model **V**, where the Cr–O bond lengths increase from 1.9 Å to the corresponding Cr···OH bond lengths of 4.7 or 3.2 Å (Figure 2a). These large increases of bond distances suggest a pronounced release of strain upon C–H activation. In general, sites associated with the most favorable reaction energies are also associated with low activation barriers (*e.g.* +26 kcal mol⁻¹ for Cr–O(3) site of model **V**, Figure 2a), and typically correspond to the formation of Cr vinyl complexes with an OH group far from the Cr center, suggesting more significant strain release. More endoergic C–H activation across the Cr–O(3) bond of model **IV** (+11 kcal mol⁻¹, Figure 2b) is associated with a higher activation barrier (+41 kcal mol⁻¹) and relatively small Cr–O bond length increase from 1.8 Å to 2.1 Å. These results illustrate how the energetics of C–H bond activation strongly depend on the local structure of the Cr^(III) site.

Initiation *via* ethylene insertion into a Cr–O bond follows similar trends: the most strained Cr^(III) sites are associated with a lower barrier to ethylene insertion. For instance, ethylene insertions into the Cr–O(2) or into the Cr–O(3) bond of model **V** are associated with the most exoergic reaction energies (–55 and –35 kcal mol⁻¹), and the Cr–O bond lengths increase from 1.9 Å to the corresponding Cr···OC bond lengths of 3.9 or 3.1 Å (Figure 2a). For less strained sites both C–H bond activation and ethylene insertion into a Cr–O bond are competitive, while the most strained sites favor ethylene insertion and oxachromacycle intermediate. It is likely that both pathways are operative and depend on which sites are generated in the calcination step and the operating conditions.^[310]

6.1.2.4. Relation between Well-Defined Cr^(III) Silicates and the Phillips Catalyst

With the recent development of Cr^(III) silicates as a possible model for Phillips catalysts, it is necessary to list the differences and the similarities between the two systems. As the Phillips catalysts, the well-defined Cr^(III) silicates polymerize ethylene without the

need of a cocatalyst, while they are both less active for the polymerization of propylene. Both systems produce high density PE with a broad molecular weight distribution. In sharp contrast, however, Cr^(III) silicates do not display any induction period and do not change oxidation state upon contact with ethylene, indicating that Cr^(III) sites are highly active for ethylene polymerization. Well-defined Cr^(III) sites, according to EXAFS analysis, nonetheless show high PE dispersity. This conflicting information can be reconciled if one takes into account that silica is amorphous, and thus is expected to lead to a distribution of sites and thereby a broad polymer distribution. In addition, computational studies indicate that strain generated by high temperature thermal treatment of the support clearly plays a role in the initiation step: the more strained the site, the more reactive. In fact, the Phillips catalyst is known to have a strong dependence on the calcination temperature; higher temperatures typically lead to higher polymerization activities reaching a maximum in activity for a treatment at *ca.* 925 °C, after which the silica support sinters.^[9, 322] These results suggest that the dependence of polymerization activity on calcination temperature could be related to the increasing strain of the Si–O–Cr bond. These studies also show that Cr^(III) sites can initiate polymerization through different initiation mechanisms (C–H activation *vs.* insertion of ethylene into the Cr–O bond), which could explain the complexity of the Phillips catalyst. All data show that insertion of ethylene in Cr^(III) alkyl sites is very favorable.

6.2. Ziegler-Natta Polymerization Catalysts and Related Supported Systems

6.2.1. Industrial and Mechanistic Background

6.2.1.1. Ziegler-Natta Catalysts

The discovery by Karl Ziegler that ethylene polymerizes in the presence of TiCl₃ and aluminum alkyls at atmospheric pressure and without external heating was a paradigm

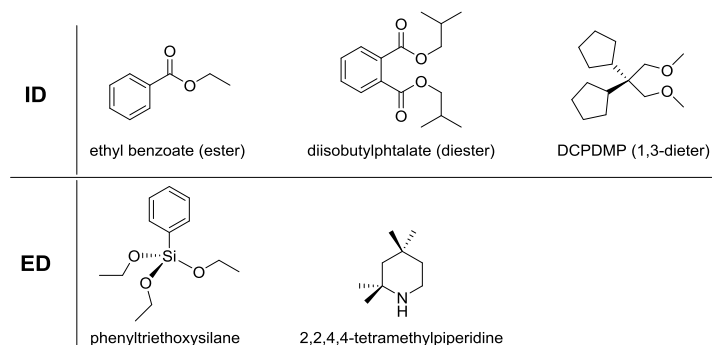
shift in the polymer industry. However, despite years of research, little is known about the nature of the active species in these systems.^[323-327] In 1954, a seminal contribution by Giulio Natta described the synthesis of isotactic polypropylene from the prochiral propylene,^[328-330] leading to a Nobel Prize in Chemistry shared with Ziegler.^[331-334] The 1st and 2nd generation Ziegler-Natta (ZN) catalysts are based on four different crystallographic forms of TiCl₃ (α , β , γ and δ) activated with diethylaluminum chloride (DEAC), δ -TiCl₃ leads to the highest activity towards olefin polymerization (Table 3).^[335] Addition of internal donors (an organic base, typically an amine or an ether) allows for the stereoselective propylene polymerization (the so-called 2nd generation of ZN catalysts), probably *via* the specific poisoning of unselective atactic sites. Nevertheless, the activity of 1st and 2nd generation ZN catalysts per mole of titanium is low with the only active centers residing at the surface of the TiCl₃ particles. One of the next breakthroughs was the immobilization of TiCl₄ on MgCl₂ particles which yielded highly active supported catalysts for the production of polyethylene and polypropylene (3rd generation). Addition of an ester as an internal donor to this catalyst also allows for stereoselective polymerization. Replacement of the ester by a diester or a diether as an internal donor corresponds to 4th and 5th generations ZN catalysts, respectively, which exhibit increasingly higher activities (Table 3). Unlike the Phillips catalyst, which relies on isolated metal sites (Section 6.1.1), the Ziegler-Natta catalysts are multicomponent systems that contain TiCl₄ and MgCl₂ as a support and require an alkylaluminum activator. The presence of internal and external donor (ID and ED) ligands allows empirical tuning of the stereoselectivity in the polymerization of α -olefins. Typically, the role of the ID is to enhance the surface area by avoiding the coagulation of MgCl₂ and to form isospecific sites in preference to non-stereospecific sites: the role of the ED is proposed to poison non-stereospecific sites and/or

to allow the conversion of non-stereospecific sites into isospecific ones.^[336] This catalyst formulation leads to the structural complexity of the active sites.

Table 3. Performances of the different generations of Ziegler-Natta catalysts in propylene polymerization. Typical examples of ID and ED are given below.^a

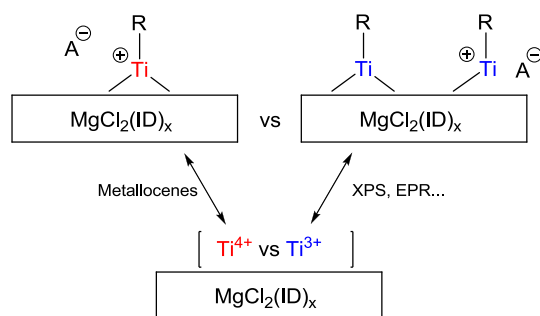
Generation	Composition	Activity (kg _{PP} g _{cat} ⁻¹)
1 st	δ-TiCl ₃ /0.33AlCl ₃ activated with DEAC	0.8–1.2
2 nd	δ-TiCl ₃ /amine or ether activated with DEAC	3–5
3 rd	TiCl ₄ /ester/MgCl ₂ activated with AlR ₃ (/ester)	5–10
4 th	TiCl ₄ /diester/MgCl ₂ activated with AlEt ₃ /silane	10–25
5 th	TiCl ₄ /diether/MgCl ₂ activated with AlEt ₃	25–35

^a 70 °C, 4 h, 0.7 MPa of propene, the polymerization tests being performed in suspension in hexane.



6.2.1.2. Active Sites in Ziegler-Natta Catalysts

ZN catalysts have been improved empirically over the years and are contribute significantly to the polymerization industry. However, the nature of the active site(s) still remains elusive (Scheme 22). The most accepted proposal is the formation of cationic Ti^(IV) alkyl species, in analogy to what is known in molecular organometallic chemistry for homogeneous metallocene catalysts.^[337-338] However, involvement of cationic or neutral Ti^(III) alkyl species cannot be ruled out at present (*vide infra*).



Scheme 22. Main hypotheses about the nature of the active sites of ZN catalysts: cationic Ti^{IV} and neutral/cationic Ti^{III} alkyl species.

Characterization of the Precatalysts. The most widely used support in ZN catalysis is MgCl_2 containing (110) and (104) terminations.^[339-340] The (110) surface contains four-coordinate Lewis acidic Mg sites, and the (104) surface contains five-coordinate Mg sites (Figure 3).^[341-353] The most advanced hybrid DFT methods that include dispersion corrections^[354-355] indicate that TiCl_4 selectively adsorbs on MgCl_2 (110) or equivalent faces: the interaction with the (104) faces leading to instable adducts.

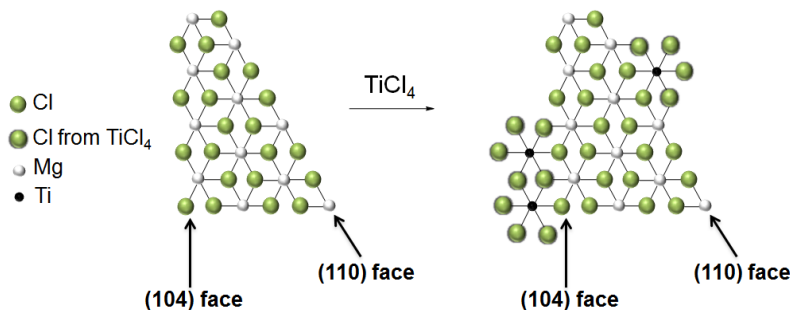
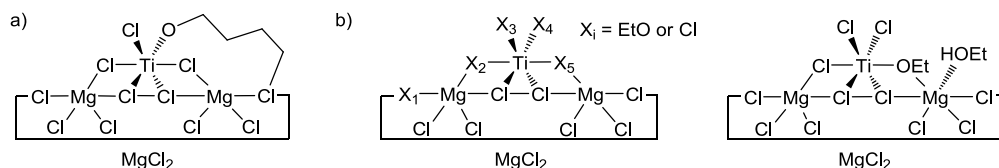


Figure 3. Interaction of TiCl_4 with the atomically flat (104) and (110) faces of MgCl_2 .

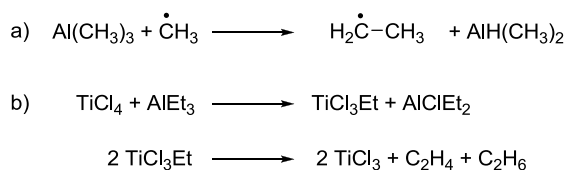
MgCl_2 used to prepare ZN catalysts often contains an additional ligand, such as THF or ethanol. Solid-state NMR studies of $\text{TiCl}_4/\text{MgCl}_2(\text{THF})_{1.5}$ ^[356-357] show that the THF ligand undergoes a Lewis acid ring opening to yield $\text{Ti}_5\text{Cl}_3(\text{O}(\text{CH}_2)_4\text{Cl})\text{MgCl}_x$ (Scheme 23a). Similar $\text{Ti}_5\text{Cl}_{3-y}(\text{OEt})_y(\text{MgCl}_x)$ species are also observed for $\text{TiCl}_4/\text{MgCl}_2(\text{EtOH})_{1.5}$ (Scheme 23b), where ethoxy groups are formed by deprotonation of ethanol.



Scheme 23. a) Major surface species on the precatalyst $\text{TiCl}_4/\text{MgCl}_2(\text{THF})_{1.5}$ and b) surface species on the precatalyst $\text{TiCl}_4/\text{MgCl}_2(\text{EtOH})_{1.5}$.

The Nature of Ti Sites after Activation. Structure determination of the active sites in $\text{TiCl}_4/\text{MgCl}_2/\text{L}$ after activation with alkylaluminum has been even more challenging. From what is known for the homogeneous metallocene catalysts, the active site has been proposed to be an electron-deficient and coordinatively unsaturated cationic $\text{Ti}^{(\text{IV})}$ alkyl species.^[336-338, 358-360] However, no direct spectroscopic evidence for cationic $\text{Ti}^{(\text{IV})}$ alkyl surface species is currently known. In contrast, $\text{Ti}^{(\text{III})}$ centers have already been evidenced.

TiCl_4 supported on MgCl_2 films epitaxially grown on Au surfaces reacts with AlEt_3 (TEA) to form an active catalyst containing titanium(III) alkyl species.^[361-363] When the contact time with TEA is extended, further alkylation or reduction to yield “ $\text{Ti}^{(\text{III})}\text{ClEt}_2$ ” and “ $\text{Ti}^{(\text{II})}\text{ClEt}$ ”, respectively, occurs. XPS and EPR analysis of model ZN catalysts on single-crystals of MgCl_2 shows that ethyl radicals are present on the catalyst surface during the activation with AlMe_3 (TMA) (Scheme 24a).^[364] In contrast, no radical is observed when using AlEt_3 as an activator, consistent with a disproportionation reaction (Scheme 24b), as previously suggested by indirect evidence.^[365-367]

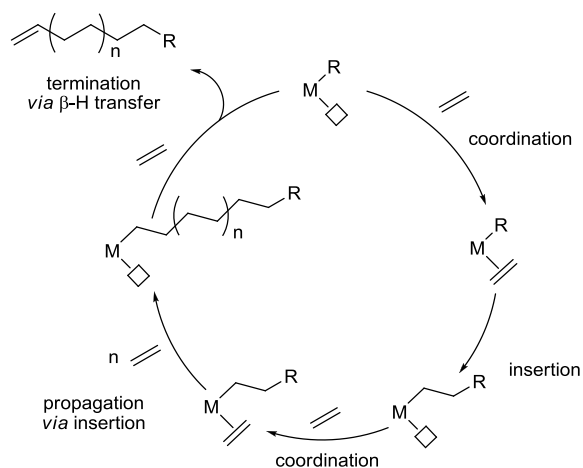


Scheme 24. a) Formation of experimentally observed ethyl radicals upon activation with AlMe_3 . b) Proposed disproportionation pathway towards the formation of $\text{Ti}^{(\text{III})}$ species upon activation with AlEt_3 .

The most recent studies on the 4th generation ZN catalysts, *i.e.* TiCl₄/dibutyl phthalate/MgCl₂ (Ti 2.0 wt%, dibutyl phthalate 8.9 wt%) activated with AlR₃ using advanced EPR methods have shown that activation leads to the formation of Ti^(III) sites.^[368-369] Two Ti^(III) sites were observed, consisting of isolated monomeric Ti^(III) chloro species. However, it is currently not known whether the actual active species, likely a Ti alkyl, corresponds to a Ti^(III) site. In addition, cationic Ti^(IV) sites are obviously EPR silent.

6.2.1.3. Homogeneous Metallocene Polymerization Catalysts

As the key role of organometallic intermediates in ZN polymerization was quickly recognized, an extensive search for organometallic complexes of early transition metals was undertaken to develop the corresponding homogeneous catalysts.^[20-21, 370] These efforts led to well-defined homogeneous catalysts based on metallocenes of group 3, 4, lanthanide and actinide metals that can be readily transformed into highly active cationic species *via* reaction with organoaluminum or other Lewis acidic reagents.^[329, 336-337, 359-360, 371-372] Isolation and crystallographic characterization of such cationic complexes aided the understanding of the mechanism of homogeneous olefin polymerization.^[338, 373] Another advancement was the discovery of methylaluminoxane (MAO)^[374] — a highly efficient cocatalyst that activates metallocenes by stepwise alkylation and alkyl abstraction reactions leading to cationic M^(IV) alkyls.^[338, 358, 360, 375-376] Classical Cossee–Arlman (coordination/insertion) mechanism was formulated in studies of these systems (Scheme 25).

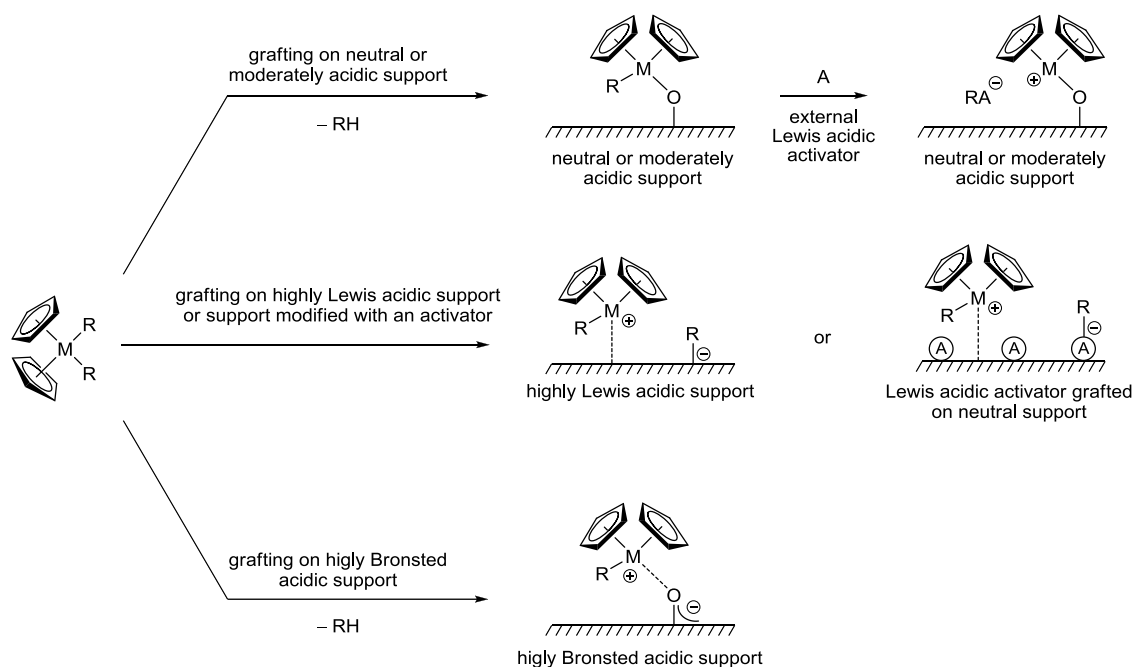


Scheme 25. Coordination/insertion mechanism of olefin polymerization.

6.2.2. Well-Defined Supported Metallocenes and Related Systems

6.2.2.1. Preamble

The first attempts to use organometallic complexes to generate supported polymerization catalysts appeared in 1970s.^[20-22, 24, 377-379] In this section, we will discuss supported single-site olefin polymerization catalysts based on perhydrocarbyl and metallocene d^0 early metal complexes, with the goal of describing the concepts rather than to be exhaustive, because many comprehensive reviews have appeared in this field.^[10-12, 360, 380-382]



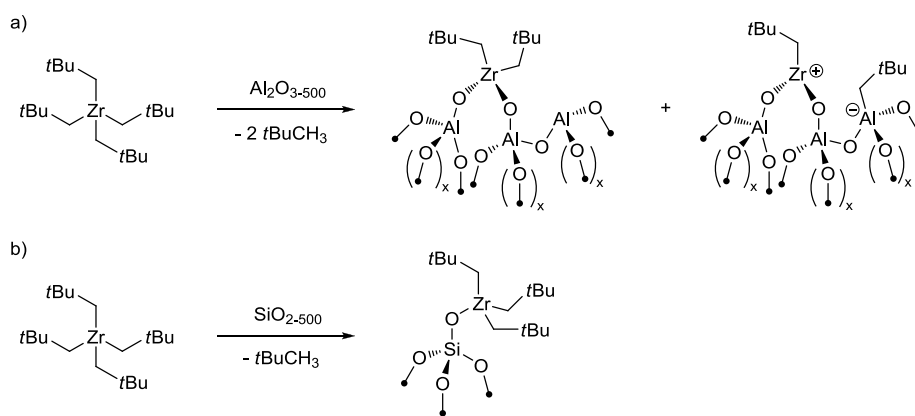
Scheme 26. Strategies to prepare active well-defined supported metallocene polymerization catalysts.

Strategies to prepare supported polymerization catalysts are schematically summarized in Scheme 26.^[46] Grafting of organometallic complexes onto highly Lewis acidic supports (MgCl_2 , dehydroxylated Al_2O_3 and $\text{SiO}_2\text{-Al}_2\text{O}_3$) generates cationic surface species *via* alkyl-abstraction by a Lewis acidic surface site (Section 6.2.2.2). These materials behave as single-component polymerization catalysts, *i.e.* do not require additional cocatalyst. Neutral covalently bonded surface species generated on neutral or moderately acidic supports (SiO_2 , MgO) display low catalytic activity unless activated with Lewis acidic reagents. The latter step gives rise to rather complex surface structures which are difficult to study and control. However, in certain cases well-defined cationic surface species were characterized in these systems when using stoichiometric amounts of strongly Lewis acidic activators such as $\text{B}(\text{C}_6\text{F}_5)_3$ (Section 6.2.2.2). Alternatively, the surface of the neutral support can be modified with an activator prior to grafting of the catalyst precursor (Section 6.2.2.3).^[337, 358] Interaction of metal alkyls with highly Brønsted acidic sulfated oxides leads to protonolysis of M-alkyl bond yielding cationic species, while the negative

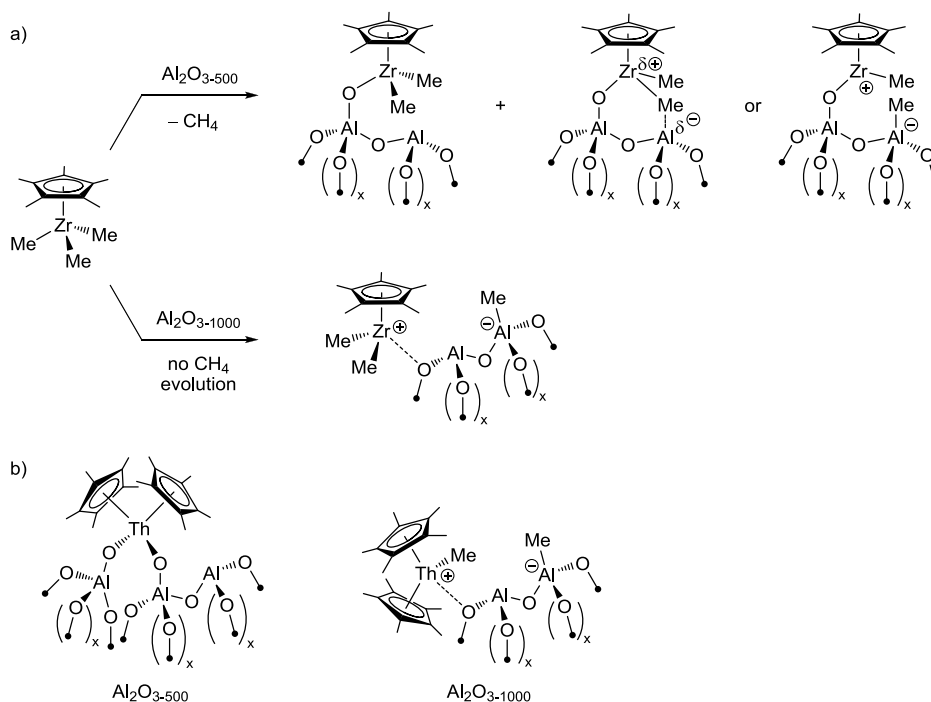
charge is delocalized at the surface (Section 6.2.2.4). Highly electrophilic surface hydrides represent a special class of single-component polymerization catalysts that will be discussed in Section 6.2.2.5.

6.2.2.2. *Well-Defined Complexes Supported on Non-Modified Supports*

As shown in Scheme 26 active cationic polymerization sites can be generated on highly Lewis acidic surfaces, such as MgCl_2 and alumina, *via* abstraction of an alkyl ligand from the metal complex by a Lewis acidic surface site, while grafting onto silica leads to neutral surface species that require further activation with an external Lewis acid. Thus, the reaction of dehydroxylated alumina with homoleptic $\text{Zr}(\text{allyl})_4$, $\text{Zr}(\text{CH}_2\text{Ph})_4$, $\text{Zr}(\text{CH}_2\text{SiMe}_3)_4$ and $\text{Zr}(\text{CH}_2\text{OCH}_3)_4$ gives active catalysts.^[20-21] Detailed study of the reaction of $\text{Zr}(\text{CH}_2t\text{Bu})_4$ with partially dehydroxylated alumina ($\text{Al}_2\text{O}_{3-500}$) shows that neutral and cationic species, $(\text{Al}_5\text{O})_2\text{Zr}(\text{CH}_2t\text{Bu})_2$ and $[(\text{Al}_5\text{O})_2\text{Zr}(\text{CH}_2t\text{Bu})]^+[\text{Al}_5\text{CH}_2t\text{Bu}]^-$, are generated on the surface (Scheme 27a); the latter explains the high polymerization activity.^[383] Similar results were found for the corresponding Hf system^[384-385] and other related molecular complexes $\text{MX}_x\text{R}_{4-x}$ ($\text{M} = \text{Zr, Hf, Ti}$; $\text{X} = \text{halide}$; $\text{R} = \text{allyl, benzyl, tetramethylsilyl, } x = 0-3$).^[20, 24, 386-387] The cationic species, $[(\text{Al}_5\text{O})_2\text{M}(\text{CH}_2t\text{Bu})]^+[\text{Al}_5\text{CH}_2t\text{Bu}]^-$, are proposed to be formed by protonolysis of $\text{Zr}(\text{CH}_2t\text{Bu})_4$ by surface Al_5OH groups, followed by transfer of one alkyl group from the grafted metal site to an adjacent aluminum Lewis acidic site. Grafting $\text{Zr}(\text{CH}_2t\text{Bu})_4$ on dehydroxylated silica forms the inactive $(\equiv\text{SiO})\text{Zr}(\text{CH}_2t\text{Bu})_3$ surface site (Scheme 27b),^[370] which strongly supports that the alkyl abstraction by the support is critical to obtain active catalysts.



Scheme 27. Grafting of $\text{Zr}(\text{CH}_2\text{tBu})_4$ onto partially dehydroxylated a) alumina and b) silica.



Scheme 28. a) Interaction of Cp^*ZrMe_3 with highly and partially dehydroxylated alumina. b) Surface species formed upon grafting $\text{Cp}^*_2\text{ThMe}_2$ on highly and partially dehydroxylated alumina.

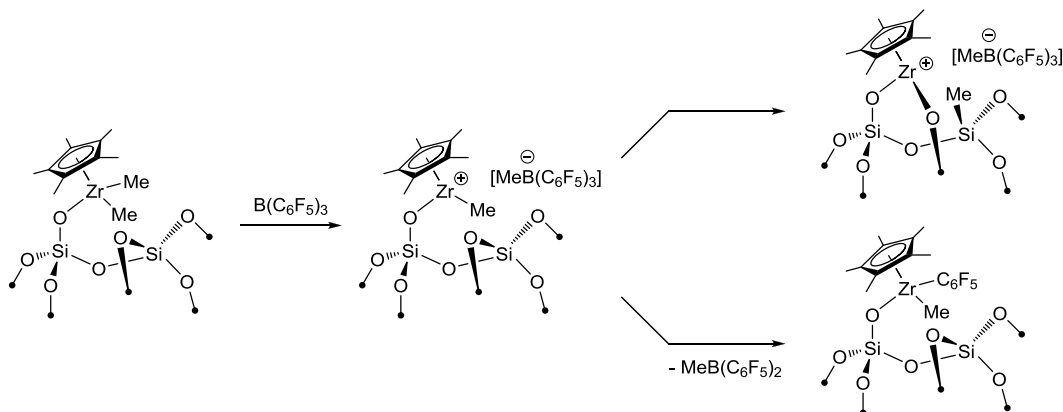
Similar behavior and activation routes have been reported for the corresponding metallocenes: Cp^*ZrMe_3 reacts with silica to form a well-defined supported metallocene that is inactive in polymerization unless activated by external Lewis acid.^[388-390] In contrast, the corresponding silica-alumina^[388] and alumina-supported^[388, 391] systems are active in ethylene polymerization, especially when highly dehydroxylated alumina is used.^[391] The

effect of thermal treatment on activity correlates with the increase in density of strongly Lewis acidic sites upon thermal treatment at high temperatures.^[306] For example, the reaction of Cp*ZrMe₃ with Al₂O₃₋₁₀₀₀ generates [Cp*ZrMe₂]⁺[Al₅Me]⁻, while the same reaction with Al₂O₃₋₅₀₀ leads to a mixture of neutral mono-grafted (≡Al₅O)ZrCp*Me₂ and partially cationic surface complex where one of the methyl groups is interacting with an adjacent Al site (Scheme 28a).^[391] The same behavior was observed for Cp₂ZrMe₂.^[388, 391]

Similar reactivity was found for organoactinides Cp*₂MMe₂ (M = Th or U) grafted on MgCl₂₋₃₀₀^[392] and Al₂O₃₋₁₀₀₀.^[392-395] Lewis acidic sites abstract Me⁻ groups and the resulting cationic species [Cp*₂M–Me]⁺ interacts with the surface either *via* electrostatic forces or weak μ-Cl, μ-O or μ-CH₃ bridges. This proposal is supported by chemical reactivity and specific spectroscopic signatures of cationic species observed in solid-state NMR experiments.^[392-395] Up to *ca.* 50% [Cp*₂M–Me]⁺ sites are active on MgCl₂.^[392] Scheme 28b shows the reaction of Cp*₂ThMe₂ with alumina dehydroxylated at different temperatures.^[393-395] Alumina dehydroxylated at very high temperatures forms [Cp*₂Th–Me]⁺ by methyl transfer from the actinide to surface aluminum site. A small fraction of [Cp*₂Th–Me]⁺ sites are very active in polymerization of ethylene. Partially dehydroxylated alumina, containing Al–OH Brønsted sites, reacts by protonolysis of the Th–Me bond to form a bis-grafted neutral species that has much lower polymerization activity (Scheme 28b). Similarly, grafting of Cp*₂ThMe₂ on silica^[392, 394, 396] and MgO^[392] leads to neutral surface complexes with low activity.

Activation of silica-supported organometallics with external Lewis acids to form catalytically active cationic sites (Scheme 26) is widely applied but characterization of the resulting surface sites is rarely possible. (≡SiO)ZrCp*Me₂ reacts with B(C₆F₅)₃ to form well-defined cationic surface complex [(≡SiO)ZrCp*Me]⁺[MeB(C₆F₅)₃]⁻, which is active in ethylene polymerization (Scheme 29).^[388, 390] However, [(≡SiO)ZrCp*Me]⁺[MeB(C₆F₅)₃]⁻

undergoes fast decomposition by alkyl transfer to a neighboring siloxane bridge to form inactive $[(\equiv\text{SiO})_2\text{ZrCp}^*]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ or by C_6F_5 transfer from the borate to the Zr center to form inactive $(\equiv\text{SiO})\text{ZrCp}^*(\text{C}_6\text{F}_5)\text{Me}$ and $\text{MeB}(\text{C}_6\text{F}_5)_2$ (Scheme 29).^[389-390]



Scheme 29. Activation by the Lewis acidic $\text{B}(\text{C}_6\text{F}_5)_3$ additives to a silica-supported metallocene catalyst and subsequent deactivation.

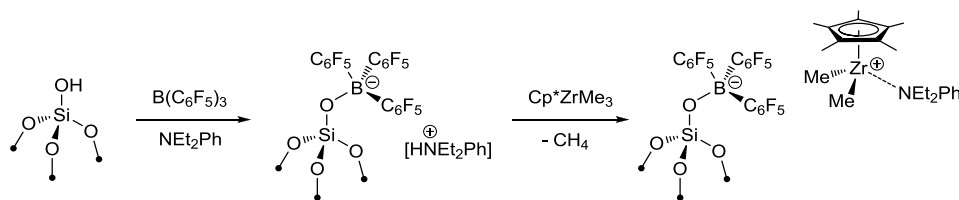
6.2.2.3. Generation of Cationic Species on Modified Supports

Lewis acidic activators can be attached to the surface of the support prior to grafting of the organometallic precatalyst (Scheme 26). The most widely applied approach is immobilization of MAO on high surface area supports which produces a solid cocatalyst.^[397-399] Reacting supported MAO with a molecular complex generates polymerization active materials that behave similarly to metallocene complexes activated by MAO in solution.^[400] However, due to complex nature of MAO itself and the resulting supported species, these catalysts are not strictly single-site catalysts. The nature of the surface sites obtained upon contact of MAO with partially dehydroxylated silica was shown only recently; FTIR and solid-state NMR have revealed the presence of $(\text{X}-\text{O})_3\text{AlMe}$ species ($\text{X} = \text{Si}$ or Al) in different configurations as well as the presence of $\text{Si}-\text{Me}$ species due to the opening of siloxane bridges.^[401]

Activating supports based on silica-supported fluorinated aluminum species were prepared by either reacting AlEt_3 with silica before a subsequent fluorination with NH_4SiF_6

or directly by reacting AlEt_2F with silica. In the former case, a thermolysis under argon and a combustion step is necessary before fluorination so that an aluminum oxide species is formed at the silica surface.^[402] These supports are comparable with supported MAO systems in terms of activity observed when treated with $\text{EtInd}_2\text{ZrCl}_2$ and $\text{Al}i\text{Bu}_3$ as alkylating agent, the reported activities being $10^6\text{--}10^8 \text{ g}_{\text{PE}} \text{ mol}_{\text{Zr}}^{-1} \text{ h}^{-1}$ at 80°C under 4 bar of ethylene.^[402] Being interesting supports, these materials require more rigorous characterization of surface sites.

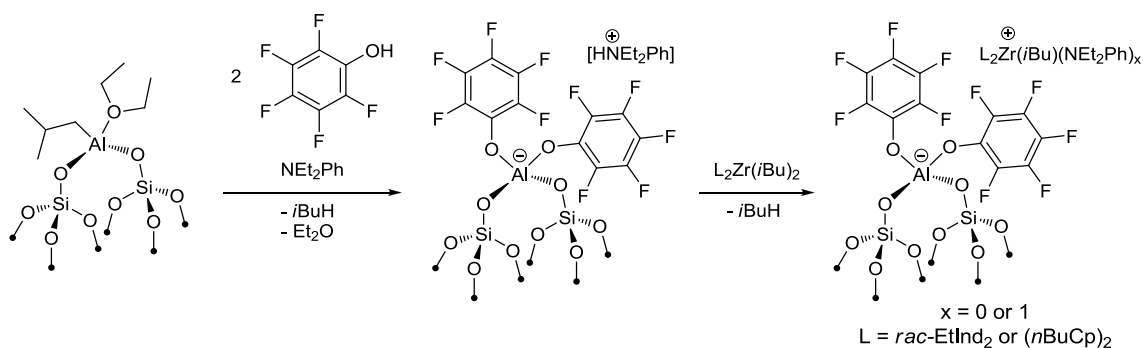
The reaction of surface silanols of silica with $\text{B}(\text{C}_6\text{F}_5)_3$ in the presence of tertiary amines yields well-defined surface species $[\text{Et}_2\text{PhNH}]^+[(\equiv\text{SiO})\text{B}(\text{C}_6\text{F}_5)_3]^-$ that can behave as Brønsted acid containing non-coordinating anion attached to the support, and thus can be used to generate cationic surface species upon reaction with alkyl complexes (Scheme 30).^[403-404] Contacting Cp^*ZrMe_3 with $[\text{Et}_2\text{PhNH}]^+[(\equiv\text{SiO})\text{B}(\text{C}_6\text{F}_5)_3]^-$ leads to protonolysis of Zr–Me bond and generates the active $[\text{Cp}^*\text{ZrMe}_2(\text{NEt}_2\text{Ph})]^+[(\equiv\text{SiO})\text{B}(\text{C}_6\text{F}_5)_3]^-$ catalyst (Scheme 30).^[390, 405-407] The presence of the amine during grafting of $\text{B}(\text{C}_6\text{F}_5)_3$ is necessary, otherwise the coordination of $\text{B}(\text{C}_6\text{F}_5)_3$ to the surface silanol is reversible, which leads to leaching of Zr species active in polymerization.^[406]



Scheme 30. Formation of the surface species $[\text{Et}_2\text{PhNH}]^+[(\equiv\text{SiO})\text{B}(\text{C}_6\text{F}_5)_3]^-$ and its subsequent reaction with Cp^*ZrMe_3 to yield $[\text{Cp}^*\text{ZrMe}_2(\text{NEt}_2\text{Ph})]^+[(\equiv\text{SiO})\text{B}(\text{C}_6\text{F}_5)_3]^-$ surface species.

The silica-supported analog of $[\text{Ph}_3\text{C}]^+[\text{Al}(\text{OC}_6\text{F}_5)_4]^-$ ^[408] was synthesized by the reaction of $(\equiv\text{SiO})_2\text{Al}(i\text{Bu})(\text{Et}_2\text{O})$ ^[409-410] with pentafluorophenol in the presence of diethylaniline to form $[(\equiv\text{SiO})_2\text{Al}(\text{OC}_6\text{F}_5)_2]^-[\text{HNEt}_2\text{Ph}]^+$ (Scheme 31).^[411]

$[(\equiv\text{SiO})_2\text{Al}(\text{OC}_6\text{F}_5)_2]^- [\text{HNEt}_2\text{Ph}]^+$ reacts with *rac*-EtInd₂ZrCl₂ or (*n*BuCp)₂ZrCl₂ in the presence of Al(*i*Bu)₃ to give active ethylene polymerization catalysts (Scheme 31). The activities at 80 °C under 4 bar of ethylene of *rac*-EtInd₂ZrCl₂ and (*n*BuCp)₂ZrCl₂ contacted with $[(\equiv\text{SiO})_2\text{Al}(\text{OC}_6\text{F}_5)_2]^- [\text{HNEt}_2\text{Ph}]^+$ are $8.8 \cdot 10^6$ and $4.3 \cdot 10^6$ g_{PE} mol_{Zr}⁻¹ h⁻¹, respectively. The polymers have properties similar to those obtained from Zr-based silica-supported MAO industrial catalysts.^[401, 412]



Scheme 31. Formation of $[(\equiv\text{SiO})_2\text{Al}(\text{OC}_6\text{F}_5)_2]^- [\text{HNEt}_2\text{Ph}]^+$ and its reaction with zirconocene complexes.

6.2.2.4. Generation of Cationic Species on Sulfated Oxides

Cationic species can form when respective catalyst precursors are grafted onto Brønsted acidic sulfated oxide supports.^[413-419] Characterization of the generated species and computational analysis, as well as polymerization studies, suggest that the surface anionic sites are charge-delocalized and weakly coordinating (Scheme 26). The reaction of Cp*ZrMe₃ with sulfated alumina (Figure 4A) yields weakly coordinated $[\text{Cp}^*\text{ZrMe}_2]^+$ cationic species (Figure 4B) as supported by the characteristic resonance associated with cationic Zr–Me⁺ in the ¹³C CP MAS NMR spectrum and the long Zr–O contact from X-ray absorption spectroscopy.^[417-419] Similar observations were found for reactions of organozirconium species with sulfated zirconia^[414] and sulfated tin oxides.^[418, 420] In some cases up to 100% of the sites are active.^[414-415, 418, 420]

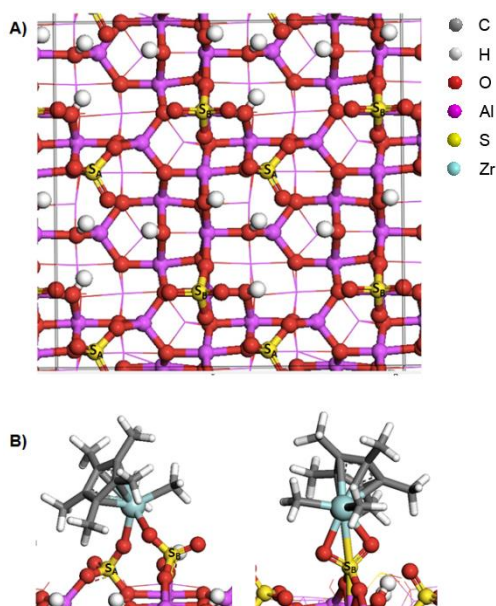


Figure 4. A) 2×2 unit cell of sulfated γ - Al_2O_3 model based on DFT calculations. B) $\text{Cp}^*\text{ZrMe}^{2+}$ complex on the S_A - S_B sites (left) and S_B sites.

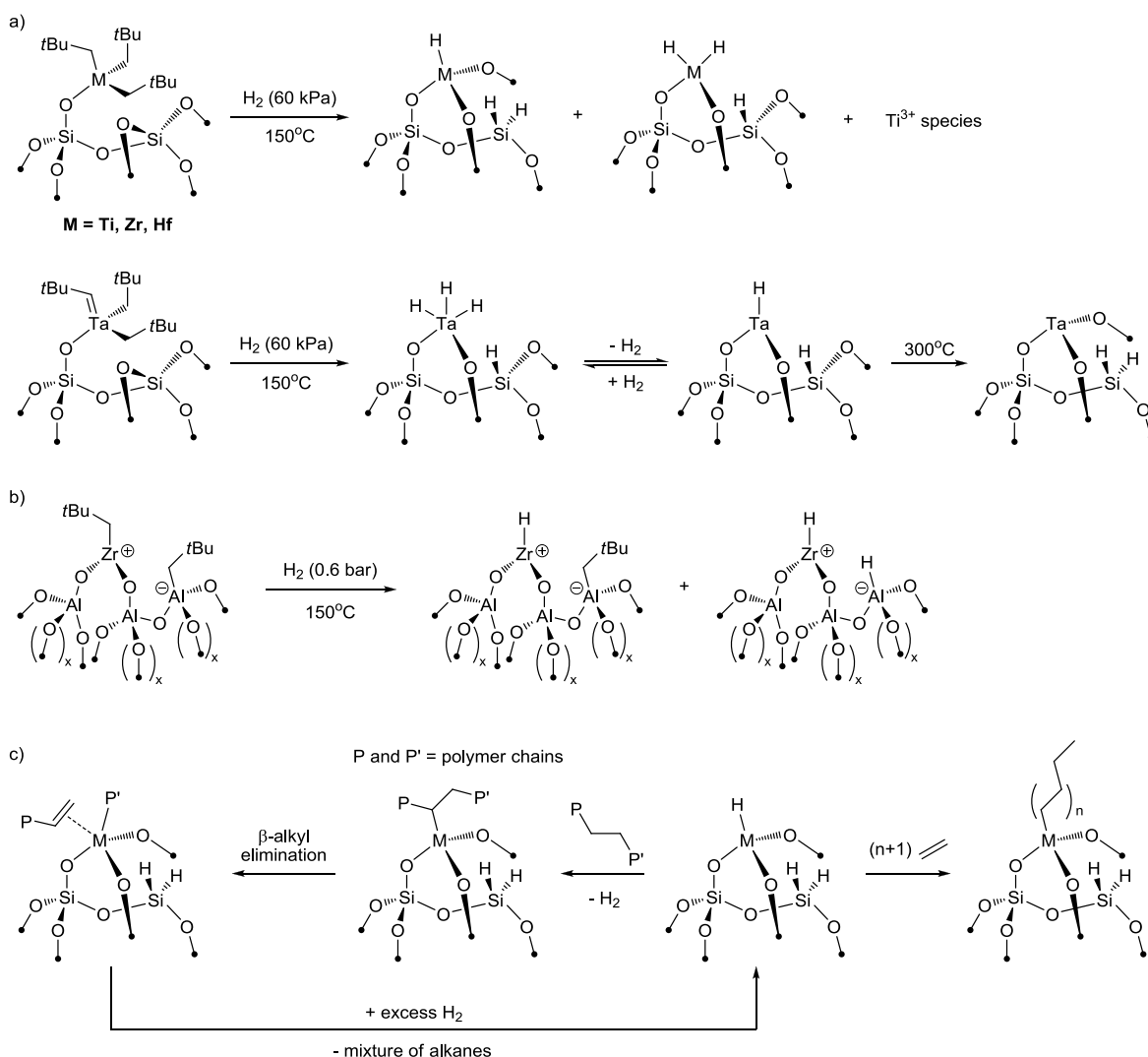
6.2.2.5. Supported Metal Hydrides as Catalyst Precursors

Supported early transition metal hydrides^[64] were discovered and tested in ethylene polymerization in late 1970s.^[421-422] Early studies have shown that grafting of $\text{Zr}(\text{allyl})_4$ - Br_x ($x = 0, 1$ and 2) on silica partially dehydroxylated at $200\text{ }^\circ\text{C}$ affords $(\equiv\text{SiO})_2\text{Zr}(\text{allyl})_2$ - Br_x .^[20-21, 377] While not very active, the silica-supported systems show enhanced activity under H_2 and ethylene, possibly because of the formation of hydride species. For instance, $(\equiv\text{SiO})_2\text{Zr}(\text{allyl})_2$ at $80\text{ }^\circ\text{C}$ in toluene under 10 atm of ethylene and 10 atm of H_2 is 38 times more active than the parent $\text{Zr}(\text{allyl})_4$. The polymerization activity of silica-supported Zr allyl species treated by H_2 is proportional to the amount of $\text{Zr}^{(\text{IV})}$ hydride sites, suggesting that the latter are the active sites.^[421]

Surface hydrides are obtained by reacting partially dehydroxylated silica, alumina, and silica-alumina with early transition metal alkyl complexes, typically $\text{M}(\text{CH}_2\text{R})_4$ ($\text{M} = \text{Ti, Zr}$ and Hf ; $\text{R} = \text{vinyl, Ph}$ or $t\text{Bu}$), followed by a treatment under H_2 at 100 – $200\text{ }^\circ\text{C}$. The surface hydrides are clearly observed by IR spectroscopy with the specific appearance of

$\nu_{\text{M-H}}$ bands in the 1900–1600 cm^{-1} region.^[43, 64] Above 150–200 °C, these bands gradually disappear, while the Si–H bands increase in intensity, indicating that hydrides are transferred to the surface and that the metal migrates into the oxide support.^[211, 423]

For example, grafting of $\text{Zr}(\text{CH}_2\text{tBu})_4$ onto partially dehydroxylated silica yields $(\equiv\text{SiO})\text{Zr}(\text{CH}_2\text{tBu})_3$ that reacts with H_2 giving $(\equiv\text{SiO})_3\text{ZrH}$ and $(\equiv\text{SiO})_2\text{ZrH}_2$ in a 60:40 ratio with the concomitant formation of $\equiv\text{SiH}$ and $=\text{SiH}_2$ species (Scheme 32a).^[424] $(\equiv\text{SiO})_3\text{ZrH}$ and $(\equiv\text{SiO})_2\text{ZrH}_2$ react with ethylene with consumption of Zr–H bands according to IR. The scenario is very similar in the case of Ti^[425] and Hf,^[426] though a significant amount of Ti^(III) sites is also formed under these conditions.^[24, 427-430] With Ta, a mixture of mono- $(\equiv\text{SiO})_2\text{Ta-H}$ and tris-hydride $(\equiv\text{SiO})_2\text{TaH}_3$ has been reported.^[212] Surface hydrides can also be generated on silica-alumina and alumina (Ti^[431], Zr^[432-433], Hf^[426, 434], Ta^[435]). It has been proposed that the electrophilicity of the Zr and Ti hydrides can be exacerbated by using silica-alumina in place of silica,^[431-432] and formation of cationic zirconium hydrides has been postulated on alumina (Scheme 32b).^[433] All these supported metal hydrides polymerize ethylene.^[430, 436] Noteworthy, depolymerization of polyethylene under H_2 has also been reported for Zr (Scheme 32c).^[432] In the case of Ti, a significant amount of Ti^(III)–H sites is formed that is proposed to be very active in ethylene polymerization.^[437-438]



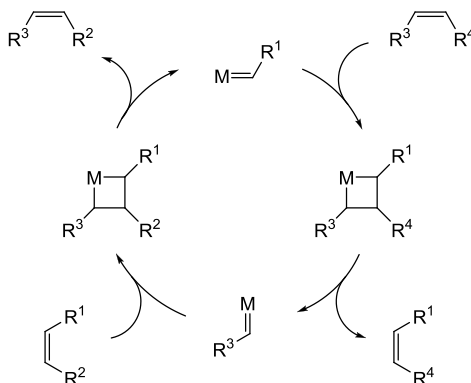
Scheme 32. a) Formation of silica-supported metal hydrides. b) Formation of alumina-supported zirconium hydrides. c) Polymerization of ethylene and depolymerization of polyethylene by supported metal hydrides.

7. Alkene Metathesis

7.1. Industrial and Mechanistic Background

The first metathesis catalysts based on group 6 metal oxides dispersed on high surface area supports^[2-3, 439-442] were discovered in 1960s by Phillips Petroleum.^[443] The Phillips Triolefin Process was originally designed to convert propylene into ethylene and 2-butenes using silica-supported tungsten oxide (WO_3/SiO_2).^[2-3, 443] Its reverse, licensed by Lummus Global as Olefins Conversion Technology (OCT), was subsequently developed in

1970s, and has gained much interest in recent years with the increasing propylene demand. WO_3/SiO_2 has also been used for the production of 1-hexene from butenes (Lummus' Comonomer Production Technology, CPT) and neohexene, an important intermediate in the synthesis of Tonalide[®] and Terbinafine[®].^[3] WO_3/SiO_2 is the most commonly used industrial olefin metathesis catalyst due to its resistance to traces of oxygenate poisons in the feed, longer lifetimes compared to Mo and Re systems, and easy regeneration to remove coke.^[444-446] WO_3/SiO_2 typically operates at temperatures above 400 °C. Molybdenum metathesis catalysts are used in the Shell Higher Olefins Process (SHOP) that involves alumina-supported molybdates ($\text{MoO}_3/\text{Al}_2\text{O}_3$) in tandem with oligomerization and isomerization catalysts.^[2-3] $\text{MoO}_3/\text{Al}_2\text{O}_3$ is active at temperatures of 100–200 °C. In contrast to Mo- and W-based systems, $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ shows room temperature activity^[447] and can catalyze metathesis of functionalized olefins when activated with SnMe_4 .^[448-449] It has been employed in the Meta-4 process for propylene production,^[3, 450-451] and in the dimerization of cyclic alkenes such as cycloheptene and cyclooctene.^[452]



Scheme 33. Chauvin olefin metathesis mechanism.

The olefin metathesis mechanism proposed by Chauvin in 1971^[453] is now widely accepted (Scheme 33). It involves metal alkylidenes and metallacyclobutanes as key reaction intermediates that interconvert *via* [2+2] cycloaddition/cycloreversion steps. A variety of well-defined molecular catalysts have been developed based on this

mechanism.^[454-459] Modern homogeneous metathesis catalysts based on d^0 metals and Ru d^6 complexes show outstanding activities and selectivities, and have found their ways beyond academic and research laboratories to industrial applications.^[460-462] In contrast to d^0 systems, homogeneous Ru metathesis catalysts have no ill-defined heterogeneous industrial counterparts and will not be discussed here. However, supported Ru-based catalysts have been prepared *via* SOMC,^[463] SHC,^[40, 464-467] and adsorption^[468-471] techniques.

Although the Chauvin mechanism is believed to be operative for the aforementioned industrial heterogeneous catalysts, the expected alkylidene and/or metallacyclobutane intermediates have never been observed in these systems and the mechanisms of their generation are still a matter of debate. Numerous studies accumulated a vast array of data regarding the effects of metal precursor, loading, and properties of the support, as well as a number of empirical recipes for catalyst activation. However, the complexity of industrial catalysts prevents a systematic analysis of these data. Controllable generation of well-defined surface sites using SOMC allows for independent investigation of these parameters. Below we will discuss the current knowledge about active sites of the industrial metathesis catalysts and relate these findings to well-defined supported systems. The catalytic systems based on Re and group 6 metals will be discussed in Sections 7.2 and 7.3.

7.2. Supported Re Metathesis Catalysts

7.2.1. Surface Sites in Re_2O_7 -Based Catalysts

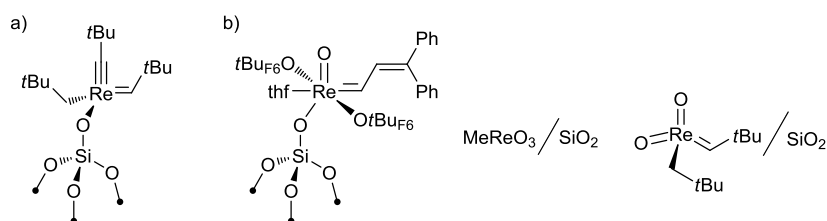
Re_2O_7 -based heterogeneous metathesis catalysts are not active on silica, but only on the supports containing Lewis acid sites, such as Al_2O_3 and $\text{SiO}_2\text{-Al}_2\text{O}_3$.^[444] While the role of the Lewis acid sites is not known, the surface species present in $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ corresponds to isolated perrhenate species coordinated to adjacent Al sites.^[472]

Experimental and computational studies indicate that the most active sites most likely correspond to $\text{Re}^{(\text{VII})}$ oxo species bound to Lewis acidic Al_{III} and Al_{IV} sites, while other combinations of Al sites are inactive (the roman number in subscript indicates the coordination number of surface Al^{3+} sites).^[472] In addition, it is well-known that $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ is active towards functionalized olefins like oleates upon pre-activation with SnMe_4 .

7.2.2. Well-Defined Supported Re Metathesis Catalysts

7.2.2.1. Silica-Supported Re-Based Catalysts

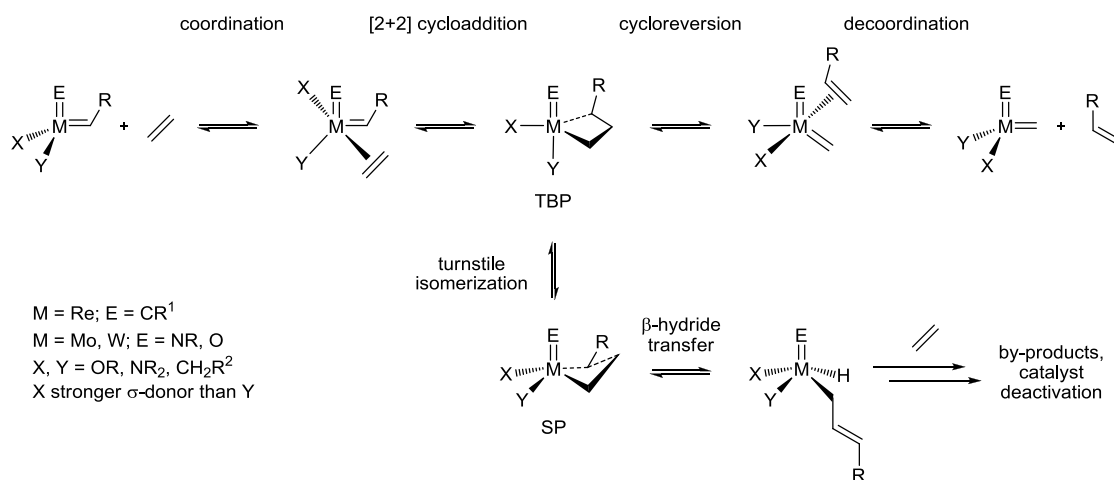
The reaction of $\text{Re}(\equiv\text{C}t\text{Bu})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_2$ ^[473] and SiO_{2-700} results in the formation of a stable silica-supported $\text{Re}^{(\text{VII})}$ alkylidene complex, $(\equiv\text{SiO})\text{Re}(\equiv\text{C}t\text{Bu})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$, active in the metathesis of olefins, including ethyl oleate, at room temperature in the absence of cocatalyst/activator (Scheme 34a).^[474-476] This result shows that silica is not intrinsically a poor support for Re-based heterogeneous catalysts, and suggests that the role of Lewis acid sites in $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ is to facilitate the formation of the alkylidene species.^[477] Several other combinations of Re precursors and silica, shown in Scheme 34b, are inactive in metathesis illustrating the effect of the ancillary ligand set.^[478-480]



Scheme 34. a) Metathesis-active silica-supported Re alkylidene complex. b) Some representative Re species on silica inactive in metathesis.

The high activity of $(\equiv\text{SiO})\text{Re}(\equiv\text{C}t\text{Bu})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$ originates from the dissymmetry of the metal center, which facilitates coordination/decoordination of the olefin

(Scheme 35), according to computational studies.^[481-486] This dissymmetry induces a distortion of the tetra-coordinated metal site towards a trigonal pyramidal geometry, facilitating olefin coordination, and it also destabilizes metallacyclobutane intermediates, which results in efficient metathesis catalysis. This mechanism is general and applies to all tetra-coordinated d^0 -based metathesis catalysts, including homogeneous ones.



Scheme 35. Elementary steps and decomposition pathways involved in olefin metathesis catalyzed by Mo, W and Re d^0 alkylidene complexes.

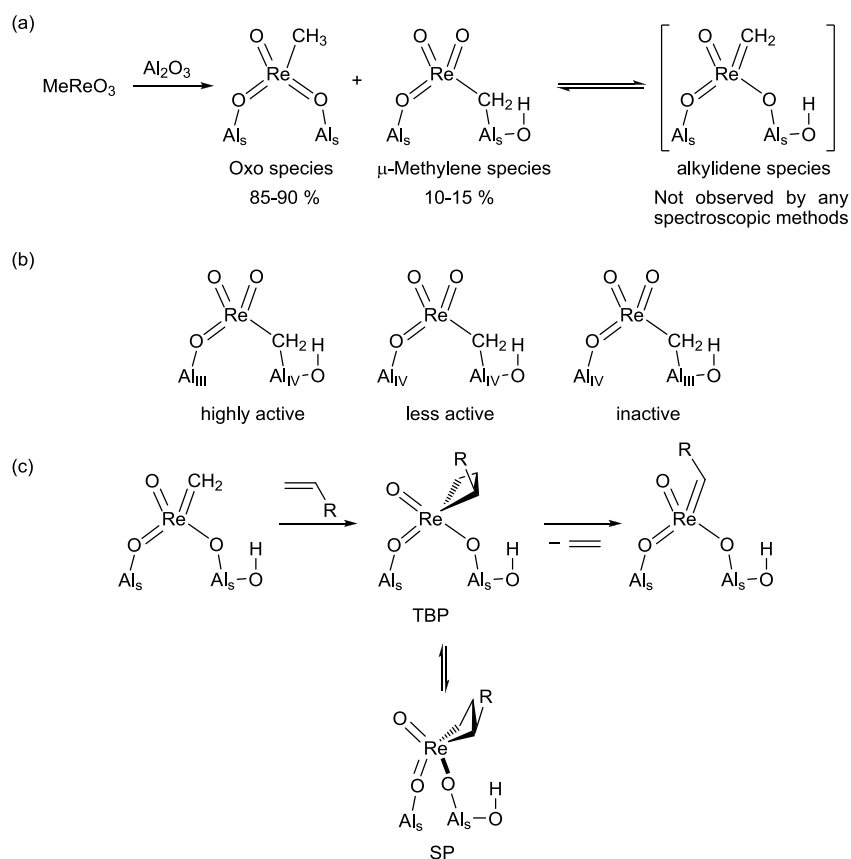
7.2.2.2. Alumina-Supported Re-Based Catalysts and Related Systems

Methyltrioxorhenium supported on Al_2O_3 ($\text{MeReO}_3/\text{Al}_2\text{O}_3$) can be used as a model for the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$. MeReO_3 is only active in metathesis when contacted with molecular or solid Lewis acids.^[487] The catalytic activity of supported MeReO_3 is related to the presence of Lewis acidic sites in the support.^[478, 488-497] The structures of the surface sites of $\text{MeReO}_3/\text{Al}_2\text{O}_3$ were investigated in detail using a combination of IR, EXAFS, solid-state NMR and DFT calculations on periodic model of γ -alumina. These studies show that MeReO_3 chemisorbs onto the surface to form an oxo-bound site (85–90%) and μ -methylene species (10–15%) (Scheme 36a).^[498-500] The oxo species contains two of the oxo ligands bound to adjacent Al sites. The μ -methylene species is formed *via* C–H bond activation of the methyl ligand in MeReO_3 on an Al–O site; in this species one of the Re=O groups is

coordinated to an adjacent Al site. Reacting ^{13}C -enriched $\text{MeReO}_3/\text{Al}_2\text{O}_3$ with natural abundance ethylene results in disappearance of a ^{13}C NMR signal associated with the μ -methylene species, indicating that this site is responsible for catalytic activity.

Detailed descriptions of the alumina supports^[305-306] and $\text{MeReO}_3/\text{Al}_2\text{O}_3$ ^[501-502] showed that the Al sites coordinated to MeReO_3 are essential for the formation of alkylidene and metallacyclobutane intermediates. The most active μ -methylene Re sites contain a $\text{Re}=\text{O}$ bound to a strongly Lewis acidic tri-coordinated Al site (Al_{III}), and the μ -methylene fragment bound to a four-coordinated Al (Al_{IV}). The reverse combination of Al sites (μ -methylene fragment bound to Al_{III} and $\text{Re}=\text{O}$ bound to Al_{IV}) forms inactive Re sites because of the very strong coordination of the μ -methylene to Al_{III} site (Scheme 36b). MeReO_3 bound to two Al_{IV} sites leads to low activity or inactive metal sites. As found for $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$,^[472] Al_{III} sites play a critical role in high activity of alumina-supported Re-based metathesis catalysts. It is thus not surprising that the activity of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ and $\text{MeReO}_3/\text{Al}_2\text{O}_3$ depends on the pre-activation temperature; the highest activity is found for activation temperature of *ca.* 700 °C,^[502-503] at which the highest density of Al_{III} sites is generated.^[306]

Though the μ -methylene species exchanges with ethylene and propylene (Scheme 36c),^[499] indicating that this site is an active site precursor, a resonance associated with an alkylidene has not yet been observed by solid-state NMR. However, *in situ* solid-state NMR of the catalyst measured under ethylene pressure provides a spectral signature assigned to metallacyclobutane in a trigonal bipyramidal (TBP) geometry as the most abundant reaction intermediate. Square-based pyramidal (SP) metallacycle is also observed, but not the alkylidene species (Scheme 36c).^[502]

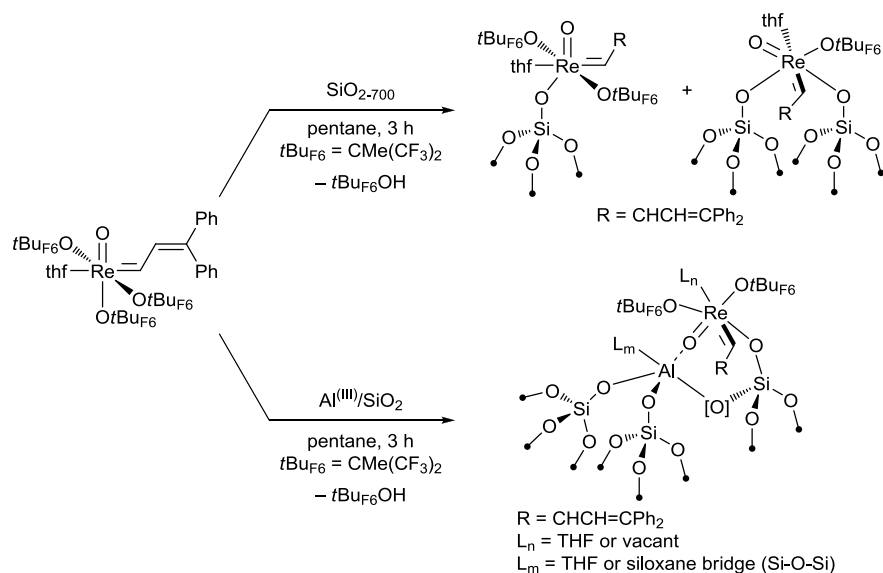


Scheme 36. a) Grafting of MeReO_3 on Al_2O_3 . b) Molecular level structures of μ -methylene sites bound to different combinations of the Al sites. c) Proposed mechanism of metathesis of rhenium alkyldene species with external olefin.

$\text{MeReO}_3/\text{Al}_2\text{O}_3$ shows catalytic properties similar to $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ activated with SnMe_4 . Both catalysts are active in both ethylene and ethyl oleate self-metathesis, while $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ is not active towards these olefins in the absence of activators.^[444, 448-449, 504] Solid-state NMR studies of $\text{SnMe}_4/\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ and $\text{MeReO}_3/\text{Al}_2\text{O}_3$ obtained using various labeling strategies indicate that μ -methylene sites are formed in both cases.^[505] This result indicates that the role of SnMe_4 is to convert the surface perhenate into MeReO_3 which is then activated on alumina to form μ -methylene sites.

The role of Lewis acid sites in $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts suggests that other Re alkyldenes that are inactive on silica may be active in the presence of these “activating” sites. For example, the reaction of $\text{Re}(=\text{O})(=\text{CH}-\text{CH}=\text{CPh}_2)(\text{O}i\text{Bu}_{\text{F6}})_3(\text{THF})$ ($\text{O}i\text{Bu}_{\text{F6}} =$

OC(CF₃)₂Me) with silica generates the inactive well-defined oxo-alkylidenes shown in Scheme 37.^[480] In contrast, reacting Re(=O)(=CH–CH=CPh₂)(OtBuF₆)₃(THF) with silica incorporating Al^(III) surface sites (Al^(III)/SiO₂), prepared by dispersing Al[OSi(OtBu)₃]₃ onto a dehydroxylated silica surface followed by thermolysis, results in oxo-alkylidene sites that are active in metathesis. Solid-state NMR spectroscopy indicates that the Al sites bind ligands and probably Re=O, but further studies are clearly needed to understand the exact role of the alumina support for the activation of the metal sites. This result suggests that Lewis acidic aluminum sites can be essential in the design of Re-based heterogeneous catalysts.



Scheme 37. Grafting of Re(=O)(=CH–CH=CPh₂)(OtBuF₆)₃(THF) on SiO₂₋₇₀₀ and Al^(III)/SiO₂.

7.2.3. Relation between Re₂O₇/Al₂O₃ and Well-Defined Re-Based Catalysts

In conclusion, silica is an appropriate support for Re metathesis catalysts, providing that Re^(VII) contains an alkylidene and an appropriate set of σ -donating ligands, as in ($\equiv\text{SiO}$)Re($\equiv\text{C}t\text{Bu}$)(=CH $t\text{Bu}$)(CH₂ $t\text{Bu}$). Variation of the σ -donating ligands often leads to inactive catalysts, as in MeReO₃/SiO₂ and Re(=O)(=CH–CH=CPh₂)(OtBuF₆)₃(THF)/SiO₂. Although pathways to form the alkylidene intermediates in Re₂O₇/Al₂O₃ remain unknown,

studies of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ and $\text{MeReO}_3/\text{Al}_2\text{O}_3$ point to the essential role of Al_{III} sites, which is consistent with the optimal activation temperature of alumina support for Re-based catalysts. While the relationship between the active sites in $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ and $\text{MeReO}_3/\text{Al}_2\text{O}_3$ is not entirely clear, activation of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ with SnMe_4 generates μ -methylene species similar to that observed in $\text{MeReO}_3/\text{Al}_2\text{O}_3$.

7.3. Supported Group 6 Metathesis Catalysts

7.3.1. Surface Sites in Industrial Catalysts

A number of studies have been carried out to investigate the surface structure of WO_3/SiO_2 with various *in situ* spectroscopic methods including Raman, IR, UV-vis DRS, and XAS.^[248-249, 506] Under fully oxidized conditions di-oxo $(\equiv\text{SiO})_2\text{W}(=\text{O})_2$ and mono-oxo $(\equiv\text{SiO})_4\text{W}(=\text{O})$ sites are observed, in addition to WO_3 nanoparticles/clusters. The relative amounts of these species depend on the W loading. The di-oxo $(\equiv\text{SiO})_2\text{W}(=\text{O})_2$ species are dominant below 8% WO_3 , and are probably the source of the active sites.^[446] The molecular structure of fully oxidized Mo catalysts on different supports (SiO_2 , Al_2O_3 and $\text{SiO}_2\text{-Al}_2\text{O}_3$) was also extensively studied by *in situ* Raman, IR, UV-vis DRS, and XAS. Based on these methods^[507] and DFT calculations,^[508-509] surface di-oxo $(\equiv\text{SiO})_2\text{Mo}(=\text{O})_2$ units are dominant on silica. Similar surface species $(\text{Al}_5\text{O})_2\text{Mo}(=\text{O})_2$ are mainly present on alumina at low surface coverage, while both isolated surface di-oxo $(\text{Al}_5\text{O})_2\text{Mo}(=\text{O})_2$ and oligomeric mono-oxo $(\text{Surf-O})_4\text{Mo}(=\text{O})$ sites are formed at higher coverage.^[510-513] At coverages above one monolayer ($4.6 \text{ Mo}/\text{nm}^2$), crystalline MoO_3 nanoparticles are also found.^[514] A number of mechanisms of the formation of alkylidenes from surface oxo species has been proposed.^[2, 442, 515-516] Most of them involve reduced metal sites that are possibly formed *via* reduction of $\text{M}^{(\text{VI})}$ oxo species in the presence of olefin under the reaction conditions.

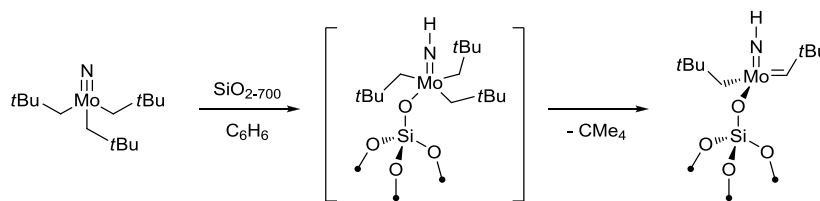
7.3.2. Well-Defined Supported Group 6 Metathesis Catalysts

7.3.2.1. Preamble

The first attempts to apply organometallic precursors to prepare supported metathesis catalysts date back to 1970s using WMe_6 ^[517] and other perhydrocarbyl complexes^[518] that can generate surface alkylidenes *in situ*. This approach has been recently re-investigated using advanced characterization methods (Section 7.3.2.2).^[519-526] Supported alkylidynes were also shown to be active metathesis catalyst precursors.^[527-532] These systems and their possible activation pathways have been recently discussed in detail.^[441] Supported tungsten hydrides represent a special class of *in situ* generated olefin metathesis catalysts (Section 7.3.2.3).^[224-225, 533-540] An alternative strategy has focused on direct grafting of molecular alkylidene complexes onto the surface of oxide supports. Preliminary reports appeared in early 2000s,^[541-542] and application of modern characterization techniques eventually allowed for precise control of the structures of these surface species and gave rise to the generation of remarkably active well-defined silica-supported Mo ^[543-549] and W ^[550-555] imido-alkylidenes and more recently W oxo-alkylidenes^[556-560] (Section 7.3.2.4). In 1970-80s Yermakov^[561-564] and Iwasawa^[565-566] were first to use organometallic precursors ($\text{Mo}(\text{C}_3\text{H}_5)_4$ and $\text{W}(\text{C}_4\text{H}_7)_4$) to prepare well-defined supported Mo and W oxides relevant to industrial systems and discriminate the activities of different oxidation states. These studies suggested that neither fully oxidized $\text{Mo}^{(\text{VI})}/\text{W}^{(\text{VI})}$ nor highly reduced $\text{Mo}^{(\text{II})}/\text{W}^{(\text{II})}$ species were responsible for metathesis activity and that active sites likely arose from oxidation state +4. Recent advances describing redox chemistry of well-defined supported W oxo sites are discussed in Section 7.3.2.5.^[567]

7.3.2.2. Catalysts Based on Well-Defined Silica-Supported Alkyl Complexes

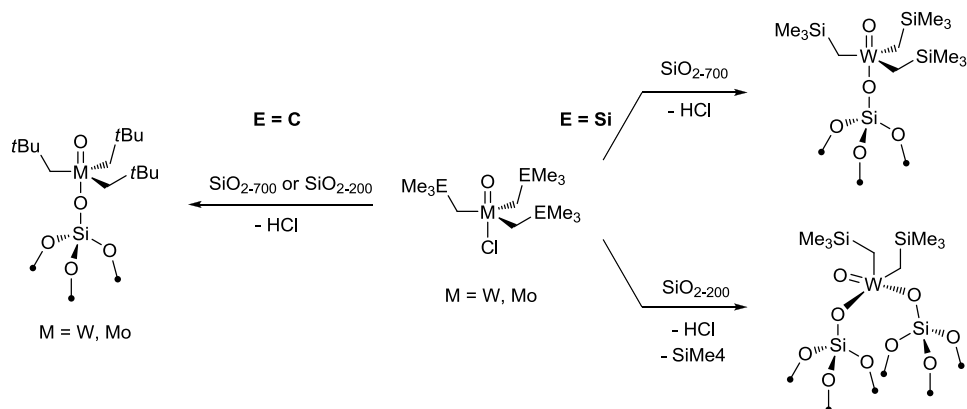
In analogy to molecular organometallic chemistry, it was speculated that α -elimination of silica-supported alkyls could generate surface alkylidene species. Indeed, one of the first active well-defined supported imido-alkylidene catalysts was obtained by grafting $\text{Mo}(\equiv\text{N})(\text{CH}_2t\text{Bu})_3$ on silica.^[531, 568] Grafting proceeds *via* protonation of the nitrido ligand giving a penta-coordinated intermediate $(\equiv\text{SiO})\text{Mo}(=\text{NH})(\text{CH}_2t\text{Bu})_3$ that undergoes α -H abstraction at one of the neopentyl ligands to form 2,2-dimethylpropane and $(\equiv\text{SiO})\text{Mo}(=\text{NH})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$ (Scheme 38). This catalyst is active in metathesis of propene, 1-octene and ethyl oleate.



Scheme 38. Grafting of $\text{Mo}(\equiv\text{N})(\text{CH}_2t\text{Bu})_3$ on SiO_{2-700} .

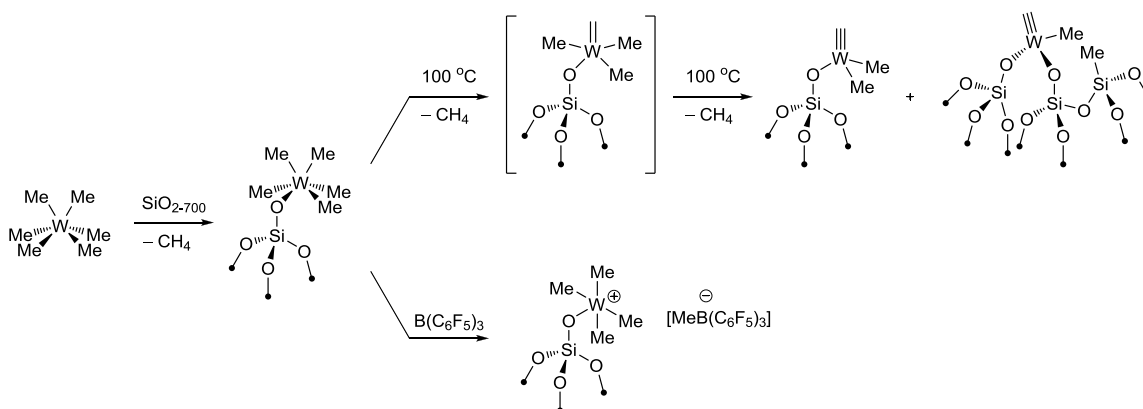
$\text{W}(=\text{O})(\text{CH}_2t\text{Bu})_3\text{X}$ ($\text{X} = \text{CH}_2t\text{Bu}$ or Cl) reacts with SiO_{2-700} to form $(\equiv\text{SiO})\text{W}(=\text{O})(\text{CH}_2t\text{Bu})_3$.^[521-522] The same monopodal surface species is formed when $\text{W}(=\text{O})(\text{CH}_2t\text{Bu})_3\text{Cl}$ is grafted on SiO_{2-200} .^[524] On the contrary, grafting of isoelectronic $\text{W}(=\text{O})(\text{CH}_2\text{SiMe}_3)_3\text{Cl}$ on SiO_{2-700} and SiO_{2-200} leads to monopodal and bipodal surface complexes, respectively (Scheme 39).^[524-525] Catalytic metathesis performance in a flow of propene at 80 °C for both neosilyl systems $(\equiv\text{SiO})_x\text{W}(=\text{O})(\text{CH}_2\text{SiMe}_3)_{4-x}$ (18,000 and 24,000 TON after 25 h for $x = 1$ and 2, respectively) is significantly better than that of $(\equiv\text{SiO})\text{W}(=\text{O})(\text{CH}_2\text{CMe}_3)_3$ (6,000 TON after 25 h). The analogous Mo system $(\equiv\text{SiO})\text{Mo}(=\text{O})(\text{CH}_2t\text{Bu})_3$ shows high activity in propene metathesis at 60 °C (90,000 TON; 25 h).^[526] In addition, the supported tungsten oxo-alkyl complex has also been generated *in situ* by grafting WOCl_4 on SiO_{2-200} followed by alkylation with SnMe_4 ; this also results in

active metathesis catalyst.^[523] Though not observed spectroscopically, alkylidenes are likely formed *in situ* in all these systems.



Scheme 39. Grafting of $M(=O)(\text{CH}_2\text{CMe}_3)_3\text{Cl}$ ($M = \text{W}, \text{Mo}$) and $\text{W}(=O)(\text{CH}_2\text{SiMe}_3)_3\text{Cl}$ on silica.

Grafting WMe_6 on silica forms $(\equiv\text{SiO})\text{WMe}_5$ that yields methylidene and methylidyne surface species by α -H abstraction explaining its activity in olefin metathesis (Scheme 40).^[519] Treatment of $(\equiv\text{SiO})\text{WMe}_5$ with $\text{B}(\text{C}_6\text{F}_5)_3$ leads to cationic $[(\equiv\text{SiO})\text{WMe}_4]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$, which has good activity in self-metathesis of terminal and internal olefins and ROMP of cyclooctene at room temperature.^[520]

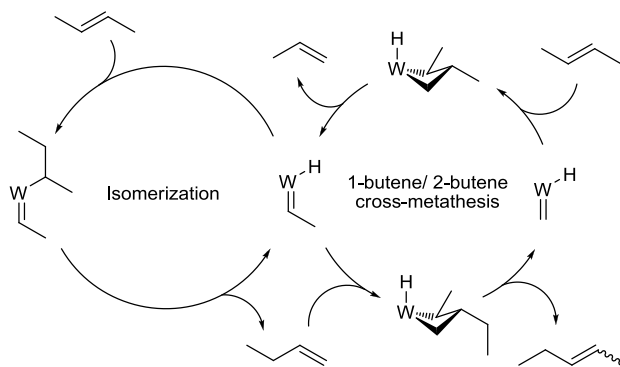


Scheme 40. Grafting and further transformations of WMe_6 on silica.

7.3.2.3. Supported W Hydrides

Grafting of $\text{W}(\equiv\text{C}t\text{Bu})(\text{CH}_2t\text{Bu})_3$ on $\text{Al}_2\text{O}_{3-500}$ followed by H_2 treatment at $150 \text{ }^\circ\text{C}$ generates supported $\text{W}^{(\text{VI})}$ hydrides.^[533] Similar species are probably formed in the

corresponding silica-alumina-supported system.^[534] These W–H complexes are active in olefin metathesis and other catalytic transformations. For example, $\text{WH}_3/\text{Al}_2\text{O}_{3-500}$ operates as a “bi-functional single active site” W carbene-hydride catalyst forming propylene from 2-butene *via* isomerization of 2-butene to 1-butene followed by cross-metathesis of 2-butenes and 1-butene (Scheme 41).^[535-540] Similarly, $\text{WH}_3/\text{Al}_2\text{O}_{3-500}$ also converts ethylene to propylene (ETP reaction, see Section 5)^[224].



Scheme 41. Proposed mechanism of formation of propylene from 2-butene catalyzed by alumina-supported tungsten hydrides.

7.3.2.4. Well-Defined Silica-Supported Alkylidene Complexes

Well-Defined Silica-Supported Mo Imido-Alkylidenes. Some of the first active homogeneous metathesis catalysts were based on molecular Mo imido-alkylidene complexes of general type $\text{Mo}(=\text{NR}^1)(=\text{CHR}^2)(\text{X})_2$ (X = alkoxide, aryloxy or amide).^[454] Symmetrical $\text{Mo}(=\text{NR}^1)(=\text{CHR}^2)(\text{OR}^3)_2$ containing electron-withdrawing alkoxide ligands resulted in more active catalysts than those containing electron-donating alkoxides.^[569-570] The most active MAP (monoalkoxide-pyrrolide)^[571-575] and MAC (monoalkoxide-chloride)^[576] catalysts also implement electronic dissymmetry at the metal center — a key factor in generating highly active metathesis catalyst as discussed in Section 7.2.2.1.^[482-486]

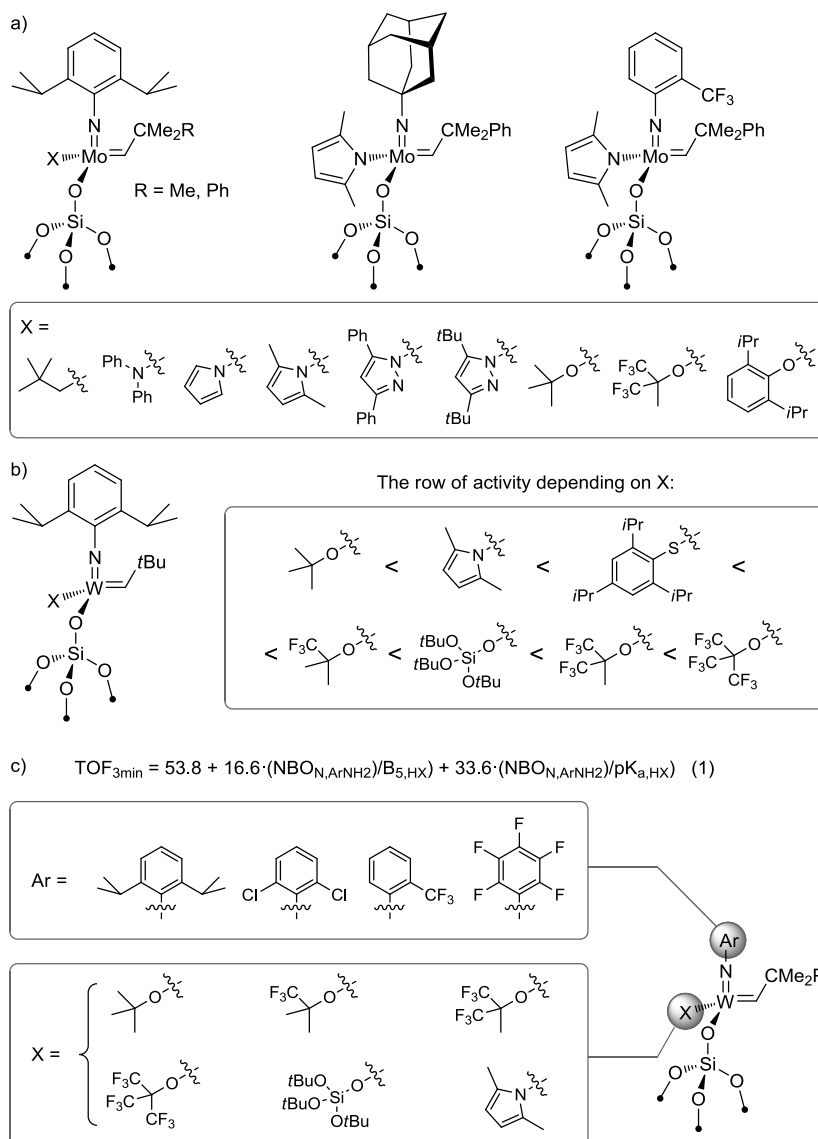
The first fully characterized heterogeneous Mo catalyst was obtained by grafting $\text{Mo}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_2$ (Ar = 2,6-*i*Pr₂C₆H₃) on SiO_{2-700} to form well-defined $(\equiv\text{SiO})\text{Mo}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$.^[543, 547] The silica-supported complex is more stable

and as active in metathesis of propene, 1-octene, and ethyl oleate as the analogous molecular siloxide model complex $((t\text{BuO})_3\text{SiO})\text{Mo}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$, and far more stable and active than the parent $\text{Mo}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_2$. However, $(\equiv\text{SiO})\text{Mo}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$ forms all butene isomers in propene metathesis. The formation of 1-butene suggests that the presence of the pendant alkyl ligand facilitates β -H transfer in the metallacycle intermediate to form olefin byproducts and induce deactivation of the catalyst (Scheme 35). This process is particularly favored in the presence of ethylene.^[483-484] Replacing the alkyl X ligand in $(\equiv\text{SiO})\text{Mo}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{X})$ by an alkoxide or amide increases the selectivity and stability of the catalysts. The family of well-defined Mo-based silica-supported imido-alkylidenes reported to date is presented in Scheme 42a and includes complexes with various amide (X = Ph₂N,^[545] pyrrolyl,^[545] 2,5-dimethylpyrrolyl (Me₂Pyr),^[544] pyrrazoly^[549]) and alkoxide (X = OtBu,^[546, 548] OC(CF₃)₂Me,^[548] O-2,6-*i*Pr₂C₆H₃^[548]) X ligands. Variation of the imido ligand provides an additional tool for tuning the activity of the catalyst.^[544] Overall, in the flow conditions of propene metathesis these catalysts can reach remarkable turnover numbers (TON) of 100,000–200,000 after 25 h with initial turnover frequencies (TOF) up to 500–800 min⁻¹. Silica-supported Mo catalysts also catalyze metathesis of functionalized olefins such as ethyl oleate. A detailed comparison of the catalytic activities of these systems can be found in Supplementary Material (Tables S1–S2). Such a dramatic improvement of the catalytic performance of supported catalysts compared to their molecular counterparts is probably associated with the decreased bimolecular decomposition due to site isolation along with dissymmetrization of the metal center upon substitution of one of the X ligands with the surface siloxy group, similarly to the effect observed for the silica-supported Re complex and the corresponding homogeneous MAP catalysts.

Well-Defined Silica-Supported W Imido-Alkylidenes. Similarly to Mo a wide series of well-defined silica-supported W imido-alkylidene complexes of general structure $(\equiv\text{SiO})\text{W}(=\text{NAr})(=\text{CHR})(\text{X})$ were prepared (Scheme 42b,c). Comparison of the performance of Mo and W complexes bearing the same ligand sets (*e.g.* for Ar = 2,6-*i*Pr₂C₆H₃ and X = CH₂*t*Bu^[550-551] or Me₂Pyr^[552]) in the metathesis of propene shows that W catalysts display higher stability than the corresponding Mo systems^[548] but are *ca.* one order of magnitude less active in terms of initial turnover frequencies (see Tables S1–S2). This behavior is associated with the formation of stable unsubstituted W SP metallacyclobutanes in presence of ethylene (Scheme 35). According to DFT calculations, SP metallacycles are the resting states in case of W,^[486] and were observed experimentally by solid-state NMR using labeled ethylene.^[552-553, 555] In fact, in the absence of ethylene $(\equiv\text{SiO})\text{M}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{OC}(\text{CF}_3)_2\text{Me})$ catalysts (M = W *vs.* Mo) show very similar activities in metathesis of internal olefin (*cis*-4-nonene).^[553]

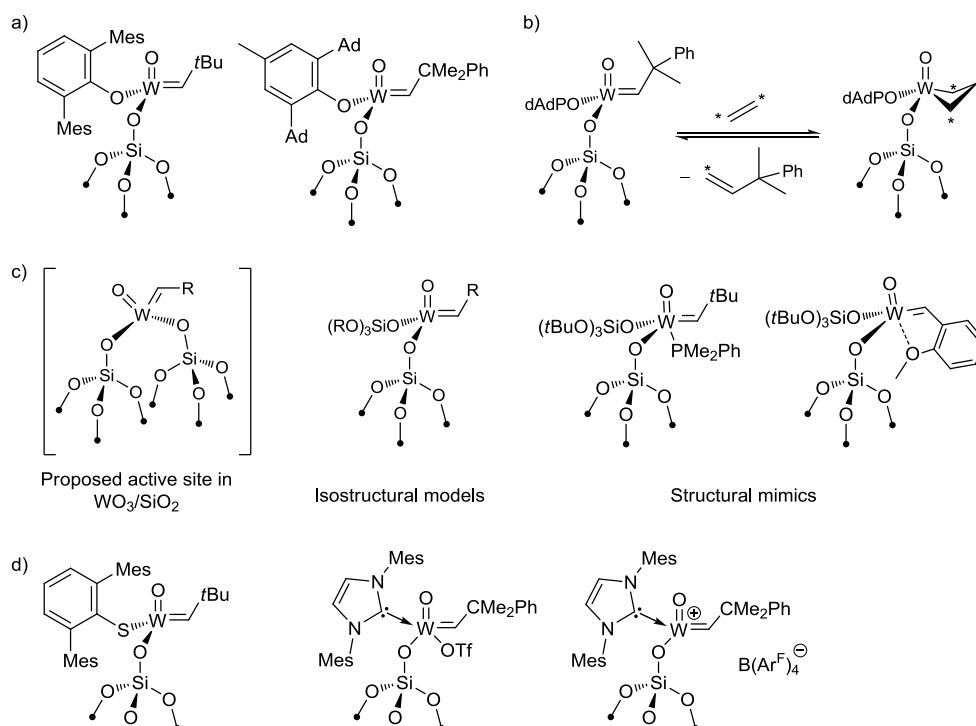
The effect of X ligand on the catalytic activity in self-metathesis of *cis*-4-nonene was investigated in a series of catalysts $(\equiv\text{SiO})\text{W}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{X})$ (Ar = 2,6-*i*Pr₂C₆H₃; X = *Ot*Bu, OC(CF₃)Me₂ (*Ot*Bu_{F3}), OC(CF₃)₂Me (*Ot*Bu_{F6}), OC(CF₃)₃ (*Ot*Bu_{F9}), OSi(*Ot*Bu)₃, SAR' (Ar' = 2,4,6-*i*Pr₃C₆H₂), Me₂Pyr; Scheme 42b).^[553-555] The observed activities are as follows: *Ot*Bu < Me₂Pyr < SAR' < *Ot*Bu_{F3} < OSi(*Ot*Bu)₃ < *Ot*Bu_{F6} < *Ot*Bu_{F9}, which parallels the decrease of the σ-donating ability of the X ligand. A systematic investigation of the influence of both the imido and X ligands in $(\equiv\text{SiO})\text{W}(=\text{NAr})(=\text{CHCMe}_2\text{R})(\text{X})$ (Ar = 2,6-*i*Pr₂C₆H₃, 2,6-Cl₂C₆H₃, 2-CF₃C₆H₄, C₆F₅; X = *Ot*Bu, *Ot*Bu_{F6}, *Ot*Bu_{F9}, OSi(*Ot*Bu)₃, Me₂Pyr; R = Me or Ph; Scheme 42c)^[555] shows that initial turnover frequencies in metathesis of *cis*-4-nonene can be correlated with the steric and electronic parameters of the parent ligands. Quantitative structure–activity relationship analysis of this wide series of well-defined heterogeneous catalysts shows that the activity is optimal when combining X

and NAr ligands of the opposite electronic character. A straightforward evaluation of the electronics and sterics of the ligands can be obtained from readily available parameters, such as NBO charge of the nitrogen atom in ArNH₂, pK_a of HX, and Sterimol B₅ parameter of X (Scheme 42c, eq. 1).^[555]



Scheme 42. a) Well-defined silica-supported Mo imido-alkylidene metathesis catalysts reported to date. b) The effect of the X ligand on the catalytic activity of $(\equiv\text{SiO})\text{W}(=\text{N}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)(=\text{CH}t\text{Bu})(\text{X})$ in *cis*-4-nonene self-metathesis. c) Evaluation of the effect of imido and X ligands on the catalytic activity of silica-supported W imido-alkylidenes in *cis*-4-nonene self-metathesis.

Well-Defined Silica-Supported W Oxo-Alkylidenes. The active sites of classical WO_3/SiO_2 catalysts are proposed to contain oxo and alkylidene moieties. The first tungsten oxo-alkylidene complex $\text{W}(=\text{O})\text{Cl}_2(=\text{CH}t\text{Bu})(\text{PEt}_3)_2$ was reported in 1980.^[577-578] However, base-free well-defined tungsten oxo-alkylidenes $\text{W}(=\text{O})(=\text{CH}t\text{Bu})(\text{OR})_2$ ($\text{R} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$ (HMT), $2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2$ (HIPT)) were only prepared recently.^[579] $\text{W}(=\text{O})(=\text{CH}t\text{Bu})(\text{OHMT})_2$ is active at room temperature with $\text{TOF}_{3\text{min}}$ of 3 min^{-1} but deactivates relatively fast. The corresponding well-defined oxo-alkylidene surface complex, $(\equiv\text{SiO})\text{W}(=\text{O})(=\text{CH}t\text{Bu})(\text{OHMT})$ (Scheme 43a),^[556] is significantly more active and stable ($\text{TOF}_{3\text{min}}$ 280 min^{-1} at 0.02 mol%; *cis*-4-nonene; batch). $\text{W}(=\text{O})(\text{CH}t\text{Bu})(\text{dAdPO})_2$ (dAdPO = 2,6-bis-adamantyl-4-methylphenoxide) contains sterically larger ligands and, when grafted on silica, forms $(\equiv\text{SiO})\text{W}(=\text{O})(=\text{CH}t\text{Bu})(\text{dAdPO})$ (Scheme 43a).^[557] $(\equiv\text{SiO})\text{W}(=\text{O})(=\text{CH}t\text{Bu})(\text{dAdPO})$ is more active than all silica-supported imido-alkylidene catalysts reported before ($\text{TOF}_{3\text{min}}$ 325 min^{-1} ; 0.02 mol%; *cis*-4-nonene; batch) and stable to 50 ppm catalyst loading. Several silica-supported complexes with structure very similar to the proposed active sites in WO_3/SiO_2 catalysts have been prepared, $(\equiv\text{SiO})\text{W}(=\text{O})(=\text{CHR})(\text{OSi}(\text{O}t\text{Bu})_3)(\text{L})$, where the siloxide ligand replaces aryloxy (Scheme 43c).^[558]



Scheme 43. a) Silica-supported W oxo-alkylidene metathesis catalysts containing bulky aryloxy ligands (HMTO and dAdPO). b) SP metallacycle formed in the reaction of $(\equiv\text{SiO})\text{W}(=\text{O})(=\text{CHCMe}_2\text{Ph})(\text{dAdPO})$ with ^{13}C labeled ethylene. c) Proposed active sites of the industrial WO_3/SiO_2 catalysts and their structural mimics prepared by SOMC. d) Silica-supported W oxo-alkylidenes containing strongly σ -donating ligands.

DFT calculations suggest that oxo-alkylidenes are better catalysts than imido-alkylidenes because deactivation by β -H transfer from the SP metallacycle (Scheme 35) is energetically disfavored in presence of oxo ligand.^[485] However, while highly active for internal olefins, $(\equiv\text{SiO})\text{W}(=\text{O})(=\text{CH}t\text{Bu})(\text{OHMT})$ and $(\equiv\text{SiO})\text{W}(=\text{O})(=\text{CH}t\text{Bu})(\text{dAdPO})$ show poor activity towards terminal olefins as a result of formation of ethylene and stable unsubstituted SP metallacycles (*vide supra*). The SP metallacyclobutane $(\equiv\text{SiO})\text{W}(=\text{O})(\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dAdPO})$ prepared by contacting the catalyst with ^{13}C labeled ethylene (Scheme 43b) shows induction behavior in *cis*-4-nonene metathesis, consistent with the rate-limiting decomposition of $(\equiv\text{SiO})\text{W}(=\text{O})(\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dAdPO})$ to form $(\equiv\text{SiO})\text{W}(=\text{O})(=\text{CH}_2)(\text{dAdPO})$ and the inhibition of catalysis by ethylene. In fact, when

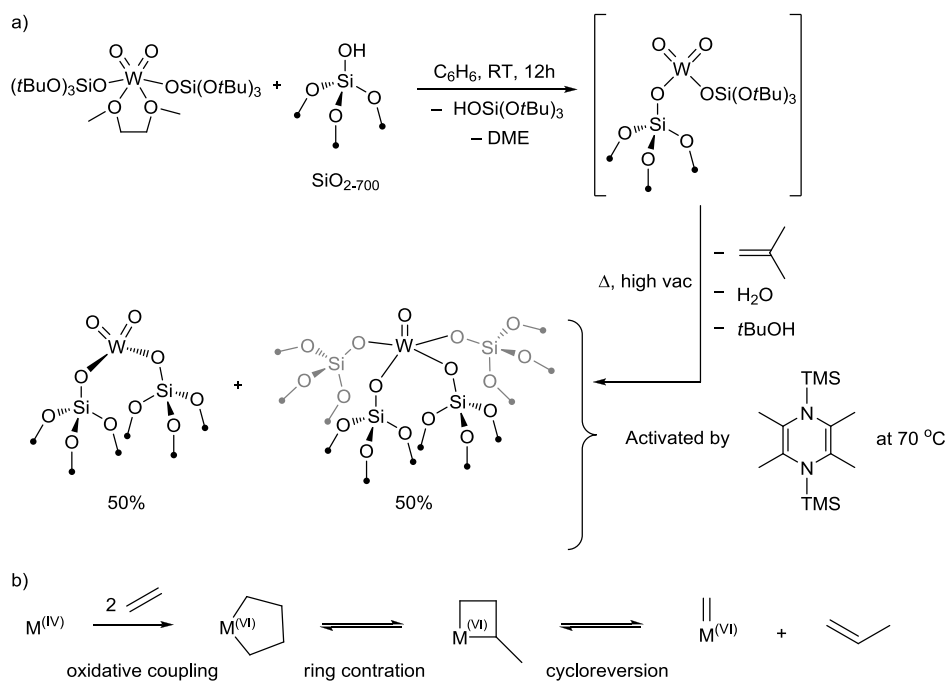
evolved ethylene is being removed from the reaction mixture by carrying out the metathesis in boiling substrate, the catalyst also shows high activity and stability in metathesis of terminal olefins (>75,000 TON for 1-hexene).

The formation of stable metallacycles can be disfavored by increasing the dissymmetry at the metal site, in particular by introducing ligands that are stronger σ -donors than surface siloxy ligand.^[482, 486] Indeed, replacing the aryloxy by isoelectronic arylthiolate ligand (Scheme 43d) led to significant improvement of the catalytic activity towards terminal olefins.^[559] Recent development of neutral and cationic W oxo-alkylidene complexes bearing strongly σ -donating *N*-heterocyclic carbene (NHC) ligand^[580] allows for generation of the corresponding silica-supported systems: $[(\equiv\text{SiO})\text{W}(=\text{O})(\text{CHCMe}_2\text{Ph})(\text{IMes})(\text{OTf})]$ and $[(\equiv\text{SiO})\text{W}(=\text{O})(\text{CHCMe}_2\text{Ph})(\text{IMes})]^+[\text{B}(\text{Ar}^{\text{F}})_4]^-$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, $\text{B}(\text{Ar}^{\text{F}})_4 = \text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4$) (Scheme 43d).^[560] The combination of strong σ -donating NHC ligand with weak σ -donating surface silanol group in the cationic $[(\equiv\text{SiO})\text{W}(=\text{O})(\text{CHCMe}_2\text{Ph})(\text{IMes})]^+[\text{B}(\text{Ar}^{\text{F}})_4]^-$ system results in remarkably high activity and stability in propene metathesis reaching over one million turnovers within 6 days.^[560]

7.3.2.5. Activation of Well-Defined Supported $\text{W}^{(\text{VI})}$ Oxo Complexes

As shown above, well-defined silica-supported W alkylidenes are highly active at room temperature, implying that the low activity and high operating temperature of the industrial WO_3/SiO_2 system (>400 °C) is due to the difficulty in generating the active oxo-alkylidene from inactive W oxo species. Well-defined $\text{W}^{(\text{VI})}$ oxo species have been recently prepared by grafting $\text{WO}_2(\text{OSi}(\text{O}t\text{Bu})_3)_2(\text{DME})$ ^[581] on SiO_{2-700} followed by thermal treatment, yielding well-defined $(\equiv\text{SiO})_2\text{W}(=\text{O})_2$ and $(\equiv\text{SiO})_4\text{W}(=\text{O})$.^[567] $(\equiv\text{SiO})_2\text{W}(=\text{O})_2$

and $(\equiv\text{SiO})_4\text{W}(=\text{O})$ are inactive in metathesis below 400 °C. However, these species can be activated at low temperature *via* treatment with organosilicon reductant 2,3,5,6-tetramethyl-1,4-*bis*(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene ($\text{Me}_4\text{-BTDP}$).^[567] More than half of $\text{W}^{(\text{VI})}$ oxo sites are reduced to $\text{W}^{(\text{IV})}$ (along with trace amounts of $\text{W}^{(\text{V})}$) after activation with $\text{Me}_4\text{-BTDP}$ at 70 °C (Scheme 44a). Exposure of the reduced material to ethylene resulted in propylene evolution, together with the observation of metallacyclopentane and metallacyclobutane species by ^1H and ^{13}C solid-state NMR. These findings indicate that oxidative coupling of ethylene followed by ring-contraction is involved in the formation of $\text{W}^{(\text{VI})}$ oxo-alkylidene species (“oxidative coupling mechanism”, Scheme 44b).^[516] This study provides a molecular rationale on how alkylidenes could form from oxo species in the classical industrial catalysts.



Scheme 44. a) Grafting and thermal decomposition of $\text{WO}_2(\text{OSi}(\text{O}t\text{Bu})_3)_2(\text{DME})$ on $\text{SiO}_2\text{-700}$. b) Proposed mechanism of the formation of alkylidene active site.

7.3.3. Relation between Well-Defined and Industrial Catalysts

In homogeneous catalysis, alkylidene species are key intermediates in olefin metathesis. The structures and activities of different alkylidene complexes are well-understood. Even though the active sites in the industrial catalysts are thought to be structurally similar to their homogeneous analogs, clear spectroscopic evidences are still missing due to the harsh operating conditions and very small amounts of active sites (<5% in general) making most spectroscopic studies hard to be interpreted. Therefore, little is known about the exact structure of active sites and the real mechanisms of their activation, propagation and deactivation. By synthesizing well-defined surface-supported catalysts through SOMC approach, one can mimic the structure of surface species or proposed active sites in industrial catalysts. Moreover, these well-defined catalysts have typically >50% and up to 100% active sites making them ideal models for spectroscopic and structure–activity correlation studies, thus providing unique opportunities for developing industrial catalysts *via* a more rational approach.

The development of well-defined supported olefin metathesis catalysts started from grafting of perhydrocarbyl molecular precursors (alkyl, alkylidene or alkylidyne), amenable to generate alkylidenes — the proposed active species in the Chauvin mechanism. In particular, well-defined alkylidene complexes have allowed understanding the origin of catalytic performance of each system, pointing at subtle ligand electronic effects. This level of molecular understanding has led to the development of homogeneous and heterogeneous catalysts with unprecedented activities. Today well-defined oxo-alkylidene W complexes, the closest in structure with the proposed active sites for WO_3/SiO_2 , display very high activity and stability at room temperature, in contrast to the industrial catalysts that work only above 400 °C unless pre-activated. This showed that oxo-alkylidene species are intrinsically very active in metathesis but are difficult to generate from oxo species. Using

organosilicon reducing agents, it is now possible to generate at low temperatures highly active species from W oxo sites through a transient reduction of $W^{(VI)}$ into highly reactive $W^{(IV)}$ sites. Such reduction processes are probably involved in industrial catalysts upon reaction with olefin at 400 °C. Therefore, well-defined model supported catalysts provide molecular understanding of industrial catalysts and enable further improvement of these systems.

8. Conclusion

Molecular-level understanding of surface sites is a key step to the detailed understanding of heterogeneous catalysts and to the more rational development of catalytic processes. SOMC has been an essential tool to bridge the gap between homogeneous and heterogeneous catalysis^[42] by applying characterization methods used in both molecular and surface science. In this review, we have shown that SOMC can also relay critical information about the possible structure of active sites in key industrial catalysts, which rely on ill-defined isolated metal sites on oxide surfaces, and that “well-defined systems” can be used to reveal subtle complexities of amorphous supports, such as the generation of strain and defect sites, thus providing information about the role of activation temperature and other factors related to elementary steps in catalyst preparation.^[582]

Thanks to many major developments in recent years, in particular in spectroscopic and microscopic methods complemented by computational modelling, SOMC has reached the maturity to bridge another gap and to help understanding and developing industrial catalysts through a more rational approach. To be noted, the major developments in operando spectroscopy,^[583] environmental microscopy,^[584-585] and solid-state NMR spectroscopy, including Dynamic Nuclear Polarization^[586] Surface Enhanced NMR Spectroscopy (DNP SENS),^[587-589] have allowed gaining unprecedented molecular level understanding of surface sites. For example, DNP SENS together with computational

chemistry provides detailed structural information about the arrangement of atoms at the surface of materials,^[590] specific structures and coordination environments^[591-593] and even 3D conformation of surface species.^[594-595] Similarly, Extended X-Ray Adsorption Spectroscopy (EXAFS) seems to be particularly well-suited to provide unique information about single-site catalysts under a broad range of operating conditions (temperature and pressure), since such catalysts contain mainly one type of surface sites,^[43] and can be complemented by other spectroscopic methods such as IR, Raman and UV-vis.^[596] While still rarely used to study single-site catalysts, operando XAS combined with complementary spectroscopic methods and computational approaches will help understanding well-defined systems and by comparison provide insights in the corresponding industrial catalysts. In particular, single-site catalysts prepared by SOMC provide ideal benchmark for both advanced spectroscopic and computational methods,^[597] a key step to ascertain possible surface structures allowing refining models. Together with surface science techniques, which are bridging the pressure gap, one can foresee that SOMC will provide molecular level understanding of surface sites of industrial catalysts that will allow the ultimate bridge between model systems and industrial catalysts.

Thanks to SOMC and advances in spectroscopy, many highly active and structurally characterized single-site catalysts have emerged, having in some cases reached activities greater than their molecular analogs. In few cases, in particular with supported metallocenes, this has translated into industrial catalysts, even if only scarce data is available in the open literature and remains industrial concealed information. However, catalysts prepared by SOMC still remain mostly laboratory curiosities. While providing unprecedented insights about the surface chemistry of many oxides and catalytic transformations, including for the corresponding industrial catalysts, there are only few examples today that have been transposed to industrial set-ups as discussed above, the

prototypical examples being single-site supported polymerization catalysts. Besides the cost, a probably more important issue that is rarely discussed in academia is the stability of single-site catalysts under industrial conditions (stability to different feeds, temperatures and other operating conditions, possibility of regeneration, ...). A critical aspect will be to render catalysts prepared by SOMC more robust and possibly amenable to simple preparation and regeneration steps, one of the key assets of classical heterogeneous catalysis. With several catalysts reaching 1'000'000 turnovers, the field is now mature enough to enter back in industry, where it started.^[21, 243, 378] One could expect courageous entrepreneurs to take the lead, foster the partnership between academia and industry, to bridge the gap between laboratory to pilot and production plant scales. All elements for success are there, and ready to develop well-defined supported catalysts in industrial settings.

9. References

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