C−H Bond Activation and Organometallic Intermediates on Isolated Metal Centers on Oxide Surfaces

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1. Introduction

The selective activation and transformation of alkanes or aromatics have been a research goal for several decades.[1−3] Today, research in this area is strongly motivated by the need to optimize resources and to shorten the number of steps, hence the direct and selective transformation of petrochemicals into valuable products is therefore of major interest. Any of these processes will have first to rely on the selective C−H bond activation. This has been the holy grail in molecular organometallic chemistry and homogeneous catalysis for some years;[1,4,5] several success stories have appeared in the past ten years,[6−9] including progress in the direct catalytic functionalization of methane into methanol.[10−13] However,

finding stable catalytic systems using acceptable operating conditions remains a challenge. In heterogeneous catalysis, several large scale industrial processes are based on the selective C−H bond activation of alkanes and lead to the synthesis of more valuable and functionalized products in a single step, for instance the direct oxidation of butane into maleic anhydride,[14−16] the dehydrogenation of propane into propene,[17,18] or the direct transformation of liquefied petroleum gas (LPG) into aromatics.[19−24]

C−H bond activation is in fact a ubiquitous process in heterogeneous catalysis. It involves various types of mechanisms and intermediates. C−H bond activation involving carbonium and carbenium ion intermediates[3,25−27] or taking place on metal particles (supported or not) or clean metal surfaces[28−35] has been extensively reviewed in the past years. Here, we will focus on processes involving C−H bond activation of alkanes and aromatics on isolated metal centers of surfaces on oxide materials leading to organometallic species and/or intermediates. The review is divided into two main sections focusing on the C−H bond activation on oxide materials and related systems (section 2) and on well-defined organometallic complexes supported on oxide materials (section 3). Section 2 is subdivided into four parts describing C−H bond activation on bulk oxides, bulk metal halides, supported transition-metal oxides, and metal-exchange zeolites.

2. Oxide Materials and Related Systems

2.1. Bulk Oxides

2.1.1. Stoichiometric C−H Bond Activation and H/D Exchange Processes

H/D exchange processes in D_2/alkane and CH_4/CD_4 mixtures are catalyzed by various metal oxides (M_xO_y), and in most cases they take place via C−H bond activation and formation of a metal-alkyl intermediate (Scheme 1a). A comprehensive study of the reactivity of oxides in H/D

Scheme 1. (a) Formation of Metal−Alkyl Intermediates by C−H Bond Activation on M−O$_S$, with O$_S$ Designating the O Atoms of the Oxide Surface and (b) Related Activation of H$_2$
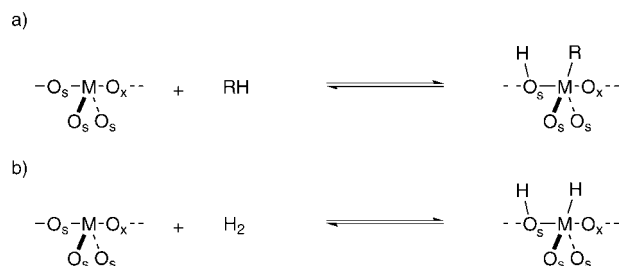
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exchange processes shows that oxide materials can be divided into four main categories:[36,37] those with (1) no activity: Nb_2O_5, MoO_3, SiO_2, SnO_2, Tb_4O_7, WO_3, and Y_2O_3, (2) low activity: CeO_2, Fe_2O_3, Mn_2O_3, and TiO_2, (3) moderate activity: Al_2O_3, CaO, Gd_2O_3, La_2O_3, MgO, Nd_2O_3, Pr_6O_{11}, Sm_2O_3, Yb_2O_3, and ZrO_2, and (4) higher activity: Cr_2O_3, Ga_2O_3, and ZnO. Note that this trend is similar to what has been observed for the activity of these oxides in hydrogenation[38−41] or in the H/D exchange reaction of a H_2/D_2 mixture (Scheme 1b).[42] This probably indicates that the active sites are likely the same in all these cases. Additionally, the primary product of the reaction of D_2 and CH_4 is CH_3D, which is in agreement with a stepwise incorporation of deuterium.[37,43] Note that the activity in H/D exchange reactions of these oxides can be related to neither the Lewis acidity nor the Lewis basicity of the oxide materials.

In particular, H/D exchange and C−H bond activation processes have been extensively studied on alumina in the past 40 years.[44−60] All these studies agree that H/D exchange takes place (1) on a small amount of surface sites (defect sites), *ca.* $0.02−0.04/nm^2$ (to be compared with an OH density of 4 OH/nm^2 after dehydroxylation at 500 °C), which are formed upon thermal treatments above 400 °C, and (2) via the heterolytic splitting of the C−H bond on highly reactive Al−O surface sites (σ-bond metathesis or ambiphilic C−H activation).[61] The most recent study combining experiment (titration, IR, and solid state NMR) and theory showed that, in the case of methane, C−H bond activation occurs on Al_{III} sites, the most unsaturated and reactive Al sites, and generates surface Al_SOH and $Al_{IV}−CH_3$ species (Scheme 2).[60] It has also been proposed that other alkanes should react in similar ways with these sites and could be further converted into alkenes.[62] Similarly to CH_4, H_2 reacts with the same $Al_{III}O$ sites but also with the less reactive $Al_{IV}O$ sites.[60]

It is probable that C−H bond activation on other oxides takes place via similar processes and involves organometallic intermediates. This includes aluminosilicates, whether amorphous or crystalline (zeolites),[59,63] which display analogous

Scheme 2. Heterolytic Splitting of H-X on Al−O_S Sites (Defect Sites): (a) X = CH_3 and (b) X = H (S = surface) and *x* = 0 or 1. (c) σ-bond Metathesis Transition State
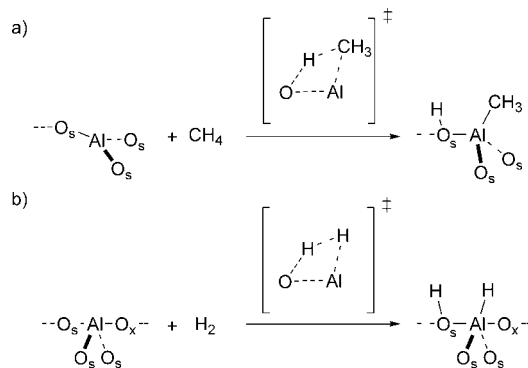

reactivity toward H_2 and alkanes. In fact, similar activation energies for the H/D exchange process were also measured. It is therefore likely that H/D exchange processes take place via heterolytic splitting of C−H and H−H bonds on highly reactive Al sites, a process involving lower activation barriers (50−80 kJ/mol) than those involving carbonium or carbenium ions (typically E_a of 120−150 kJ/mol).

Finally, the C−H bond activation of alkyl fragments can also occur during the chemisorption of organometallic compounds on alumina (grafting). While grafting typically takes place via reaction of the surface hydroxyls with the reactive M−C bond,[64−67] in the particular case of $MeReO_3$, it was shown that grafting occurred via either coordination of the oxo ligand on Lewis acid sites or C−H bond activation of the methyl group on defect sites.[68−70] This yields $[CH_3ReO_3 \rightarrow Al_S]$ and $[Al_SCH_2ReO_3]$ as the major and the minor surface species, respectively (Scheme 3a). In view of the high activity of this system in alkene metathesis and labeling experiments,[68,69,71,72] it was also shown that the μ-methylidene species $[Al_SCH_2ReO_3]$ correspond to the active sites of the catalyst (Scheme 3b). It is noteworthy that other supports such as nobia,[73] silica−alumina,[71] and zeolite[74] can be used to activate CH_3ReO_3, and one could propose that similar active species are formed on these supports via C−H bond activation of the methyl group on reactive M−O_S sites. Finally, C−H bond activation processes yielding μ-methylidene surface species have also been proposed to explain the formation of minor species in the chemisorption of $Cp_2M(CH_3)_2$ on highly dehydroxylated alumina (Scheme 3c, M = U and Th).[66,75,76]

2.1.2. Alkane Dehydrogenation on Metal Oxides

In alkane dehydrogenation, one possible reaction pathway involved the formation of a metal−alkyl intermediate, which undergoes β-H elimination and generates an alkene. Of various oxides, Ga_2O_3, whether supported or not, catalytically dehydrogenates alkanes such as ethane and propane into the corresponding alkenes in the absence of O_2,[77−81] a reactivity closely related to what is observed with Ga-exchange zeolites (*vide infra* section 2.4). Note that Cr_2O_3 or Fe_2O_3 display a much lower activity and that Al_2O_3 and SiO_2 are almost inactive for this reaction.[82,83] This order of reactivity parallels again this observed for H/D exchange reactions (*vide supra*). Moreover, it has been shown that cofeeding CO_2 typically increases both the activity and the stability of these nonoxidative dehydrogenation catalysts; possibly because CO_2 plays the role of a mild oxidant and prevents coke formation.[80,81,84,85] A detailed mechanistic investigation of the dehydrogenation

Scheme 3. (a) Formation of the Active Sites of MeReO₃/Al₂O₃ via C−H Bond Activation. (b) Formation of the Key Carbene Intermediates and Alkylidene Exchange Reaction (π-Bond Metathesis). (c) Grafting of Cp*₂M(CH₃)₂ on Dehydroxylated Alumina (M = U or Th)
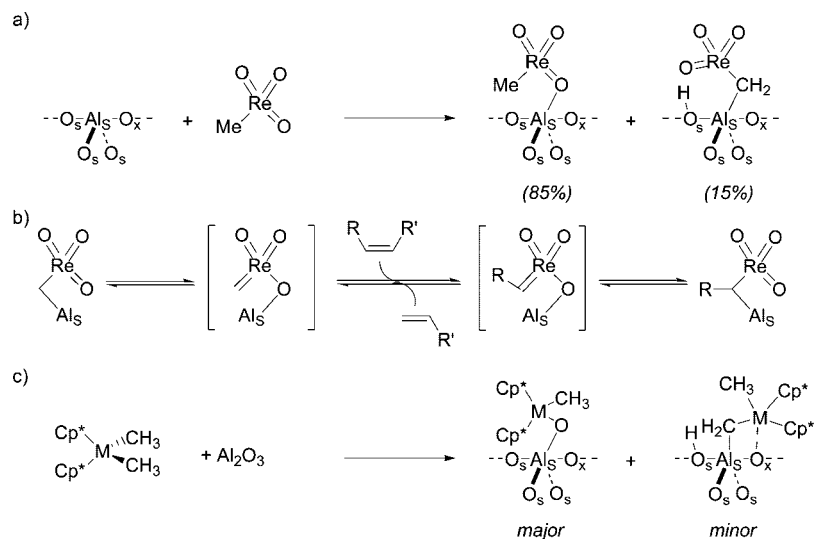

Scheme 4. Possible Mechanisms of Alkane Dehydrogenation on Ga₂O₃: (a) Formation of Alkenes; (b) Formation of H₂
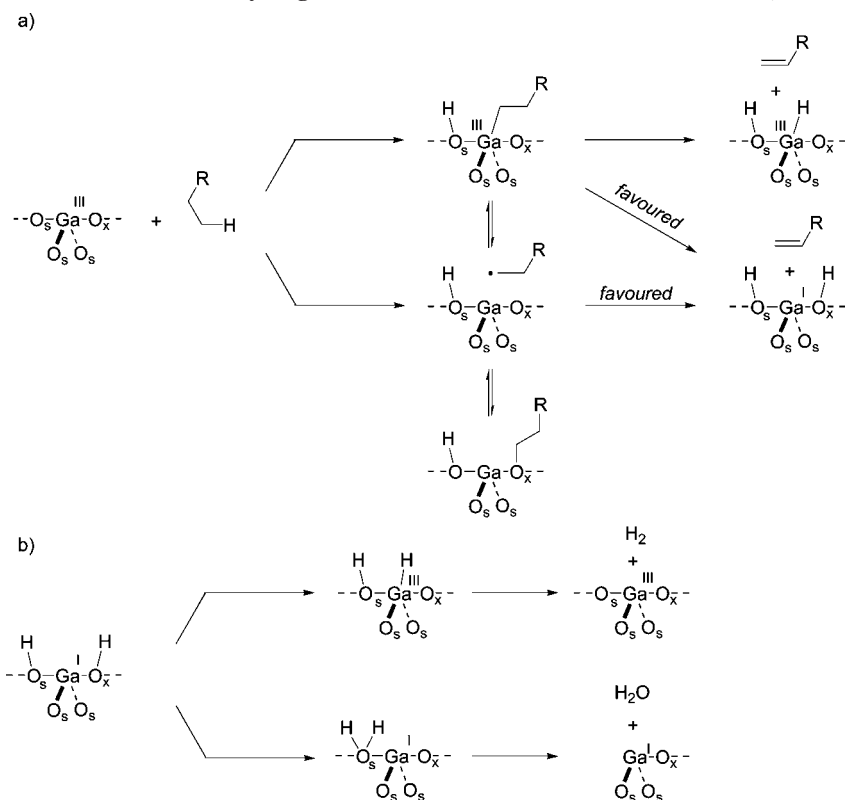
process by periodic DFT calculations shows that the C−H bond activation can take place via either heterolytic splitting on highly reactive Ga−O$_S$ or H-abstraction on a reactive O$_S$ site, leading to an adsorbed alkyl radical intermediate and a surface hydroxyl, with the latter process being slightly favored (Scheme 4).[86] Both pathways can converge toward Ga−alkyl intermediates, which were observed experimentally,[87] but the radical mechanism can also yield Ga−alkoxy species. Calculations also show that all these intermediates, i.e. the adsorbed alkyl radical and the Ga−alkyl and the Ga−alkoxy species, can readily yield propene via further H-transfer: (i) from the radical intermediate [a subsequent H-transfer by another O$_S$ atom, yielding propene and a reduced Ga-center, is preferred over the formation of Ga−H],

(ii) from the alkoxy species [H-transfer to an adjacent surface oxygen with a concomitant reduction of Ga is also favored compared to H-transfer to a surface Ga leading to Ga−H (not shown), but the most favored pathway is the cleavage of the O−C bond and the formation of the radical], and (iii) from the alkyl species [β-H transfer forming Ga−H and propene is also disfavored compared to H-transfer to adjacent O atoms].

The most likely mechanism for propane dehydrogenation into propene on Ga₂O₃ takes place via H-transfer on O sites and a concomitant reduction of surface Ga-centers. As already pointed out, metal−alkyl intermediates have been observed[87] but could only correspond to dormant species of the overall catalytic cycle. The thus-generated alkyl radical

Scheme 5. Oxidation of Butane into Maleic Anhydride on VPO Catalyst: (a) Reaction Intermediates; (b) Most Commonly Accepted Mechanism for the Formation of 2-Butene

Scheme 6

Scheme 7

E = NH for ammoxidation (O$_2$/NH$_3$)
E = O for oxidation (O$_2$)
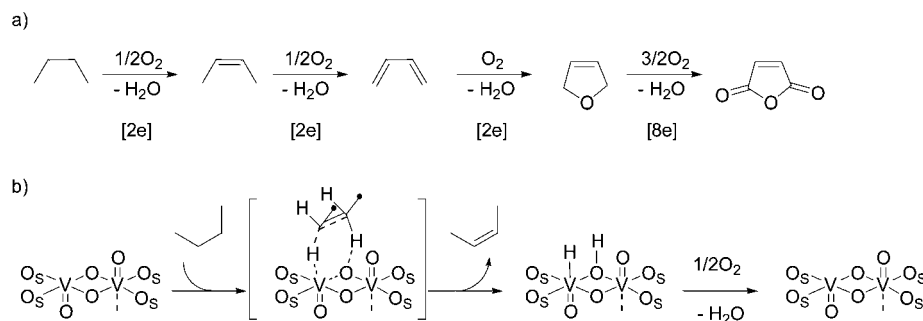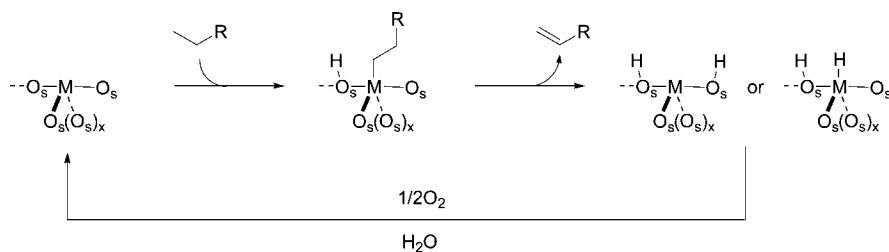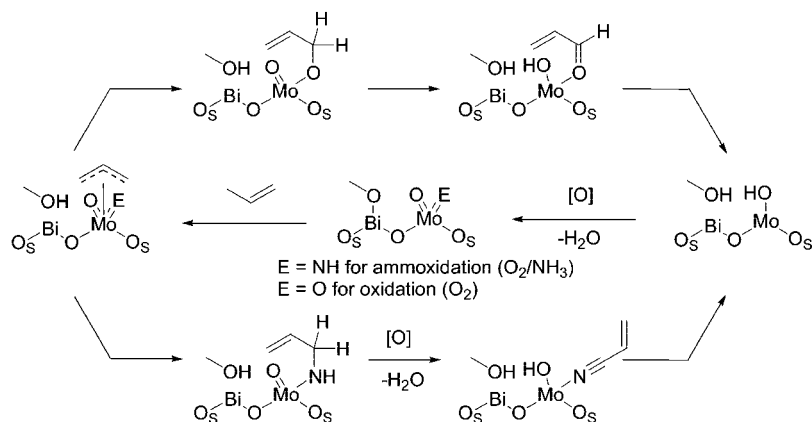
generates via H-transfer the alkene and Ga^{III}—H. This intermediate can then decompose into H$_2$ to regenerate the initial surface sites (Ga^{III}). However, H-transfer can also lead to the formation of strongly adsorbed H$_2$O: this process is easier than the formation of H$_2$, even if overall H$_2$ formation is easier than that of gaseous H$_2$O. Note that the competitive formation/desorption of H$_2$O leads to a modification of the reduction of Ga sites (Ga^{I}). This would explain the fast deactivation of Ga$_2$O$_3$ as well as the beneficial effect of added H$_2$O[88] and CO$_2$, with the former inducing H$_2$ desorption and the latter reoxidation of Ga centers.[80,81,84,85] Note that the dehydrogenation activity of Ga$_2$O$_3$ (compared to those of Al$_2$O$_3$ and SiO$_2$ for instance) could be related to the ease of formation of reduced surface species, i.e. Ga^{I}. While the dehydrogenation of alkanes on Ga$_2$O$_3$ is promising, rapid deactivation is still a major problem. Improved stabilities have been obtained by using solid solution in alumina[83] or by using supported systems.[88,89]

2.1.3. Oxidative Dehydrogenation and Selective Oxidation of Alkanes

All selective oxidations of alkanes start by C—H bond activation, which is often the rate-limiting step, and this key

step is usually an H-abstraction by surface oxygen species yielding radical intermediates, which are further transformed into the products via multiple steps, and no evidence for metal—alkyl intermediates has been found. It typically involves the *Mars van Krevelen* mechanism, i.e. the oxidation of the alkane by the metal oxide and reoxidation of the solid by molecular oxygen. This area has been comprehensively reviewed,[14−17,90−92] and only a few examples will be discussed thereafter, mainly to illustrate the current possible mechanisms involved in the C—H bond activation step.

The direct and selective conversion of alkanes into oxygenates by oxidation with molecular oxygen has been a great challenge for decades. Note that high selectivities are usually achieved for very specific substrates, which yield very stable products, e.g. propane → acrylic acid, butane → maleic anhydride, xylene → phtalic anhydride.... The most noteworthy example of this series is probably the direct conversion of butane into maleic anhydride with high selectivities (up to 97% at 65% conversion), and it is in fact a commercial process.[14,93] One of the best catalytic systems is based on vanadium phosphate (VPO), which is also used to convert selectively *o*-xylene into phtalic anhydride. Butane oxidation into maleic anhydride corresponds to a 14-electron oxidation

process and involves several key stages: formation of butenes, then butadiene, and 1,4-dihydrofuran, which is then subsequently converted into maleic anhydride (Scheme 5a).[90,94] While the actual elementary steps of such a complicated process and the nature of the active sites are still matters of debates, the rate determining step is the C−H bond activation of butane. The most commonly accepted mechanism involves the conversion of butane into 2-butenes via a concerted abstraction of two hydrogen atoms on V^{IV}−O species (Scheme 5b),[95,96] which is followed by the reoxidation of the active phase by O_2 (the *Mars van Krevelen* mechanism). Alternative mechanisms have been proposed, such as the H-abstraction of butane by activated O_2 coordinated to V^{IV} centers, which leads to strongly adsorbed 2-butene or 2-butanone, which can then be converted into butadiene via Brönsted acid catalysis.[97]

The oxidative dehydrogenation of alkanes (ODH) is also another important reaction.[98] One of the key problems is that the oxidation of the alkene product is often easier (faster) than that of the starting alkane. This consequently requires operating the process at low conversions in order to reach high selectivities. ODH can be carried out on various bulk metal oxides (e.g., V_2O_5), *albeit* in very low yield per pass. In fact, the corresponding supported systems give usually much higher activity and selectivity; they are discussed in more detail in section 2.3 (*vide infra*). Of several other systems that have been investigated, MOP (M = Ti, Zr, V, Fe),[99,100] $VMgO_x$,[98,101,102] $VSiZrO_x$,[103,104] and CrSiMO (M = Al or Zr)[105] show relatively high selectivities. In all cases, the C−H bond activation has also been identified as the rate determining step. Note again that ODH, and in particular that of ethane, necessitates relatively high temperatures (above 600 °C), for which homogeneous gas phase reactions can be predominant. It has been proposed that C−H bond activation probably leads to M−alkyl intermediates (not observed), which readily decompose to the corresponding 1-alkene by abstraction of a β-H of the alkyl chain by a surface oxygen atom (Scheme 6). An alternative concerted 2H-abstraction mechanism can be proposed by analogy with what has been proposed in the selective oxidation of alkanes on VPO catalysts (*vide supra*, Scheme 5b).[98,103] The selectivity of dehydrogenation vs formation of oxygenated products has been correlated to the distance between sites, which implies the need for site isolation.

The conversion of propene into acrolein and acrylonitrile (ammoxidation) using bismuth−molybdate catalysts is a well-known process (eqs 1 and 7),[106,107] and the corresponding ammoxidation process of propane has been developed (eq 3).[92,108] This process involves propene as a key intermediate, and the subsequent elementary steps are those of propene ammoxidation. Note however that the ammoxidation of propane requires much higher reaction temperatures (>500 °C) and longer residential time than that of propene and that the conversion of propane into propene is not catalyzed and involves mainly a gas phase reaction. In all these processes, propene, whether the reactant or generated *in situ*, is converted via a C−H bond activation involving a H-abstraction to generate a stabilized propenyl radical (Scheme 7).[109] Considering the number of subsequent steps, the selectivity is therefore a critical issue, and it relies on site isolation of active phases (note the difference with single-site catalysts): a too high density leads to combustion of propene and a too low density to the formation of allyl radical, thus leading to C_6 byproduct.[110] Several catalysts can be used, including the well-

known ammoxidation catalyst $MoBiO_x$, but more complex systems have been developed involving multicomponent oxides based on Mo−V−Nb−Ta−Sb−Te....[111−113] Similarly, the conversions of propane into acrylic (eq 4) and of 2-methylpropane into methacrylic acid (eq 5) have been studied in detail with similar types of catalysts: VPO, bismuth-molybdate catalysts, and multicompenent oxide catalysts, e.g. Mo−V−Te(Sb).[114,115]

$$\text{(1)} \quad \ce{->[O_2][-H_2O]} \quad \text{CHO}$$

$$\text{(2)} \quad \ce{->[O_2, NH_3][-H_2O]} \quad \text{CN}$$

$$\text{(3)} \quad \ce{->[O_2, NH_3][-H_2O]} \quad \text{CN}$$

$$\text{(4)} \quad \ce{->[O_2][-H_2O]} \quad \text{COOH}$$

$$\text{(5)} \quad \ce{->[O_2][-H_2O]} \quad \text{COOH}$$

$$2\ \text{CH}_4 \quad \ce{->[O_2][-H_2O]} \quad \begin{matrix} y \\ z \\ 1\text{-}2y\text{-}2z \end{matrix} \quad \begin{matrix} \diagup\diagup \\ \diagdown \\ \text{CO}_x \end{matrix} \quad \text{(6)}$$
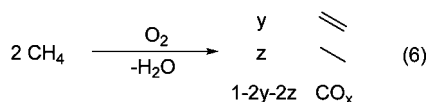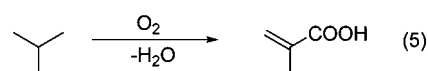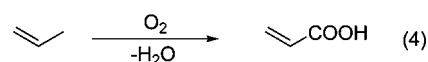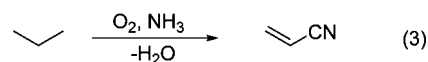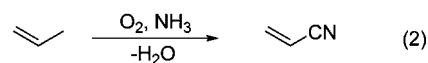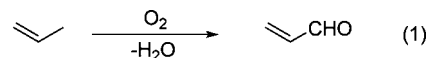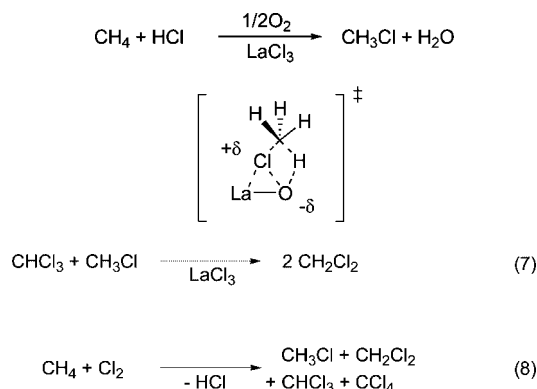
Finally, oxidative coupling of methane into ethylene has also been extensively studied (eq 6), and it is catalyzed by bulk oxides and particularly alkaline earth oxides (MgO)[116,117] or rare earth oxides (La_2O_3),[106] typically doped with alkali ions (Li).[118,119] While M−alkyl intermediates might be formed at lower temperatures,[120] the key step of this reaction is a H-abstraction, the formation of radical intermediates, and subsequent gas phase reactions.[121−123] This limits the selectivity of this reaction: currently, 80% C_2 selectivity at 20% conversion (with a projected maximum of 30% yield).[124]

2.2. Bulk Metal Halides

It is noteworthy that bulk metal halides and, in particular, $LaCl_3$ catalyze several processes involving C−H bond activation: for instance, the selective transformation of methane into chloromethane (Scheme 8)[125] and the hydrogen−chlorine exchange between chlorinated hydrocarbons; for example, $CHCl_3$ and $CHCl_3$ are transformed into $2CH_2Cl_2$ (eq 7).[126] In contrast to the chlorination of methane by Cl_2, which involves a radical chain reaction (eq 8), the reaction catalyzed by $LaCl_3$ yields selectively CH_3Cl. The conversion of methane into chloromethane, catalyzed at 400 °C by $LaCl_3$, requires HCl and O_2,[125] and the C−H bond activation occurs at the surface of the material on LaClO sites, which are generated by the partial oxidation of the surface chloride of $LaCl_3$ by O_2. The oxide is then transformed back into the chloride material by exchange with HCl, and water is desorbed. In the absence of O_2, LaClO is consumed and $LaCl_3$ becomes inactive.

Scheme 8. Selective Chlorination of Methane by HCl/O$_2$ Catalyzed by LaCl$_3$ and the Proposed C—H Bond Activation Step

$$CH_4 + HCl \xrightarrow[\text{LaCl}_3]{1/2 O_2} CH_3Cl + H_2O$$

$$CHCl_3 + CH_3Cl \xrightarrow{\text{LaCl}_3} 2\ CH_2Cl_2 \qquad (7)$$

$$CH_4 + Cl_2 \xrightarrow[- \text{HCl}]{} \begin{array}{l} CH_3Cl + CH_2Cl_2 \\ + CHCl_3 + CCl_4 \end{array} \qquad (8)$$

2.3. Supported Transition-Metal Oxides

These systems have been widely studied in the past decades, in particular because of their catalytic properties, which allow a broad range of catalytic alkane transformations: alkane dehydrogenation[18,127] and oxidative dehydrogenation as well as selective oxidation of alkanes.[98,128−131] Of several catalysts, supported group 5 and 6 metal oxides, typically VO$_x$,[101,132,133] NbO$_x$,[134] CrO$_x$,[18,127] MoO$_x$, and WO$_x$,[135] are particularly interesting. These systems are characterized by the presence of isolated sites or small clusters at a low surface coverage; with bulk oxides being formed only at higher surface coverage (above a monolayer).[106,110] Independently of the catalysts and the reactions, the C—H bond activation is often the rate determining step. We will discuss in a first part the dehydrogenation of alkanes and then in a second part both the oxidative dehydrogenation and selective oxidation of alkanes into oxygenates, because they have common reaction intermediates.

2.3.1. Dehydrogenation of Alkanes

The CATOFIN process, which is used to produce propene and isobutene from the corresponding alkanes, is performed with catalysts based on chromium oxide supported on alumina.[18,127] Despite the complexity of the surface state of the catalysts, a consensus has been emerging: the active sites probably correspond to an isolated Cr^{3+} in a pseudo-octahedral environment (Scheme 9a).[136,137] However, other active species such as small chromium oxide clusters are likely participating in the overall process. The current proposed mechanism involves the C—H bond activation on a Cr—O$_S$ bond, thus forming a Cr-alkyl intermediate, which can decompose via β-H transfer,[138,139] to form the alkene and a Cr^{III}—H surface species. While the direct elimination of H$_2$ from this species is highly disfavored, the subsequent C—H bond activation on this intermediate via a favorable σ-bond metathesis step leads to a new M—alkyl intermediate and thereby to a viable catalytic pathway (Scheme 9b). One of the problems of this process is its high endothermicity and the low associated conversion. This is compensated by the use of high reaction temperatures, which are accompanied by a deactivation of the catalyst via coke formation. Therefore, research efforts have concentrated on finding more stable catalysts using different supports (SiO$_2$, ZrO$_2$, ...)[106] or on using promoters such as CO$_2$, which can displace the equilibrium and slow down coke formation for silica supported systems.[140,141]

Scheme 9. Proposed Mechanisms of Alkane Dehydrogenation on Supported Chromium Oxides
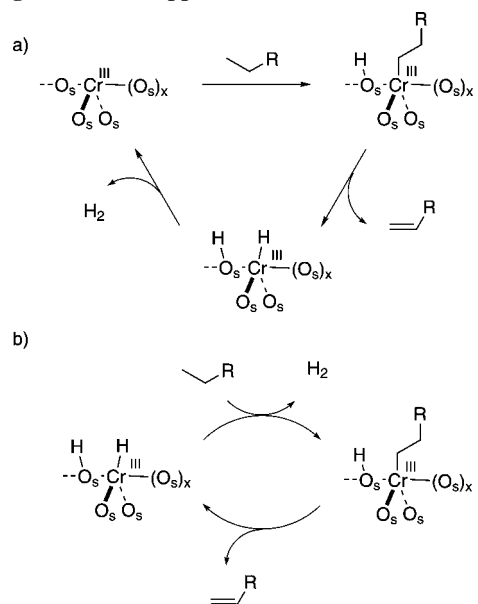

2.3.2. Oxidative Dehydrogenation and Selective Oxidation of Alkanes

It is possible to increase the yield of alkane dehydrogenation using molecular oxygen as coreactant to displace the thermodynamic equilibrium by oxidation of coproduct H$_2$ into H$_2$O.[131] However, despite years of research, the yields are still limited, and this reaction needs to operate at low conversions to avoid large amounts of overoxidation products (CO$_x$). The best catalyst used for the oxidative dehydrogenation of alkane (ODH), and typically that of propane, is based on VO$_x$ supported on oxide materials,[98,130,131,133] but MoO$_x$ supported catalysts are becoming competitive.[142−144] These types of catalysts can also be used to catalytically convert methane into oxygenates, e.g. formaldehyde, in the presence of O$_2$ or N$_2$O, *albeit* with a low yield (2−5%; high selectivity only obtained at low conversions): VO$_x$,[145−147] MoO$_x$,[148−150] WO$_x$,[151] as well as FeO$_x$.[152−154] While leading to very different products, these reactions have common reaction intermediates and have the same rate determining step, i.e. C—H bond activation.[155,156] Elementary steps for these reactions and particularly the C—H bond activation step have been a matter of debate for many years, and several reaction pathways can be proposed depending on the structure of the active sites: terminal metal oxo or μ-oxo species, isolated vs polynuclear species (Scheme 8).[157−160] First, C—H bond activation on a terminal oxo species can take place via addition of the C—H bond across the M=O bond, [2 + 2]; two approaches are possible, leading to alkyl or hydride intermediates, respectively (Scheme 10a and b). Alternatively, C—H bond activation on the terminal oxo species can lead directly to the formation of the corresponding alcohol bound to the reduced metal center (oxenoïd insertion mechanism, Scheme 10c). C—H bond activation can occur via H-abstraction, generating an alkyl radical intermediate; on bis-oxo species, typically present on MoO$_x$ systems, *syn* and *anti* approaches are possible (Schemes 10d and e). H-abstraction can also occur on μ-O bridge species (Scheme 10f). Finally, C—H bond activation can also occur via [3 + 2]- or [5 + 2]-activation for sites with gem and vicinal bis-oxo species, respectively (Schemes 10g and h). These processes involve either nonredox two-electron pro-

Scheme 10. C−H Bond Activation of Alkanes on Surface Metal Oxo Species (x = 0 or 1)

Scheme 11. (a) ODH of Propane on Silica Supported VO$_x$. (b) Proposed Mechanisms
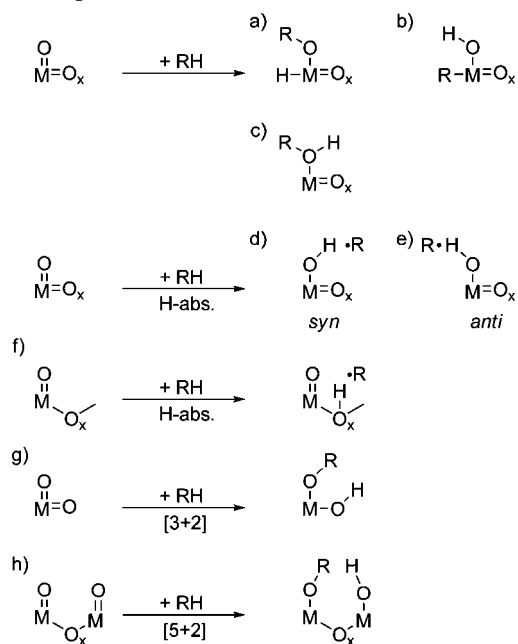
cesses (the heterolytic splitting of the C−H bond on acid−base centers), redox two-electron processes ([n + m]-processes), or a redox one-electron process generating radicals. DFT calculations on cluster models clearly show that the lowest energy barrier is usually associated with the H-abstraction process on terminal oxo species (*anti* better than *syn*) with Cr (20.0 kcal mol^{-1}) < V (35.5 kcal mol^{-1}) < Mo (45.0 kcal mol^{-1}) < W (56.8 kcal mol^{-1}).[159] However, C−H bond activation leading to a metal−alkyl intermediate (Scheme 10b) can be competitive in some cases: W (43.6 kcal mol^{-1}) < Mo (50.1 kcal mol^{-1}) < V (57.0 kcal mol^{-1}) < Cr (not found). So far, however, no metal−alkyl intermediate has been experimentally observed for these systems.

2.3.2.1. Oxidative Dehydrogenation (ODH) on Supported VO$_x$. The oxidative dehydrogenation of ethane and propane are promising processes.[131] In the specific case of the conversion of ethane into ethene, it is even competitive with steam cracking. Supported vanadium oxides are particularly noteworthy because the active sites possibly involve isolated VO species (in contrast to the other systems based on MoO$_x$ or WO$_x$). In fact, both too low and too high surface V densities are detrimental to high selectivities, and this has been associated with the combustion of the thus-formed alkenes into CO$_x$ on the support and/or the polymeric V species.[133,161−163] Such processes are particularly important for alkenes having allylic C−H bonds, e.g. propene and higher alkenes, which are more readily activated. Small clusters and particularly isolated sites on fully covered oxide surfaces have been proposed to be essential to achieve high selectivities. It is therefore not surprising that the support is an important component in the catalyst formulation, as it can more or less stabilize isolated centers, small clusters vs larger V$_2$O$_5$ crystallites. Overall, silica can be regarded as the optimal support in terms of selectivity. Another important fact is that the optimal temperature window for this process is quite narrow, and around 500 °C, lower temperatures favor combustion while unselective gas phase reactions start to be competitive at higher temperatures (>550 °C).[161,162,164] This is directly related to the easier C−H bond activation of propene, the product, which is associated with a lower
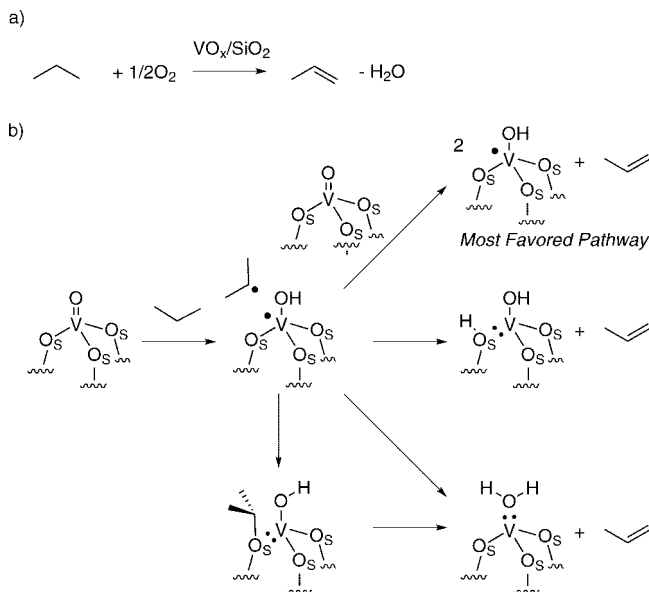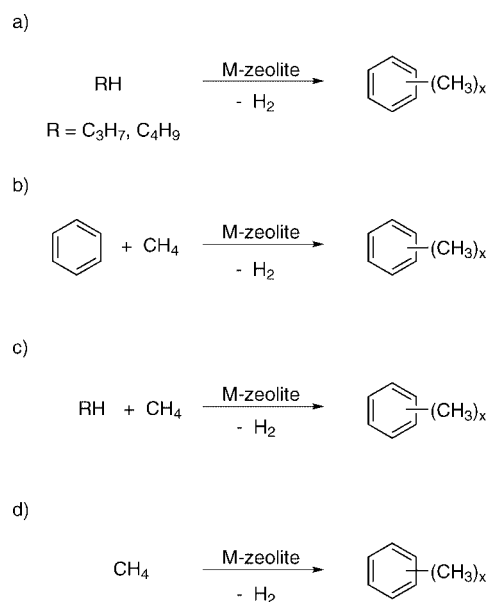
activation energy than the C−H bond activation of propane, the reactant. ODH on supported VO$_x$ also follows the typical *Mars−van Krevelen* mechanism, i.e. oxidation of the alkane with a concomitant reduction of metal oxo surface species followed by a reoxidation of the active sites by molecular oxygen and desorption of water.[165] Reoxidation of the catalyst is fast, and the rate determining step of the overall process is again the first C−H bond activation of the alkane. The terminal oxo species of V^V surface species are the most reactive O sites according to DFT calculations on a model for isolated silica supported vanadyl species (Scheme 11).[166] Similar results were obtained by periodic calculations on V$_2$O$_5$.[167,168] The most favored C−H bond activation step corresponds to a H-abstraction, which yields a radical intermediate and a reduced V^{IV}−OH species. Calculations also suggest that the formation of propene in the propane dehydrogenation is most favored via subsequent H-abstraction of the propyl radical on an adjacent isolated VO species (in place of further reduction of vanadium into V^{III}(OH$_2$)).[166,169] In all cases, reoxidation of V^{III} or V^{IV} species is always easy with O$_2$.

2.4. Metal-Exchanged Zeolites

Metal exchange zeolites (M-zeolites) have concentrated a large research effort, because of their ability to transform alkanes into alkenes and aromatics.[23,170−172] They can also be used to catalyze the alkylation of aromatics with methane,[173] the coaromatization of methane and alkanes,[174] and the direct aromatization of methane (Scheme 12).[173,175,176] While all these transformations are still subject to many mechanistic debates and detailed investigations, M−alkyl species are probably key intermediates. They are formed via C−H bond activation on isolated (M−O$_S$), dinuclear (M$_2$O$_2$), or more complex polynuclear sites (M$_x$O$_y$). These M-zeolites can be of various structures (typically identified with three letter codes: MFI, MOR, ZSM-5...)[177] and compositions, and can include a wide range of metals M, ranging from main group (Al, Ga) to transition-metal elements (Cu, Fe, Mn, Mo, Pt, W, Zn, ...). A vast research effort has focused on Ga- and Zn-zeolites because of their industrial relevance and

Scheme 12

a)

$$RH \xrightarrow[- H_2]{\text{M-zeolite}} \bigcirc(CH_3)_x$$

$$R = C_3H_7, C_4H_9$$

b)

$$\bigcirc + CH_4 \xrightarrow[- H_2]{\text{M-zeolite}} \bigcirc(CH_3)_x$$

c)

$$RH + CH_4 \xrightarrow[- H_2]{\text{M-zeolite}} \bigcirc(CH_3)_x$$

d)

$$CH_4 \xrightarrow[- H_2]{\text{M-zeolite}} \bigcirc(CH_3)_x$$

their unprecedented reactivity, and these systems will be discussed hereafter in more detail.

For instance, the Cyclar and related processes (aroforming or Z-forming) typically use Ga-zeolite to convert in a single step liquefied petroleum gas (LPG), composed of propane and butane, into H_2 and liquid aromatics, i.e., benzene, toluene, and xylenes.[19–24] Conversion of alkanes into aromatics takes place via successive dehydrogenation, oligomerization, and cyclization steps. While all these steps are not fully understood, Ga-zeolites act as a multifunctional catalyst, and one of the key steps, the formation of alkenes from alkanes, takes place at Ga sites and involves a C–H bond activation and formation of a Ga–alkyl intermediate. Ga-zeolites are also known to activate H_2[178,179] and alkanes and to catalyze H/D exchange reactions.[20] In all cases, the active sites probably result from charge-compensation of framework aluminum by mononuclear Ga ([Ga$^+$],[180,181] [Ga(=O)$^+$][180,182–184]) or dinuclear species [Ga$_2$O$_2{}^{2+}$] (Figure 1).[185–187] These species correspond to highly Lewis acidic centers, which can readily polarize and activate the C–H bond of alkanes as well as H_2 to generate Ga–R (or Ga–H) and OH surface species (Scheme 13). Model studies show that [Ga$^+$]-species have a relatively low activation barrier for C–H bond activation of ethane via heterolytic splitting followed by a rearrangement into [Ga(H)(Et)$^+$] and then the concomitant elimination of H_2 and ethene (Scheme 13a).[181] C–H bond activation on [Ga(O)$^+$] generates [Ga(R)(OH)$^+$]-species,

which can readily generate ethene and [Ga(H)(OH)$^+$]-species. However, the latter species are not prompt to eliminate H_2 to regenerate [Ga(O)$^+$], but H_2O instead, leading to a reduction to Ga$^+$ species (Scheme 13b). This shows that [Ga(O)$^+$] is probably not the active site of choice for dehydrogenation.[188] More recent experimental and computational studies point toward dinuclear Ga species as active sites (Scheme 13c), for which all steps are favored.[186,187] In particular, the easier desorption of H_2 is noteworthy and probably results from the presence of less basic O sites in the dinuclear Ga$_2$O$_2{}^{2+}$ core with respect to this of the Ga$^+$ or GaO$^+$ site.

Zn-zeolites display a very similar reactivity pattern: H_2 and alkane activation, H/D exchange, formation of aromatics from alkanes,[189,190] and the coaromatization of methane and alkane.[173] Note also that Zn-zeolites probably contain similar dinuclear structures [Zn$_2$O$_2$] (Scheme 13c).[178,179,191–197] Alkane activation (including methane) also occurs via C–H bond activation and formation of metal–alkyl intermediates, which have been experimentally observed on different Zn-zeolites.[179,195,196,198,199] Of several studies on the H/D exchange reaction of D$_2$/alkane mixtures on various Zn-zeolites,[20,200–202] a recent comparative study of H- and Zn-zeolite (zeolite = BEA) shows that Zn-BEA displays a much lower activation energy and higher rates (ca. 2 orders of magnitude) than the corresponding H-zeolite,[201] which clearly shows that the reaction mechanisms are different for the two systems, i.e. carbonium ion for H-BEA vs metal–alkyl intermediates for Zn-BEA. M-exchange zeolites and particularly those containing Mo or even Zn also catalyze the direct conversion of methane into benzene and H_2 with a high selectivity (>90%).[170,172,175,176] While the structure and the nature of the active sites are still a matter of debate, it is accepted that methane is first converted into ethylene, which is then converted into benzene through acid catalysis. Several mechanisms have been proposed for the first step involving the formation of ethylene, and they involve the following: (1) carbocations, (2) radicals, or (3) organometallic intermediates, and more specifically alkylidenes, alkylidynes, or carbides.[203] Several experiments are consistent with the formation of Mo$_2$C and imply that it could be the active species or a precursor of the active species.[204,205] It is therefore possible that C–H bond activation on MoCx species leads to the growth of an alkyl chain and the formation of alkenes, similarly to what is observed in the nonoxidative coupling of methane on silica supported tantalum hydrides (*vide infra*, section 3.4).[206] Finally, besides C–H bond activation, it is noteworthy that stable σ-RH complexes could be observed for Cu-ZSM5 (Figure 2).[207,208] From these studies, it is clear that metal–alkyl

[(Ga$^+$)$_2$]^{II} [(GaO$^+$)$_2$]^{II} [(Ga$_2$O$_2$)$^{2+}$]$^{II-SP}$

H Ga O Al Si
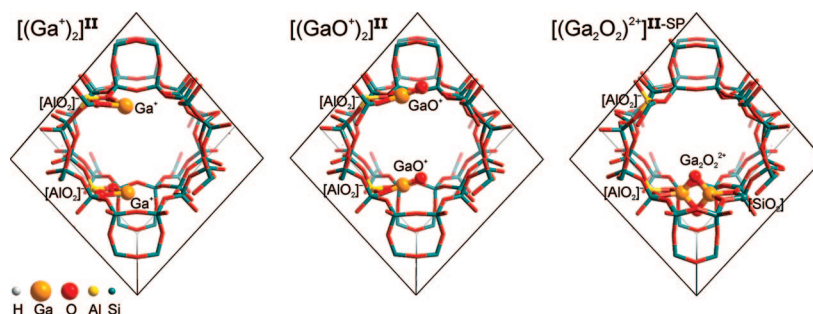
Figure 1. Computational models for Ga$^+$, GaO$^+$, and [Ga$_2$O$_2$]$^{2+}$ sites of a Ga-zeolite, e.g. zeolite = MOR. Adapted from ref 186 with the help of the authors. Copyright 2009 Royal Society of Chemistry.

Scheme 13. Dehydrogenation of Alkanes on Ga-Zeolites: (a) Ga⁺ Active Sites, (b) Ga=O⁺ Active Sites, and (c) Ga₂O₂ Active Sites
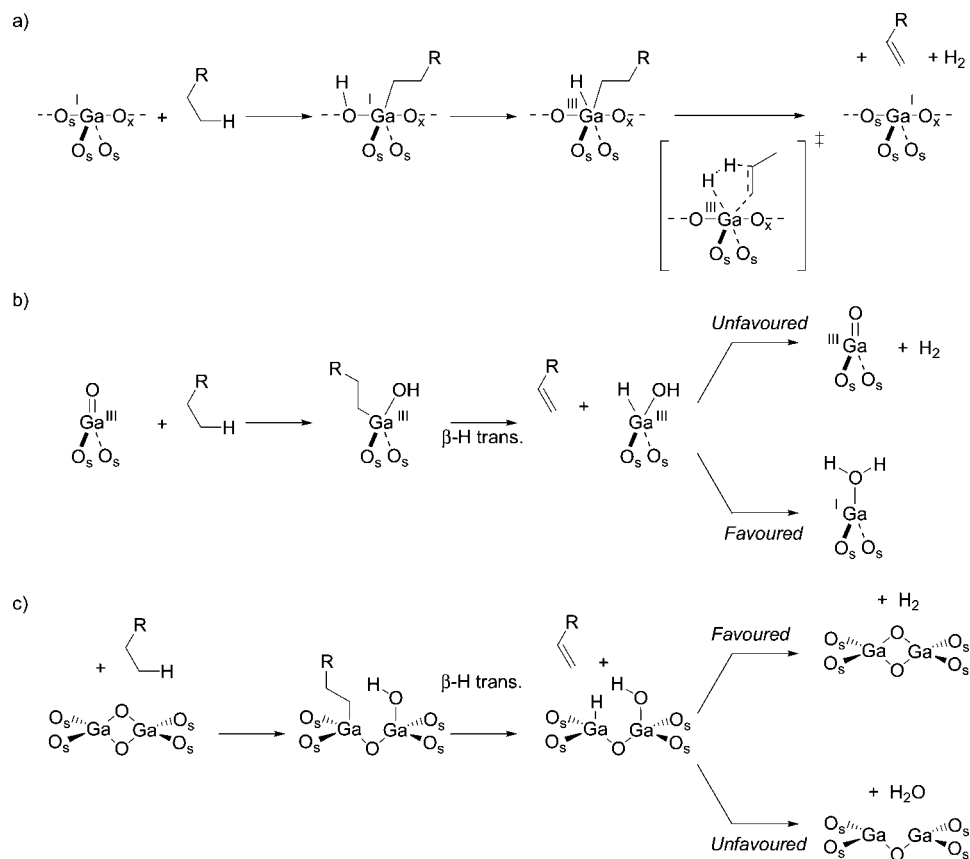
surface complexes are key reaction intermediates in the dehydrogenation/aromatization processes catalyzed by M-zeolites.

Under oxidizing conditions, metal-exchange zeolites, and, more specifically, those containing MoO_x and WO_x, catalyze the direct oxidation of methane into methanol/formaldehyde and related oxidation processes (see section 2.2).[209−212] Here, it is probable that C−H bond activation takes place similarly to what has been proposed for MoO_x and WO_x supported on oxide materials (vide supra, section 3), i.e. via H-abstraction and a radical mechanism. Moreover, Fe-zeolites are also noteworthy: they catalyze the direct and selective oxidation of benzene into phenol by N_2O.[213−215] While this reaction corresponds to the selective functionalization of an aromatic C−H bond, several mechanisms are possible, such as the direct insertion of O in the C−H bond of benzene or the

Scheme 14. (a) Selective Oxidation of Benzene into Phenol by N₂O Catalyzed by Fe-Zeolites; (b) Mechanism via Direct C−H Bond Activation; (c) Mechanism via Epoxidation
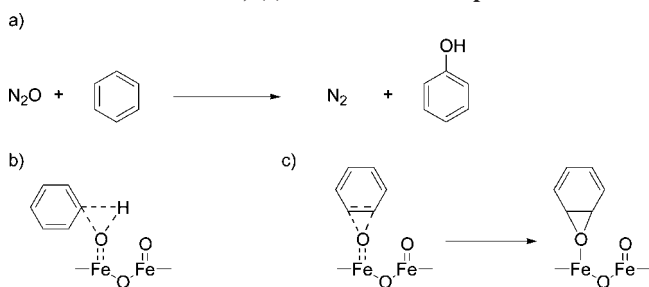
epoxidation followed by an acid catalyzed rearrangement of the unstable epoxide into phenol (Scheme 14). With methane, however, the reaction is stoichiometric, yielding stable MeO−Fe surface species, which can only yield methanol (in a stoichiometric way) upon extraction.[216]

3. Well-Defined Organometallic Complexes Supported on Oxide Materials

The controlled reaction of molecular organometallic complexes on oxide surfaces yields well-defined organometallic complexes grafted on oxides with a variety of ligands such as hydrides, alkyls, alkylidenes, and alkylidynes, which are able to react with the C−H bond of alkanes.[217] Here, we will discuss in detail stoichiometric and catalytic processes involving C−H bond activation.
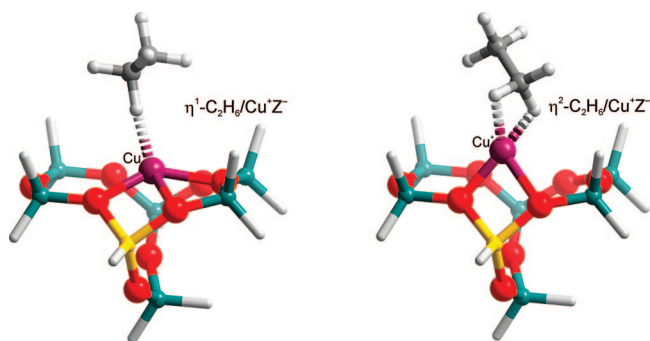

Figure 2. Computational models for σ-alkane Cu complexes in zeolites. Adapted from ref 208 with the help of the authors.

3.1. Stoichiometric C—H Bond Activation and H/D Exchange Processes

### 3.1.1. Activation of Alkanes on Silica Supported Metal Hydrides

M-alkyl surface fragments are readily formed upon the C—H bond activation of alkanes on silica supported metal hydrides. For instance, the silica supported zirconium hydrides[218−222] react with a wide range of alkanes, e.g., CH_4, C_nH_{2n+2}, and cycloalkanes, at low temperatures to yield the corresponding metal alkyl complexes and H_2,[223] as observed with analogous molecular d^0 complexes (Scheme 15a).[224] In particular, C—H bond activation of propane is faster on primary carbons and yields the most stable n-propyl surface species along with the isopropyl surface species as the minor isomer.[225] This reaction takes place via σ-bond metathesis, which formally corresponds to the transfer of a proton from the alkane to the Zr-hydride. Here, the transition state has a quasi triangular shape with an almost linear arrangement of the C atom and the two H atoms.[226−230]

The most recent spectroscopic investigations showed that the silica supported zirconium hydrides were a mixture of mono- and bis-hydrides (Scheme 15b),[231] and the study of their relative reactivity toward CH_4 showed that the bis-hydride is much more reactive,[232] which is consistent with calculations.[230] Additionally, these species catalyze H/D exchange in H_2/D_2 or CH_4/D_2 mixtures via a stepwise insertion of deuterium (Scheme 15c−e), with the former being very fast, even at temperatures below room temperature.[233] Computational studies have shown that the reaction pathway is probably a two-step mechanism involving C—H bond activation via σ-bond metathesis, thus forming a metal−alkyl intermediate, followed by hydrogenolysis (the reverse step), which regenerates the metal hydride and incorporates deuterium in the alkane (Scheme 15d).[228] A direct one-step reaction pathway is highly disfavored ($E_a > 65$ kcal mol^{-1}), because it involves a four-center transition state with a carbon in the β-position (Scheme 15e).[227]

The related silica supported tantalum hydrides are prepared in a similar way. They are mixtures of surface species (Scheme 16a), and current data are consistent with the presence of mono- and tris-hydride species.[234] This system displays a similar reactivity to zirconium hydrides, i.e. the low temperature activation of alkanes and H/D exchange reactions, through very likely the same mechanism, σ-bond metathesis (Scheme 15c and d, M = Ta).[235−238] Nonetheless, in the specific case of cycloalkanes, the cycloalkyl surface species evolved toward more highly unsaturated species through dehydrogenation processes. For instance, activation of cyclopentane yields a well-defined silica supported cyclopentandienyl tantalum species,[238] which involves successive C—H bond activation processes (Scheme 16b).[239,240] In the case of methane, it leads to the formation of Ta—CH_3, Ta=CH_2, and Ta≡CH species (Scheme 16c).[234] Computational studies suggest that the tris-hydride Ta species is probably the active species and activates alkanes via σ-bond metathesis.[241]

Finally, alumina supported Th hydride species, generated by treatment under H_2 of Th(allyl)$_4$ supported on dehydroxylated alumina, catalyze H/D exchange reaction of a D_2/alkane mixture (3−4 bar of D_2 and alkane/Th ratio = 1000, Scheme 17a and b).[242] This reaction is fast, with rates of 800−1200 h^{-1}, and is slightly selective for terminal C—H bonds (Scheme 17c). Overall, the incorporation of deuterium is not
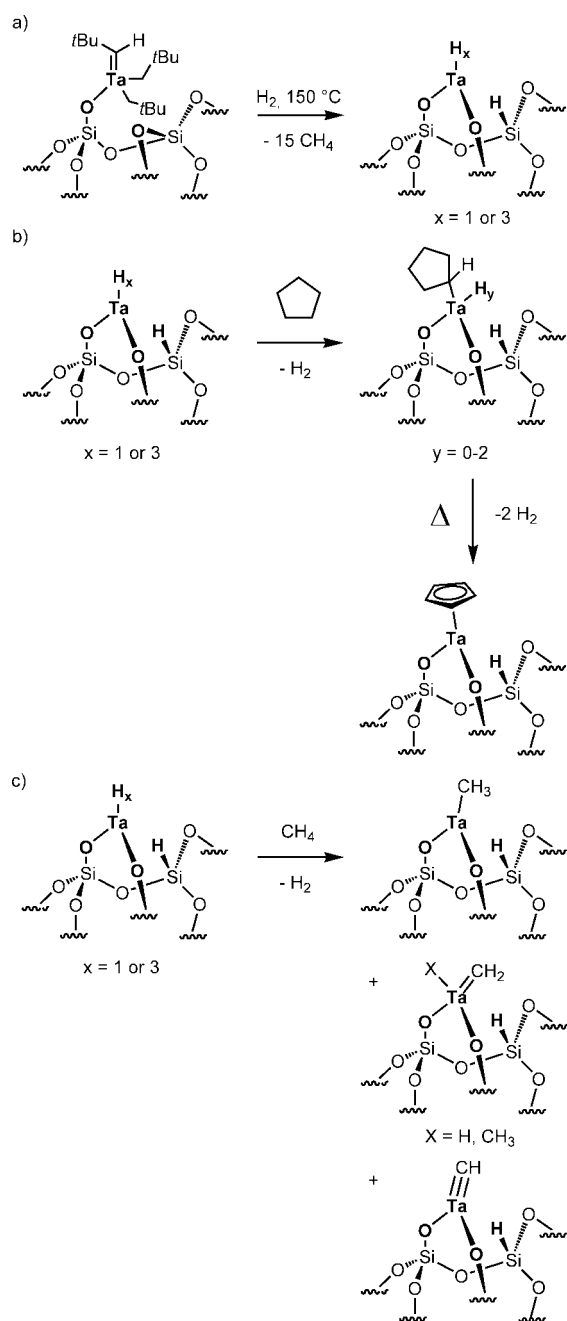
Scheme 15. (a) C—H Bond Activation of Cycloalkanes on Silica Supported Zirconium Hydrides [Zr—H]; (b) Formation and Structure of [Zr—H]; (c) H/D Exchange Reaction Catalyzed by [Zr—H] (M = Zr); (d) Stepwise Mechanism (Favored); (e) One-Step Mechanism (Unfavored)
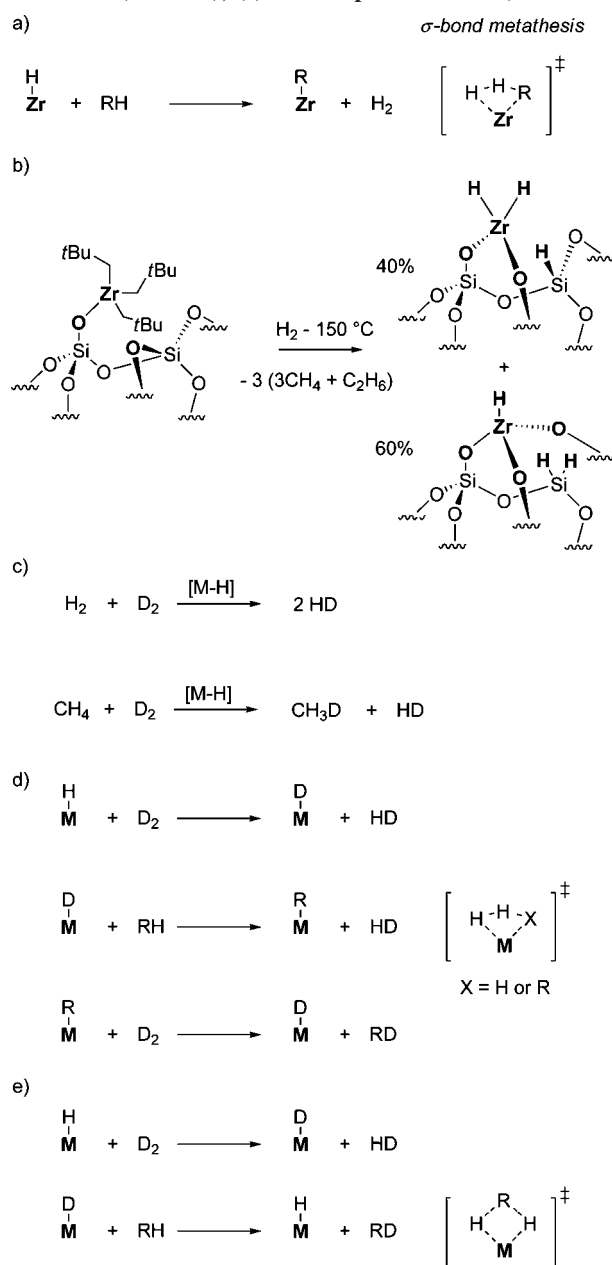
selective, and dimethylcyclohexanes undergo cis−trans isomerization during the H/D exchange process, probably via β-H transfer and a chain walking mechanism (Scheme 17d).

Like metal-hydride, metal-alkyl and metal-aryl species can activate C—H bonds, leading to the exchange of perhydrocarbyl ligand.[224,243,244] While not directly evidenced experimentally, computational studies suggest that the methyl/methyl exchange of the d^0 zirconium methyl species in the presence of methane can readily take place via σ-bond metathesis (Scheme 18a).[228] Similarly, the silica supported Ir-complex (≡SiO)Ir(Ph)(PMe$_3$)Cp* reacts with benzene to exchange its phenyl ligand, like its molecular equivalents (Scheme 18b).[245]
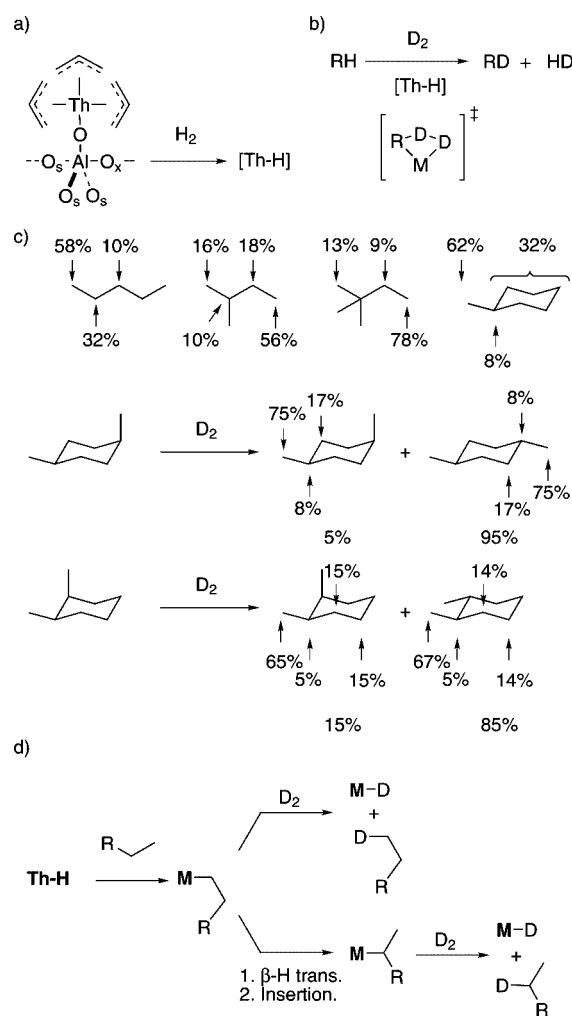
Scheme 16. (a) Formation and Structure of the Silica Supported Tantalum Hydrides [Ta−H]; (b) Reaction of [Ta−H] with Cyclopentane; (c) Reaction of [Ta−H] with CH₄

Scheme 17. Alumina Supported Th Hydrides and H/D Exchange Reactions: (a) Formation of [Th−H]; (b) H/D Exchange of D₂/Alkane Mixtures; (c) Selectivity in Isotopomer; (d) Chain Walking Mechanims of Incorporation of D at Different Positions of an Alkane


3.1.2. Activation of Alkanes on Silica Supported Metal Alkylidenes and Alkylidynes

Surface metal alkylidene species are typically formed via decomposition of bis-alkyl intermediates via α-H abstraction,[246] and the reverse step corresponds to the C−H bond activation of an alkane onto a M=C bond.[247−250] Evidence for this process has been obtained in the metathesis of alkane (CH₃CH₂R) on various well-defined metal neopentyl neopentylidene species (M = Ta,[251,252] Mo,[253,254] W,[255] and Re[254]) through the formation of cross-metathesis products with the following selectivity *t*BuCH₃ > *t*BuCH₂CH₃ > *t*BuCH₂CH₂R, while the coupling product, *t*BuCH₂CH₂CH₂R, is not detected (Table 1, entries 1−9). Note that the formation of these products requires neopentyl neopentylidene surface species and an alkane of general structure RCH₂CH₃. This implies

Scheme 18. (a) Methyl/Methane Exchange on a d⁰ Metal, e.g. M = Zr; (b) Phenyl/Benzene Exchange on Ir
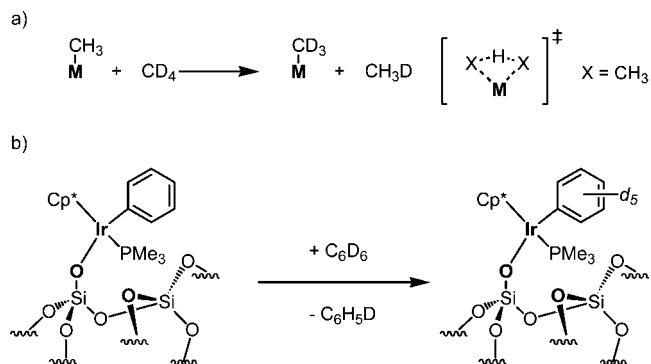
that both the neopentyl and the neopentylidene ligands are important and that β-H transfer is probably a key step. These products probably result from a stepwise mechanism involving known elementary steps of molecular organometallic chemistry (Scheme 19, R₁ = R₂ = *t*Bu): (i) C−H bond activation of RCH₂CH₃ on the metal alkylidene, thus forming an intermediate with three pendant alkyl ligands [M(CH₂*t*Bu)₂(CH₂CH₂R)],[247−250] of which one has a β-H; alternative mechanisms are possible involving the replacement of the alkyl ligand via σ-bond metathesis or the

Table 1. Quantity of Cross-Metathesis Products (equiv./M) in the Reaction of Propane with Well-Defined Alkylidene and Alkylidyne Supported Species

entry	supported metal complexes	alkane	cross-metathesis products tBuCH$_2$X			
			X = H	X = Me	X = Et	X = Pr
1	($\equiv$SiO)Ta(=CHtBu)(CH$_2t$Bu)$_2$	ethane	0.84	0.27	a	a
2	($\equiv$SiO)Ta(=CHtBu)(CH$_2t$Bu)$_2$	propane	1.05	0.30	0.11	a
3	($\equiv$SiO)Ta(=CHtBu)(CH$_2t$Bu)$_2$	2-methylpropane	1.09	0.44	a	b
4	($\equiv$SiO)Ta(=CHtBu)(CH$_2t$Bu)$_2$	butane	1.01	0.22	0.16	0.04
5	($\equiv$SiO)Ta(=CHtBu)(CH$_2t$Bu)$_2$	2,2-dimethylpropane	a	a	a	a
6	($\equiv$SiO)Mo(NAr)(=CHtBu)(CH$_2t$Bu)	propane	0.82	0.34	0.10	a
7	($\equiv$SiO)Mo(NAr)(=CHtBu)(NR$_2$)	propane	a	a	a	a
8	($\equiv$SiO)W(NAr)(=CHtBu)(CH$_2t$Bu)	propane	0.68	0.42	0.20	a
9	($\equiv$SiO)Re($\equiv$CtBu)(=CHtBu)(CH$_2t$Bu)	propane	0.50	0.59	0.22	a
10	[($\equiv$SiO)W($\equiv$CtBu)(CH$_2t$Bu)$_2$]	propane	a	a	a	a
11	[(Al$_S$O)W($\equiv$CtBu)(CH$_2t$Bu)$_2$]^c	propane	0.40	0.02	a	a
12	[($\equiv$SiO)$_{SiO2\text{-}Al2O3}$W($\equiv$CtBu)(CH$_2t$Bu)$_2$]^d	propane	0.50	0.04	a	a

^{a} Not detected, <0.01 equiv. ^{b} 2,2,4-Trimethylpentane detected in very small amounts (<0.01 equiv). ^{c} Supported on alumina. ^{d} Supported on silica−alumina.

Scheme 19. Reaction of Alkanes (RCH$_2$CH$_3$) with Alkyl Alkylidene Metal Surface Species, M(=CHR$_1$)(CH$_2$R$_2$): (a) C−H Bond Activation; (b) Rearrangement; (c) Formation of Cross-metathesis Products

yields two sets of products [M(=CHR)(H)]/tBuCH=CH$_2$ and [M(=CH$_2$)(H)]/tBuCH=CHR; (v) subsequent alkene insertion into the metal alkylidene hydride intermediates, C−H bond activation, and decomposition, generating [M(=CHR)(CH$_2$R)] and [M(=CH$_2$)(CH$_2$R)] along with the cross-metathesis products tBuCH$_2$CH$_3$ and tBuCH$_2$CH$_2$R (Scheme 19c). The higher selectivity of tBuCH$_2$CH$_3$ compared to that of tBuCH$_2$CH$_2$R would be the consequence of the more facile approach in the [2 + 2]-cycloaddition step of the alkene in the former case (1,3) compared to the latter (1,2), which is consistent with what is observed in the cross-metathesis of propene and well-defined neopentylidene surface complexes (formation of about a 3 to 1 ratio of tBuCH=CH$_2$ and tBuCH=CHMe).[256−259]

Finally, the reaction of propane with silica−alumina and alumina supported bisalkylalkylidyne W systems, namely [(Al$_S$O)W($\equiv$CtBu)(CH$_2t$Bu)$_2$] or [($\equiv$SiO)$_{SiO2\text{-}Al2O3}$W($\equiv$CtBu)-(CH$_2t$Bu)$_2$],[260−262] also yields the cross-metathesis products tBuCH$_3$ and tBuCH$_2$CH$_3$ as well as tBuCH$_2$CH$_2$CH$_3$. Nonetheless, the relative ratio of these products is very different from what is obtained by the alkyl alkylidene species and in particular the low selectivity of tBuCH$_2$CH$_2$CH$_3$ (Table 1, entries 10−12). This probably shows that the mechanisms of formation of these products differ, and could result from with C−H bond activation of propane on the metal-alkylidyne species as recently demonstrated in molecular systems.[263−265] However, recent DFT calculations suggest that C−H bond activation on these alkyl alkylidyne complexes is a high energy process, and an alternative mechanism has been proposed, which involves the formation of alkene on alumina site by dehydrogenation (*vide supra* section 2.1) and alkene metathesis on a bis-alkylidene intermediate.[62]

3.1.3. Intramolecular C−H Bond Activation Processes

Thermal decomposition of bis-alkyl surface species leads to formation of well-defined silica supported metal alkylidene complexes via α-H abstraction. This elementary step involves the intramolecular activation of the C−H bond at one of the alkyl ligands in the α-position by an adjacent ligand (here another alkyl), which corresponds to an intramolecular version of a σ-bond metathesis process.[246,266] This process is typically observed upon the grafting of molecular alkylidene complexes on silica surfaces, e.g. Ta and Re,[267−269] which first react with the surface silanols via [1,2]-addition, yielding bis-alkyl species before decomposing into the alkylidene (Scheme 20a). Note however that other grafting

formation of an alkylidyne ligand prior to C−H bond activation (Scheme 19a); (ii) decomposition of this intermediate via α-H abstraction leading to tBuCH$_3$ and a neopentylidene alkyl intermediate [M(=CHtBu)(CH$_2$CH$_2$R)] (Scheme 19b); (iii) further decomposition via β-H abstraction, generating neopentylidene hydride intermediates [M(=CHtBu)-(H)] and RCH=CH$_2$; (iv) disproportionation of these intermediates via [2 + 2]-cycloaddition and cycloreversion, which
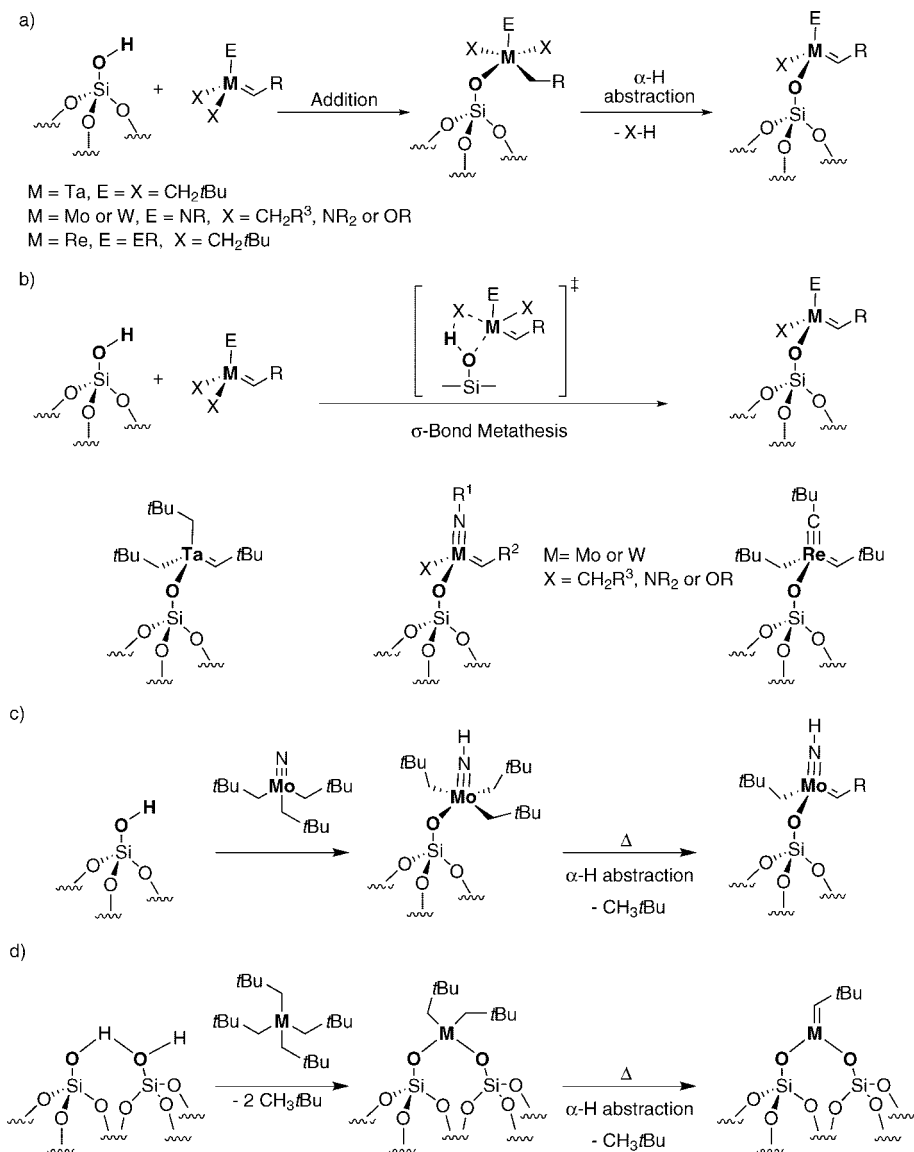
Scheme 20. Formation of Alkylidene from Bis-alkyl Surface Species via: (a) Addition of an O−H on the Alkylidene Moiety Followed by α-H Abstraction, (b) σ-Bond Metathesis, (c) Addition of an O−H on a Nitrido Moiety Followed by α-H Abstraction, and (c) Formation of a Bis-alkyl Species Followed by α-H Abstraction


pathways have been encountered; for example, grafting of Mo and W alkylidene complexes usually takes place via the direct electrophilic cleavage of σ-bonded ligands (Scheme 20b).[258,259,270] Note also that [(tBuCH$_2$)$_3$Mo(≡N)] reacts with surface silanols to generate [(≡SiO)Mo(=NH)(CH$_2$$t$Bu)$_3$], which probably decomposes into the putative surface complex [(≡SiO) Mo(=NH)(=CHtBu)(CH$_2$$t$Bu)], as evidenced by the evolution of tBuCH$_3$ and the high activity of this species in alkene metathesis (Scheme 20c).[271,272] The α-H abstraction process has also been observed upon the thermal treatment of bis(alkyl) surface species [(≡SiO)$_2$M(CH$_2$R)$_2$] (M = Ti, Zr, and Cr; Scheme 20d), which yields [(≡SiO)$_2$M(=CHR)].[273−275] Finally, the mechanism of grafting [Os(=CHtBu)$_2$(CH$_2$$t$Bu)$_2$], a d^2 complex, is also noteworthy and leads to [(≡SiO)-Os(≡CtBu)(CH$_2$$t$Bu)$_2$] via isomerization of the metal fragment from a bis-alkylidene into an alkyl alkylidyne complex (Scheme 21a).[276] One of the key steps involves an intramolecular C−H bond activation process, α-H transfer, to transform the bis-alkylidene into an alkyl alkylidyne fragment. Experimental and theoretical studies point toward two possible grafting processes: (i) isomerization of

[Os(=CHtBu)$_2$(CH$_2$$t$Bu)$_2$] into [Os(≡C$t$Bu)(CH$_2$$t$Bu)$_3$] upon coordination of a surface silanol through α-H transfers followed by σ-bond metathesis or (ii) grafting via σ-bond metathesis followed by isomerization of the metal fragment. This is in sharp contrast with the grafting of the corresponding alkylidyne complexes [M(≡CtBu)(CH$_2$$t$Bu)$_3$] of d^0 metals (M = Mo and W), which takes place via σ-bond metathesis without isomerization of the metal fragment (Scheme 21b).[67,277,278]

Intramolecular C−H bond activation processes can also explain some deactivation processes of well-defined single-site supported catalysts. For instance, one deactivation pathway of supported alkene polymerization catalyst based on lanthanides and actinides probably is due to the activation of the allylic C−H bond in place of insertion of propene, thus yielding inactive π-allyl surface complexes (Scheme 22a).[66,279,280] More recently, it was shown that C−H bond activation could lead to the deactivation of silica supported alkene metathesis catalysts.[281] From kinetic and *in situ* spectroscopic studies in combination with calculations, it was shown that the well-defined silica supported Re-based alkene metathesis catalyst decomposed, leading to degrafting, and

Scheme 21. Grafting of (a) [Os(=CHtBu)$_2$(CH$_2$tBu)$_2$] on SiO$_{2\text{-}(700)}$, Yielding [(≡SiO)Os(≡CtBu)(CH$_2$tBu)$_2$], and of (b) [M(≡CtBu)(CH$_2$tBu)$_3$] on Silica or Alumina, Yielding [(EO)M(≡CtBu)(CH$_2$tBu)$_2$] (M = Mo or W; R = tBu; and E = Si or Al of Silica or Alumina Surfaces)
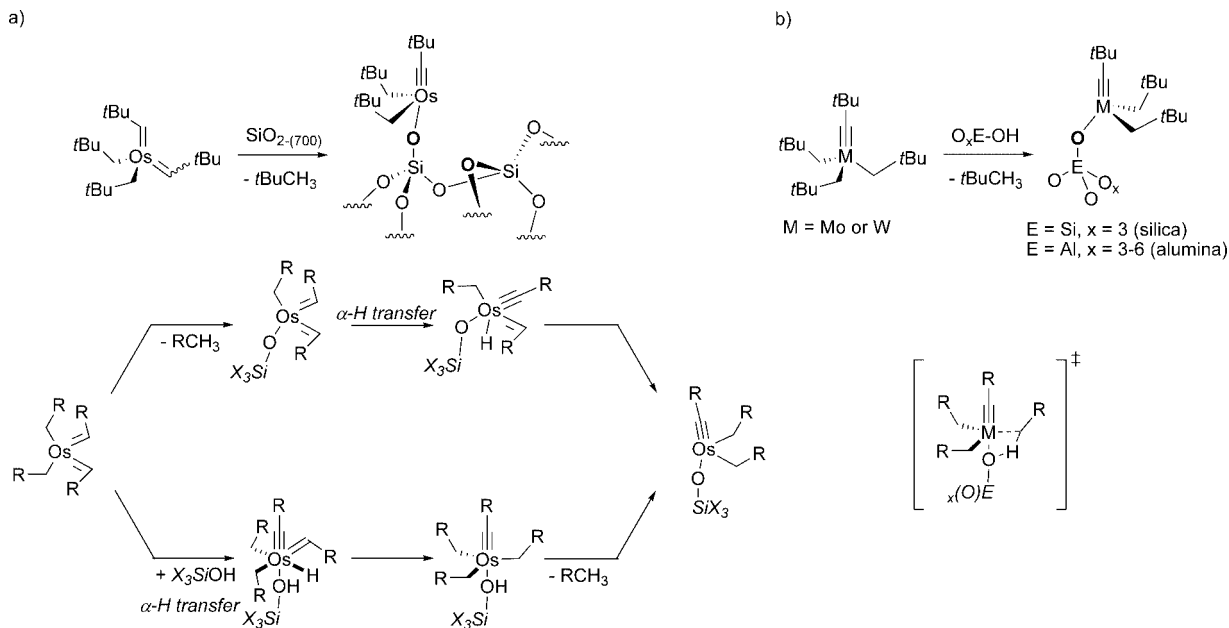
Scheme 22. (a) Deactivation of Polymerization Catalysts by Formation of π-Allyl Species; (b) Deactivation of Alkene Metathesis Catalysts by Decomposition of Metallacyclobutane Intermediates (e.g. the Well-Defined Silica Supported Re Alkylidene Complex); and (c) H/D Exchange via Chain Walking
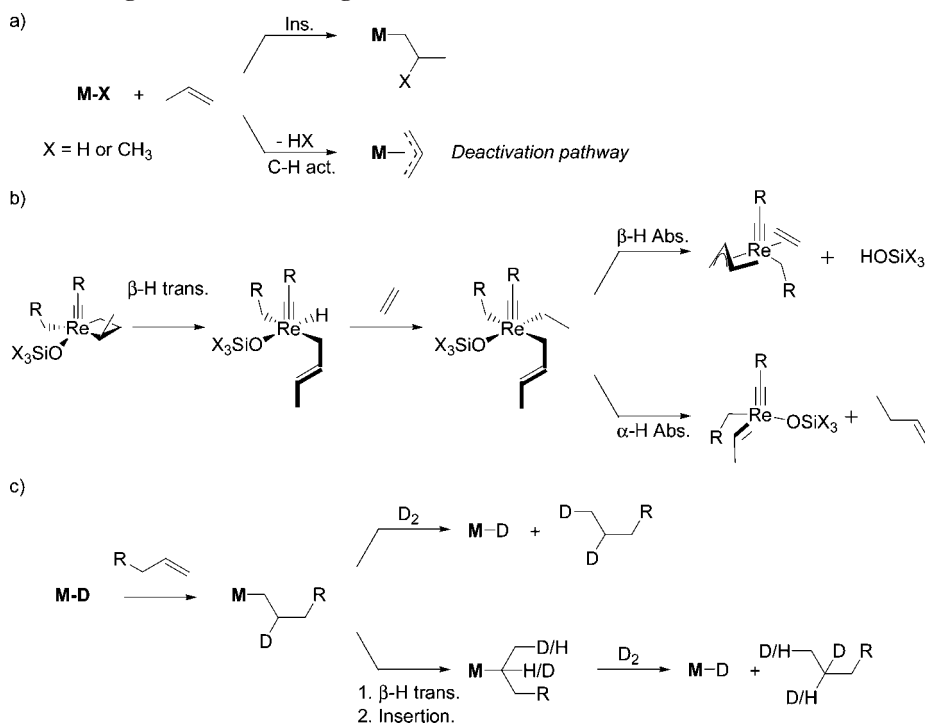
that this process is first order in ethene. The key step of this process probably involved the activation of the C−H bond in the β-position of the metallacyclobutane intermediates, a β-H transfer process (Scheme 22b). The resulting allyl hydride intermediate could then react with ethene to form a highly reactive species, which could either regenerate the catalyst via α-H abstraction between two adjacent alkyl ligands or degraft via abstraction of the β-H of the ethyl fragment by the siloxy ligand (β-H abstraction).

Additionally, β-H transfer can also lead to side reactions in hydrogenation with d^0 metal-based supported[66,242,279,280,282,283]

and homogeneous catalysts.[284−286] In the latter case, it was shown that β-H transfer can become competitive with hydrogenolysis under low pressure of H$_2$. This led to chain walking, as evidenced by the incorporation of deuterium at various positions of the alkyl chain when the reaction was performed with D$_2$ in place of H$_2$ (Scheme 22c).
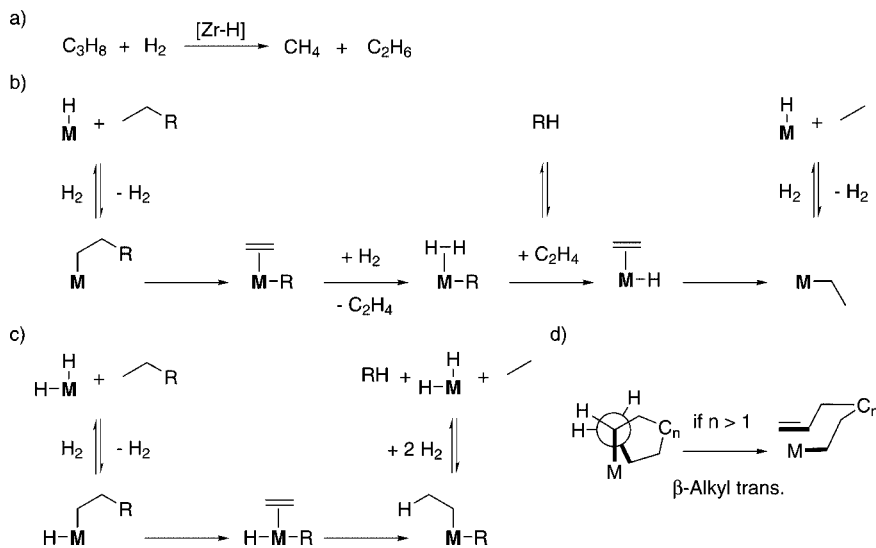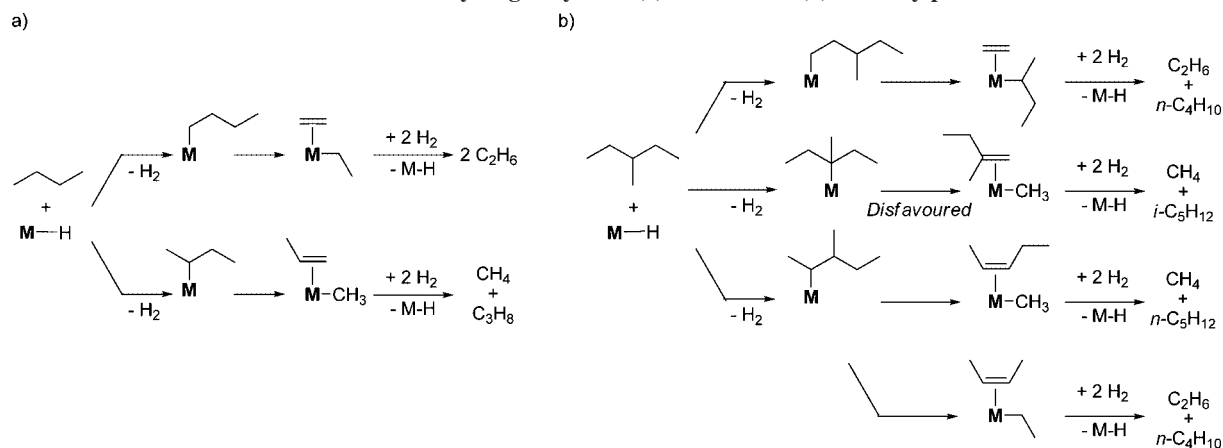
3.2. Alkane Hydrogenolysis

The hydrogenolysis of alkanes and paraffins occurs catalytically at low temperatures on metal hydrides supported

Table 2. Hydrogenolysis of Alkanes Catalyzed by Zirconium Hydride Supported on Silica: Activity and Product Distribution

reactant	activity[a]	initial product selectivity	final product selectivity
ethane	0		
propane	70	CH$_4$ (50%)	CH$_4$ (50%)
		C$_2$H$_6$ (50%)	C$_2$H$_6$ (50%)
2-methylpropane	70	CH$_4$ (52%)	CH$_4$ (67%)
		C$_3$H$_8$ (47%)[b]	C$_2$H$_6$ (33%)
butane	66	CH$_4$ (23%)	CH$_4$ (60%)
		C$_2$H$_6$ (54%)	C$_2$H$_6$ (40%)
		C$_3$H$_8$ (20%)	
2,2-dimethylpropane	66	CH$_4$ (54%)	CH$_4$ (75%)
		C$_4$H$_{10}$ (40%)[c]	C$_2$H$_6$ (25%)
2,2-dimethylbutane	d	other alkanes (90%)	d
		neo-C$_5$H$_{12}$ (<0.2%)	
		iso-C$_5$H$_{12}$ (10%)	
		n-C$_5$H$_{12}$ (<0.2%)	
3-methylpentane	36	CH$_4$ (23%)	d
		C$_2$H$_6$ (32%)	
		n-C$_4$H$_{10}$ (27%)	
		i-C$_5$H$_{12}$ (3%)	
		n-C$_5$H$_{12}$ (12%)	

[a] Activity defined as the number of turnovers per hour at low conversions. [b] Ethane (1.5%). [c] Propane (5%) and ethane (1%). [d] Not determined.

on various oxides, e.g. silica, silica−alumina, or alumina. In the case of group 4 metals and particularly Zr, based on selectivities at low conversions and the final product distribution (Table 2 and Scheme 23a, e.g. alkane = propane), the hydrogenolysis of alkanes has been proposed to take place with the following key steps: C−H bond activation of the alkane via σ-bond metathesis (*vide supra*), C−C bond activation via β-alkyl transfer, hydrogenolysis of the M−C bond, and hydrogenation of the alkene (composed of two elementary steps, insertion and hydrogenolysis, Scheme 23b).[229,230,232,287−289] In order to account for the absence of alkenes and the relatively low reaction temperatures, an alternative pathway has been proposed from calculations based on the bis-hydride surface species, which avoids the high endothermic formation of alkene intermediates, a relatively thermodynamically disfavored process (Scheme 23c).[229,230] It is clear, however, that β-alkyl transfer is the key C−C bond cleavage step, and this is further supported by the observed lack of hydrogenolysis activities toward ethane, for which the corresponding alkyl surface species (ethyl) does not possess a β-C-C bond. Moreover, cyclic alkanes having less than seven carbons (*n* < 1) do not undergo hydrogenolysis, which illustrates the requirement of a *syn-coplanar* arrangement of the M−C and C−C bonds in the β-alkyl transfer transition states (Scheme 23d).[290] Using other supports (silica−alumina[288] and alumina[291]) and group 4 metals (Ti[292] and Hf[293]) does not greatly affect the rate

Scheme 23. Hydrogenolysis of Alkane on [Zr−H]: (a) Hydrogenolysis of Propane and Final Product Distribution. (b) Proposed Elementary Steps for Mono-hydride Active Sites vs (c) a Bis-hydrides (R = CH$_3$ for Propane). (d) β-Alkyl Transfer for M-Cycloalkyl Intermediates

Scheme 24. Possible Product Formation in the Hydrogenolysis of (a) Butane and (b) 3-Methylpentane

Table 3. Hydrogenolysis of Alkanes Catalyzed by Tantalum Hydride Supported on Silica: Activity and Product Distribution

| reactant	activity[a]	initial product selectivity	final product selectivity
ethane	30	CH_4 (100%)	CH_4 (100%)
propane	12	CH_4 (55%)	CH_4 (100%)
		C_2H_6 (45%)	
2-methylpropane	24	CH_4 (55%)	CH_4 (100%)
		C_2H_6 (10%)	
		C_3H_8 (35%)	
butane	18	CH_4 (42%)	CH_4 (100%)
		C_2H_6 (38%)	
		C_3H_8 (20%)	
2,2-dimethylpropane	6	b	CH_4 (100%)
2,2-dimethylbutane	c	other alkanes (68%)	c
		neo-C_5H_{12} (31%)	
		iso-C_5H_{12} (1%)	
		n-C_5H_{12} (<0.2%)	

[a] Activity defined as the number of turnovers per hour at low conversions. [b] No selectivity at low conversion can be reported due to the competitive hydrogenolysis of 2-methylpropane. [c] Not determine.

and the product distribution, which shows that β-alkyl transfer is a general C—C bond cleavage process for d^0 group 4 metals.

It is noteworthy that this reaction can be extended to very long chain alkanes (C_{36}) and polymers, and in fact, supported Zr hydrides can readily polymerize ethene and then depolymerize the thus-formed polyethylene under H_2.[232,288] For the hydrogenolysis of linear alkanes, the observed selectivities (Table 2) showed that C—C bond cleavage is statistical and occurs at similar rates from primary or secondary alkyl Zr species; for example, the ratio of ethane/(propane + methane) $\approx$ 2 (Scheme 24a). On the other hand, it is disfavored from tertiary alkyl Zr species, as evidenced by the low selectivity in isopentane in the hydrogenolysis of 3-methylpentane (Table 2 and Scheme 24b).[255]

Hydrogenolysis of alkanes is also catalyzed at low temperatures by silica supported tantalum hydrides, but the observed selectivities at low conversions and the final product distribution are very different (Table 3 and Scheme 25a).

Scheme 25. Hydrogenolysis of Alkane on [Ta—H]: (a) Hydrogenolysis of Propane and Final Product Distribution. (b) Proposed Elementary Mono-hydride Active Sites vs (c) Tris-hydride Active Sites (R = CH_3 for Propane)
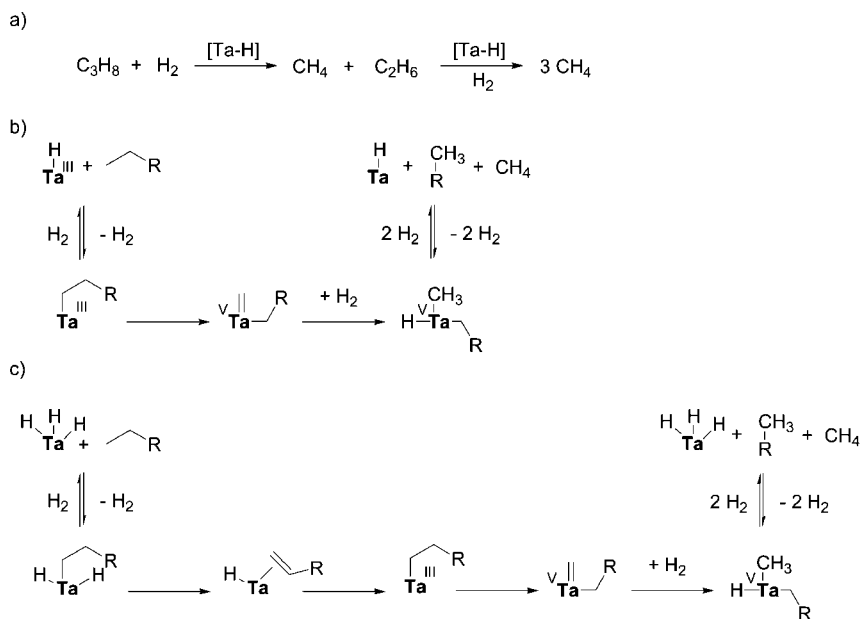
Scheme 26. Proposed Mechanism for the Catalytic Hydrogenolysis of Cyclic Alkanes with Silica Supported Tantalum Hydrides: (A) Initial C—H Bond Activation and C—C Bond Cleavage and (B) Formation of Products
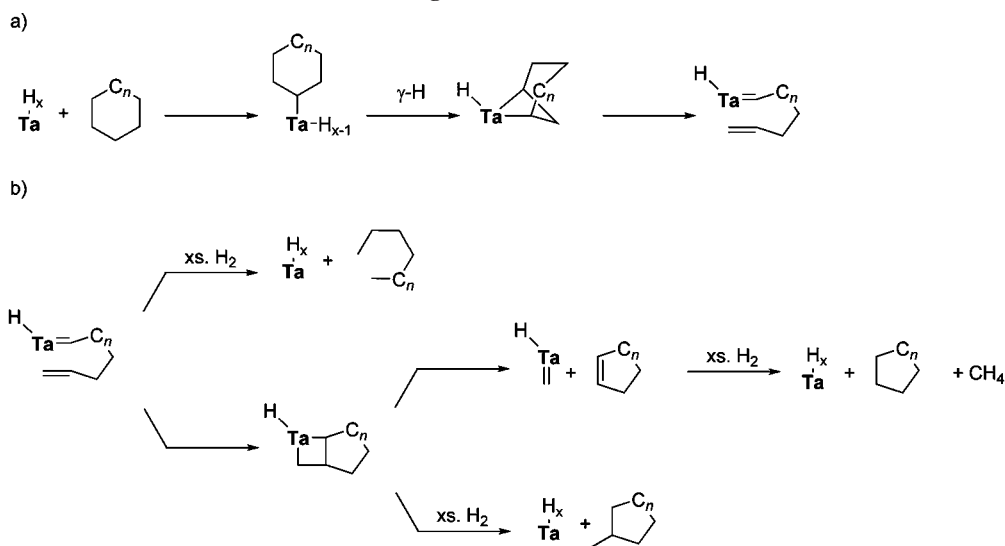
Moreover, the possibility of catalyzing the hydrogenolysis of ethane clearly shows that β-alkyl transfer cannot be the key C−C bond cleavage step in this case.[294] Here, based on these observations and calculations, the C−C bond activation step is the α-alkyl transfer,[295] and the elementary steps of hydrogenolysis are as follows: C−H bond activation, probably on a Ta^V trishydride species, via σ-bond metathesis, C−C bond cleavage through α-alkyl transfer, and hydrogenolysis (Scheme 25b−c).[296]

Moreover, various cyclic alkanes, methylcyclopentane, cyclohexane, and cycloheptane, with the exception of cyclopentane also undergo hydrogenolysis with this catalyst, albeit with much lower rates and number of turnovers.[238] Here cyclic alkanes yield lower cyclic homologues: conversion of cyclohexane into methylcyclopentane and cyclopentane, and that of cycloheptane into methylcyclohexane and cyclohexane. It has been proposed that the key step probably involved, after the formation of the cycloalkyl derivatives via C−H bond activation, a γ-H activation (Scheme 26). This yields a metallacyclobutane intermediate, which can undergo cycloreversion and subsequent steps, e.g. hydrogenolysis, hydrogenation, and rearrangement, to yield both lower cyclic and acyclic alkane homologues. The low activity of the catalyst is probably due to the formation of cyclopentane, detected in all cases, which upon C−H bond activation evolved toward cyclopentadienyl surface species (vide supra, section 3.1.1).

3.3. Alkane Metathesis

In 1997, Vidal et al. found that acyclic alkanes (C_nH_{2n+2}) are catalytically transformed into their lower and higher homologues ($C_{n−i}H_{2(n−i)+2}$ and $C_{n+i}H_{2(n+i)+2}$) in the absence of hydrogen by the silica supported tantalum hydrides (Scheme 27a−b).[297,298] Detailed mechanistic studies using different types of Ta-based catalyst precursors[251,252] and kinetic studies in flow reactors[299] showed that alkenes were primary products and that the key C−C bond cleavage and

formation steps corresponded to those involved in alkene metathesis, i.e. [2 + 2]-cycloaddition and cycloreversion (vide supra).[300−303] Several mechanistic schemes are possible, involving either two sites or one site, and they involve well-known steps of molecular organometallic chemistry.

First, the two-site mechanism is proposed to involve tantalum hydrides as key intermediates (Scheme 27c). After a first C−H bond activation to form H_2 and Ta-alkyl surface species, one site generates an alkene via a β-H transfer, thus regenerating tantalum hydrides; the other site evolves toward a Ta-alkylidene hydride via an α-H transfer.[304] The alkene, generated by the first site, then undergoes a homologation process on the second site, which leads to a different alkene and alkylidene species. Subsequent hydrogenation and hydrogenolysis steps provide a way to liberate the lower and higher alkane homologues. The selectivity in higher homologues, i.e. the presence of mainly $n − 1$ and $n + 1$ linear homologues, is fully consistent with the fact that alkene metathesis is the key homologation process and that 1-alkenes are mainly participating in the homologation process,[252,298,299] in contrast to the catalytic alkane metathesis processes based on mixtures of alkene metathesis and dehydrogenation/hydrogenation catalysts, where a broad distribution of lower and higher homologues are generated, as a result of the cross-metathesis of a broad range of alkene intermediates and, in particular, internal ones.[298,305−309]

Second, the one-site mechanism is based on tantalum alkyl alkylidene intermediates, which are formed in situ from either silica supported tantalum hydrides or neopentyl neopentylidene tantalum surface complexes (Scheme 28).[251,252] In this case, the formation and the conversion of the alkene intermediates take place within the coordination sphere of the metal center, as shown previously for the formation of cross-metathesis products, resulting from the reaction of an alkane and a neopentyl neopentylidene surface complex (Scheme 19, $R_1 = R_2 = CH_2R$).

Scheme 27. (a) General Equation for the Reaction of Alkane Metathesis; (b) Major Products in Alkane Metathesis; (c) Proposed Two-Site Mechanism for the Catalytic Metathesis of Alkanes (Only One of the Two Possible Metallacyclobutanes Is Represented); (d) Selected Catalyst Precursors (See Table 4 for Details)
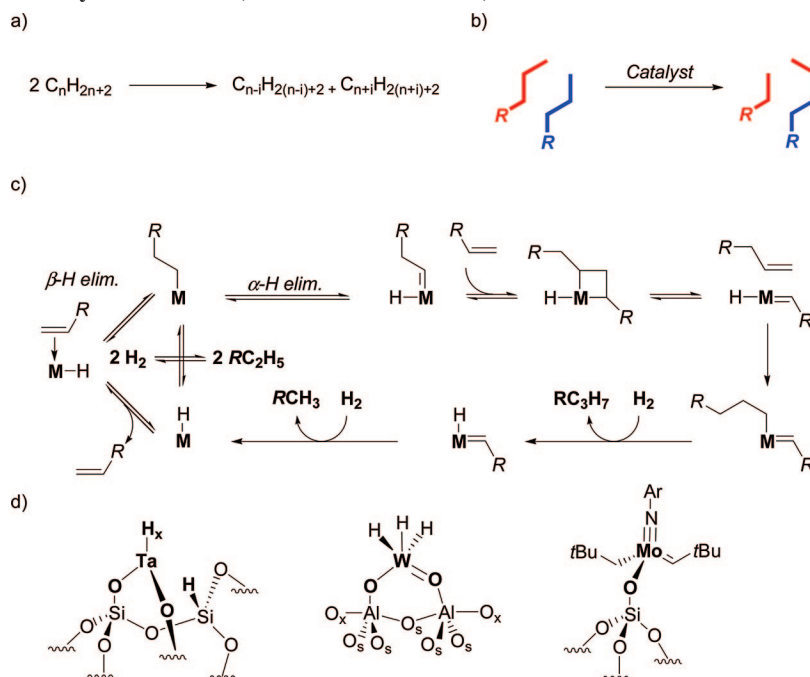
Table 4. Comparison of Catalyst Precursors in the Metathesis of Propane at 150 °C after 120 h

entry	catalyst precursors[a]	TON[b]	selectivities/%				
			C_1	C_2	C_4[c]	C_5[c]	C_6
1	Ta−H/SiO$_2$	60 (3.5)	10	46	37 (5.1)	7 (2.2)	traces
2	Ta−H/SiO$_2$−Al$_2$O$_3$	59 (4)	11.5	46.5	35.5 (4.1)	6.0 (2.2)	traces
3	Ta−H/Al$_2$O$_3$	60 (2.5)	9.5	47.5	36.5 (8.6)	6.0 (4.5)	traces
4	Ta−H/SiO$_2$−Zr	100 (3)	10	46	37	7	traces
5	W−H/SiO$_2$	8 (−)	5.5	56.0	32 (10.4)	6.5 (3.6)	traces
6	W−H/SiO$_2$−Al$_2$O$_3$	123 (8.5)	2.0	58.0	32.0 (6.7)	6.5 (3.7)	1.5
7	W−H/Al$_2$O$_3$	121 (8.5)	2.5	57.5	33.0 (7.8)	6.5 (3.8)	1.5
8	Si$_S$OTa(=CHtBu)(CH$_2$tBu)$_2$	35 (3)	13	47.5	32.5 (0.5)	6.0 (1.4)	1[d]
9	Si$_{Al}$OTa(=CHtBu)(CH$_2$tBu)$_2$	33 (−)	10.5	47.0	35.0 (3.8)	6.5 (2.3)	1[d]
10	Al$_S$OTa(=CHtBu)(CH$_2$tBu)$_2$	34 (−)	5.0	52.0	38.0 (7.0)	4.5 (3.5)	traces
11	Si$_S$OMo(≡NR)(=CHtBu)(CH$_2$tBu)	55 (1.1)	<0.2	56.0	38.0 (13)	6.0 (7.4)	0.5
12	Si$_S$OMo(≡NR)(=CHtBu)(NR$_2$)	<1	−	−	−	−	−
13	Si$_S$ORe(≡CR)(=CHtBu)(CH$_2$tBu)	13 (0.3)	3.5	56.0	39 (3.1)	4.0 (1.6)	traces
14	Si$_S$OW(≡CtBu)(CH$_2$tBu)$_2$	<1	−	−	−	−	−
15	Si$_{Al}$OW(≡CtBu)(CH$_2$tBu)$_2$	29 (0.7)	1.5	61.5	29 (7.5)	7 (4.2)	1
16	Al$_S$OW(≡CtBu)(CH$_2$tBu)$_2$	28 (1.8)	2.5	65.5	24 (7.1)	7 (3.3)	1
17	(Si$_S$O)$_2$Zr(H)$_2$	60	23	39	24 (0.5)	4.8 (1)	3.6[e]
18	(Si$_S$O)$_2$Zr(CH$_2$tBu)$_2$	−	30.5	42.3	12.7	5.7	−

[a] The names of the catalysts have been simplified as follows: M−H/oxide in entries 1−7 refers to oxide supported metal hydrides, and the chemical formula in entries 8−16 gives the structure of the surface complexes with Si$_S$, Si$_{Al}$, and Al$_S$ referring to the siloxy group of a silica surface, the siloxy group of a silica−alumina surface, and the Al group of an alumina surface, respectively. [b] TONs are here defined as the number of equivalents of propane converted per total metal after 120 h. Values in parentheses correspond to initial rates in TON/h. [c] For butanes and pentanes, the two numbers correspond in order to the selectivities of n- and i-isomers. [d] In these cases, additional products, corresponding to cross-metathesis products, are obtained: 2,2-dimethylpropane (tBuCH$_2$−H), 2,2-dimethylbutane (tBuCH$_2$−CH$_3$), and 2,2-dimethylpentane (tBuCH$_2$−C$_2$H$_5$); no tBuCH$_2$−C$_3$H$_7$ is detected (<0.1%); see Table 1. [e] Selectivities in the sum of C$_6$ to C$_{10}$ compounds.

Scheme 28. Formation of Alkyl Alkylidene Intermediates from Tantalum Hydrides
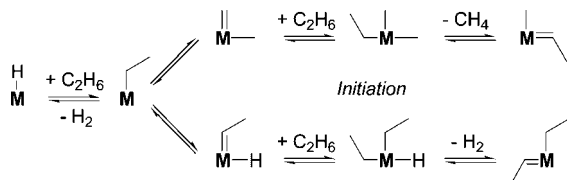
Both mechanisms are based on alkene metathesis and alkylidene hydride as a key intermediate. Today, several catalysts have been developed on the basis of well-defined metal hydrides, alkyl alkylidene, or alkylidyne surface complexes (Table 4 and Scheme 27d):

(1) Tantalum hydrides prepared on various oxide supports: silica−alumina, alumina, and tailored made supports (entries 1−4),[262,310] but they display similar activities and selectivities with the original silica supported tantalum hydrides.

(2) Tungsten hydrides supported on oxide supports (entries 5−7);[260−262] while the silica supported system is a poor catalyst because of the lack of stability of the tungsten hydrides, the silica−alumina and alumina

Scheme 29. (a) Metathesis of 2-Methylpropane; (b) Key Carbon−Carbon Bond Forming Steps from the Metallocarbene Hydride Intermediates; (c) Cross-metathesis of Ethane and Toluene
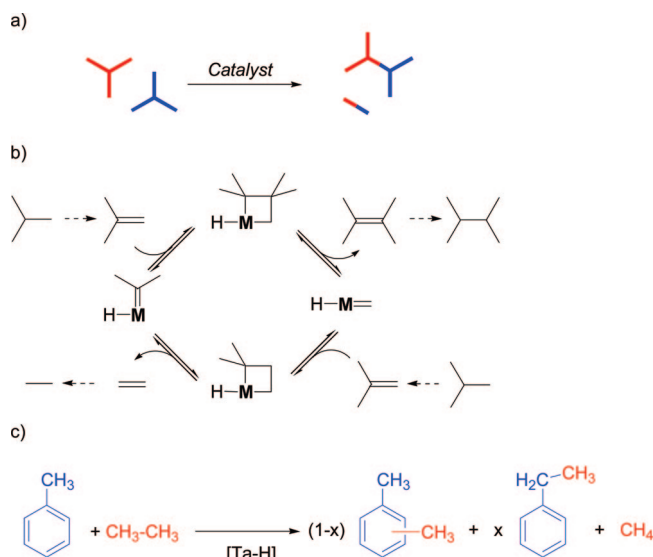
Scheme 30. Proposed Mechanism for the Catalytic Homologation of Alkanes by Oxide Supported Zirconium Hydrides
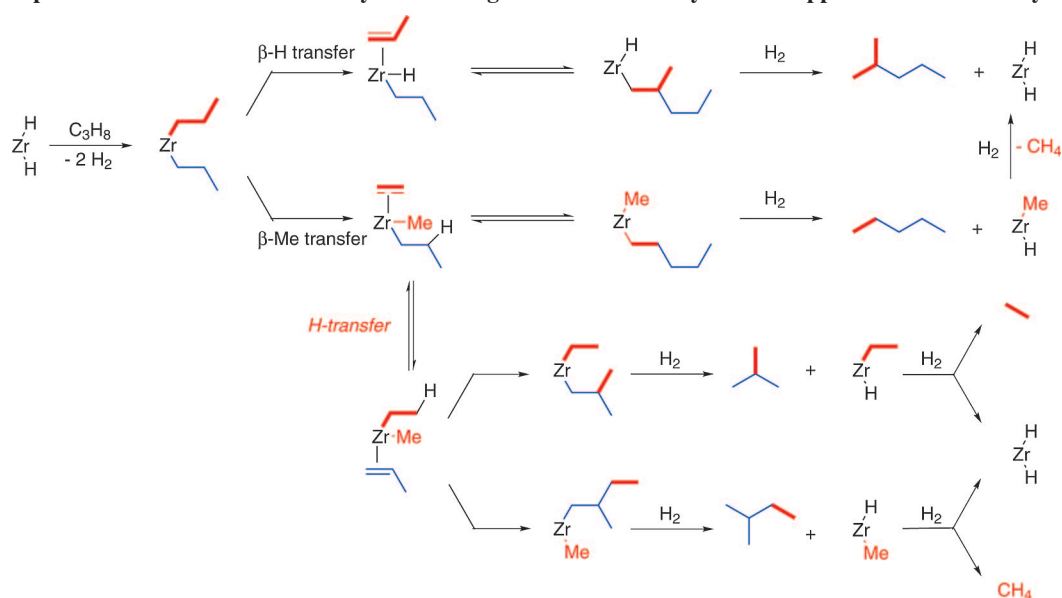
supported tungsten hydrides are more stable and selective than the corresponding tantalum hydrides.

(3) Well-defined silica supported metal alkyl alkylidene catalyst precursors; those based on Ta display similar selectivity to that of the parent tantalum hydrides but are slightly less productive (entries 8−10);[251,252] those based on Mo imido complexes have similar activity to that of the parent silica supported tantalum hydrides but higher selectivities (entry 11).[253,254] In the latter type of catalysts, it was clearly shown that both the alkylidene and the alkyl ligands were necessary to obtain catalytic activity in alkane metathesis, because the corresponding alkylidene amido complexes are inactive despite their much higher performances as alkene metathesis catalyst precursors (entry 12).[311,312] Note that Re alkyl alkylidene complexes are also active (entry 13),[254] but with much lower performances, probably because of their higher instability.[281] Overall, detailed investigations on these types of catalysts are consistent with a one-site mechanism and show that deactivation of these systems is probably due to degrafting (vide infra, Section 3.1.3),[254] preventing regeneration under H_2 as performed on the hydride based catalysts.

(4) Well-defined alkyl alkylidyne surface complexes of W, which are highly active alkene metathesis catalysts,[278,313,314] can also be used as alkane metathesis catalyst precursors (entries 14−16). While the silica supported system is inactive, probably because of a fast decomposition, the silica−alumina and alumina supported systems display activities comparable to those of the corresponding tantalum alkyl alkylidene systems (entries 8−10) and a greater selectivity for $n − 1$ and $n + 1$ homologues (entries 6−7). Overall, the current best reported catalysts are based on alumina or silica−alumina supported tungsten hydrides.

Alkane metathesis can also be used to make highly branched alkanes. For instance, the alumina supported tungsten hydrides convert selectively and catalytically 2-methylpropane into 2,3-dimethylbutane (42%) and ethane (41%) (Scheme 29a).[315] Despite the transfer of two carbons in place of one, as usually observed previously, this selectively can be explained using the same mechanism and the same

alkylidene hydride intermediates (Scheme 29b). Finally, it is also possible to carry out alkane cross-metathesis processes. For instance, ethane/toluene mixtures are catalytically converted into a mixture of ethylbenzene and xylenes by the silica supported tantalum hydride (Scheme 29c).[316] This shows that both C_{sp3} and C_{sp2} can be involved in the alkane metathesis process. Note that C_{sp2} functionalization probably involves a different type of mechanism; one possibility is the C_{sp2}-H activation on alkylidene or alkylidyne intermediates followed by an α-alkyl migration and subsequent C−H bond activation and hydrogenolysis steps to form higher alkane homologues and regenerate the active species (vide infra, Section 3.4 and Scheme 31c).

Moreover, while silica or silica−alumina supported zirconium hydrides or alkyl do not display any catalytic activity in alkane metathesis under standard conditions (150 °C and ca. 1 bar), they catalytically convert propane into higher and lower homologues under supercritical conditions (Table 4, entries 17−18).[317] However, the product selectivity and distribution are very different from catalysts based on group 5 and 6 metals: formation of mainly branched products up to decanes with a relatively high selectivity in isobutane along with methane and ethane. Here it is proposed that propane homologation takes place on a bis-hydride surface species and involves the following elementary steps (Scheme 30): (1) formation of a bis-alkyl intermediate [Zr(n-Pr)$_2$] via two σ-bond metathesis steps, (2) an homologation process yielding [Zr(C$_2$H$_5$)(i-Bu)] via successive β-alkyl transfer intramolecular H-transfer and insertion, and (3) regeneration of Zr(H)$_2$ and formation of ethane and isobutane via hydrogenolysis (σ-bond metathesis of M-C by H_2).

3.4. Catalytic Conversion of Methane

Alkane metathesis converts a given alkane into its lower and higher homologues, and in particular two ethane molecules into methane and propane. The reverse reaction implies a cross-metathesis reaction with methane and its incorporation into higher alkanes, e.g. methane and propane giving two ethane molecules. This reaction is slightly endothermic independently of temperature (ca. 10 kJ/mol), but using a large excess of methane, propane was catalytically and quantitatively converted into ethane (2 ethane

Scheme 31. Catalytic Conversions of Methane via (a) Cross-metathesis with Propane, (b) Nonoxidative Coupling, (c) C−C Bond Formation in Nonoxidative Coupling of Methane, and (d) Nonoxidative Coupling of Methane and Benzene
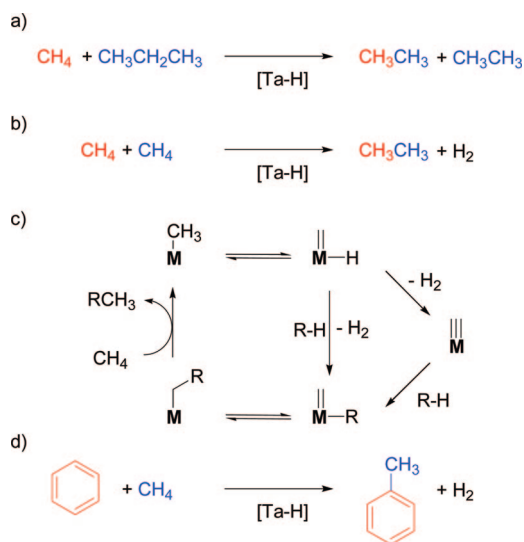
molecules per converted propane) using the silica supported tantalum hydrides, probably via the same elementary steps of alkane metathesis (Scheme 31a).[318]

With the same tantalum hydride catalyst, but in the absence of other alkanes, methane can also be catalytically converted into an equimolar mixture of ethane and H_2, which corresponds to the reaction of nonoxidative coupling (Scheme 31b).[206] This reaction is however highly endothermic and leads to very low conversions (*ca.* 0.1 and 0.2 at 300 and 375 °C, respectively). A possible mechanism involved the C−H bond activation of methane (R = CH_3 in Scheme 31c) on metal−methylidene or methylidyne intermediates;[263−265] this generates an alkyl alkylidene species, which can rearrange via α-alkyl transfer into a Ta-CH_2R. The catalytic cycle is then close upon reaction with methane, which liberates RCH_3 and regenerates Ta-CH_3. In the presence of benzene, coupling also takes place but leads to the selective formation of toluene and H_2 (Scheme 31d), and the mechanism can take place similarly to methane replacing R = CH_3 by R = Ph in the catalytic cycle.[319]

4. Conclusion

C−H bond activation of alkanes readily takes place on isolated metal centers bound to, or present on, oxide surfaces to form organometallic intermediates, and this corresponds to the key steps of numerous catalytic processes: H/D-exchange reactions, alkane hydrogenolysis and metathesis, alkane dehydrogenation, conversion of alkane into aromatics, as well as the cross-metathesis of methane and alkanes or nonoxidative coupling of methane.

First, C−H bond activation and the formation of M−alkyl species occur on M−O, M−H, and M−C bonds via σ-bond metathesis and on M−alkylidene and M−alkylidyne bonds via addition reactions, an elementary step whose transition state resembles that of a σ-bond metathesis. In contrast to molecular organometallic chemistry, C−H bond activation via oxidative addition is only rarely encountered for these systems, with one reason being that metal centers belong to main group and early transition metals, usually in their higher oxidation states. Systems based on late transition metals, e.g.

group VIII, are mainly found as particles, which were not discussed here.

Second, intramolecular C−H bond activation is also important in many catalytic processes. First, it is one of the processes which allows the formation of surface alkylidene and alkylidyne intermediates via α-H abstraction on bis-alkyl or alkyl−alkylidene species, respectively. Second, related elementary steps such as β-H abstraction and β-H transfer are also important in deactivation (degrafting) and chain transfer (alkane homologation) processes, respectively. Finally, a specific case is β-H transfer, which is the key step of (i) a chain walking mechanism, an important reaction in hydrogenation, polymerization, alkane hydrogenolysis, and possibly alkane metathesis, and (ii) deactivation mechanisms of alkene and alkane metathesis catalysts. Additionally, one should note that, in contrast to molecular organometallic chemistry, C−C bond activation is often encountered in surface chemistry, including in catalytic processes (alkane hydrogenolysis and metathesis), and this is probably due to the possibility to explore the reactivity of these surface species at higher temperatures than those for the homologous molecular complexes because surfaces and, in particular, site isolation allow the access to highly reactive—yet stable—intermediates.[320] Nonetheless, these C−C bond activation processes take place via known elementary steps of molecular organometallic chemistry (and related to those of C−H bond activation), i.e. mainly via α- and β-alkyl transfer processes, with the corresponding reverse elementary steps allowing the formation of C−C bonds and chain growth. No intermolecular C−C bond activation has been observed so far on these systems. This again shows the difference between isolated sites in high oxidation states and metal ensembles present at the surface of metal particles.

Third, it is also noteworthy that the surface chemistry and particularly C−H bond activation processes are very similar for bulk oxides and M-exchange zeolites, and this is probably an evidence for common structural features of active sites for these systems. For instance, it is possible that the structures of the defect sites in oxides are closely related to those of the active site Al and M sites of H-zeolites and M-exchange zeolites, respectively. Given the diversity of zeolite structures, it should be possible to control the nature, the density, and the accessibility of those active sites and thereby to obtain single-site catalysts. Moreover, the C−H bond activation of alkanes on the reactive sites of oxides and zeolites, which are based on main group or group 10 metals (Al, Ga, and Zn), corresponds to a σ-bond metathesis, like for single-site catalysts based on early transition metals. The analogy between the reactivity of single-site catalysts, isolated ions in metal oxides and M-exchange zeolites, shows that research effort should also be directed in bridging the gap between these systems, for instance by designing well-defined active sites bound to or incorporated in the structure of zeolites as a way to generate robust single-site catalysts.[321−324]

In contrast, under oxidative conditions (molecular oxygen or N_2O), the C−H bond activation processes are more complex; they typically involve a H-abstraction and radical-type mechanism. In fact, in some cases when high operating temperatures are used (above 500 °C), the uncatalyzed and unselective gas phase reactions can become dominant. Therefore, metal-alkyl species are often not key reaction intermediates, even if they can be detected in some cases, probably as dormant species. Yet, such radical processes can lead to highly selective transformation in specific cases, such

as the oxidation of butane into maleic anhydride. However, such cases are limited to specific substrates, and these reactions lead to otherwise low yields (low selectivity at high conversions or high selectivity at low conversion).

Overall, the level of molecular understanding of "single-site" heterogeneous catalysts in terms of structure of the active sites and reaction mechanism is close to that obtained for homogeneous systems. The detailed description of these systems has in turn been used to develop rational approaches to improve catalysts (design) and to also discover novel alkane (including methane) homologation processes. There are however open questions regarding the so-called "single-site" catalysts: what is the effect of adjacent oxygen functionalities on structure and reactivity (local environment; are they truly "single-site"?), what is the stability of these systems (deactivation, regeneration, ...), can they be used in more complex reactions involving for instance molecular oxygen (*vide infra*)?

In contrast, obtaining a detailed mechanistic understanding for the activation of alkanes on metal oxides or zeolites has been difficult and still requires a large research effort, despite many recent advances. This is due in large part to the difficulty to attain a molecular understanding of the active sites. One approach to bridge the gap between "single-site" catalysts and these systems is to improve characterization techniques,[325−333] in particular by combining advanced spectroscopic and computational studies. This requires looking at the pristine material as well as the material under working conditions (operando techniques). The thus-obtained detailed understanding of active site structures can in turn assist with design of new materials, in particular highly crystalline materials with defined chemical structures, with a control of the density of so-called "defect sites", with a defined location of sites inside the oxide matrices....[334−337] In the case of oxidative reaction processes, extra difficulties can be pointed out: very complex reaction mechanisms involving multielectron oxidation processes and molecular oxygen as well as radical or radical-like intermediates, oxide-based catalysts involving complex compositions and active site structures.... Here, despite years of research and promising industrial processes, a better molecular understanding of active sites and reaction mechanisms is probably critical to expect major advances in catalyst design. Major break-throughs could originate from a deeper understanding of C–H bond activation processes on M=O or M–O active sites with the aim to trigger C–H bond as well as O$_2$ activation at lower temperatures on metal oxides or supported metal oxides. This would assist with the design of more selective metal-based catalysts and avoid the unselective gas phase reaction processes. This also calls for a better control of the formation of active species on oxide surfaces, and one possible approach is the controlled reaction of well-defined oxide precursors including polyoxometallates.[338−340]

This review also shows that the isolated metal centers of surfaces can display unusual reactivities when compared to molecular organometallic chemistry, even if they actually obey the same rules (elementary steps)! Their reactivity is by and large due to site isolation on surfaces, which can help stabilize reactive intermediates and which allow unusual structures, e.g. low coordination, as well as the use of higher temperatures. Looking more closely at these systems can probably provide new ideas in molecular chemistry in a similar way as Nature has inspired us to design homogeneous and heterogeneous catalysts.[341−343]

6. References

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