The Role of Proton Transfer in Heterogeneous Transformations of Hydrocarbons

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Abstract: Heterogeneous catalysis is essential for the transformation of light hydrocarbons into chemical feedstocks. Many of the catalysts that mediate these transformations consist of isolated metal ions on the surface of a metal oxide support, such as silica or alumina. Due to the complexity of these catalysts, studying the active site and mechanism of these reactions is difficult. Surface organometallic chemistry (SOMC) could offer a solution to this problem by allowing the synthesis of well-defined surface organometallic species. This approach has been used to study the reactions of light hydrocarbons with isolated metal species on silica and alumina surfaces. These studies showed that proton transfers play a key role in the reactions of many hydrocarbons. The mechanisms of these reactions and their role in some common catalytic cycles are discussed.

Keywords: Heterogeneous catalysis · Proton transfer

Introduction

Heterogeneous catalysts are key components for the efficient conversion of small molecules such as H_2, CO_x, N_2, and small hydrocarbons into useful products. These catalysts consist of either supported metal nanoparticles or isolated metal ions impregnated in a metal oxide support. For example, isolated Mo, W, and Re oxides can be used as metathesis catalysts.[1] In particular WO_3/SiO_2 is the key catalyst of the Lummus process (cross-metathesis of ethylene and butenes to make propene). In addition to the Ziegler-Natta polymerization catalysts ($TiCl_4/MgCl_2/Et_3Al$), one of the main catalysts for the production of high-density polyethylene is based on dispersed Cr ions at the surface of silica (Phillips process).[2] Similarly, the Catofin process, for the dehydrogenation of light alkanes, is based on Cr(III) ions dispersed on Al_2O_3 surface.[3] The Catofin process produces alkenes, some of the most important commodity chemicals on the market, from natural materials in only one step.

Since petroleum consists of saturated hydrocarbons (having only C–H and C–C bonds), the processes that convert petroleum into useful feedstocks must involve the activation of C–H bonds. In addition,

these catalysts consist of high oxidation state metal oxo species having no metal–carbon bond, so that C–H bond activation is necessary for catalyst activation (*vide infra*). Molecular level information about the active sites and mechanistic steps in these reactions is typically lacking. One of the main reasons is that less than 10% of the metal sites in these catalysts are active, making it difficult to study the true nature of the active site of the industrial catalysts.[2]

In the past four decades, organometallic chemists have elucidated several mechanisms by which C–H bond activation can occur.[4] Some common mechanisms are shown in Eqns (1–4) (Scheme 1).[5] Low valent metals tend to do so by oxidative addition (Eqn. (1)). Proton-coupled electron transfers (PCETs), shown in Eqn. (2), tend to occur with late transition metal oxo and imido complexes in high oxidation states. However, early transition metals, such as those found in the aforementioned industrial catalysts, tend to activate C–H bonds by either a heterolytic splitting (Eqn. (3)) or the related σ–bond metathesis mechanism (Eqn. (4)). These two mechanisms both involve proton transfer from a C–H bond.

The inherent problems of site inhomogeneity and the strenuous conditions
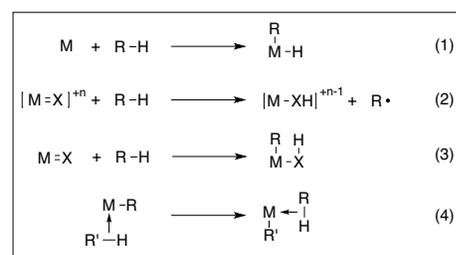
Scheme 1. Possible mechanisms of C-H bond activation.

under which the heterogeneous reactions are run, make studying the industrial catalysts in this way difficult. One solution to this problem is to generate well-defined active sites on metal oxide supports using the surface organometallic chemistry (SOMC) approach.[6] This approach involves the controlled conditioning of the surface of metal oxide supports in order to create a uniform surface site (Scheme 2). Often, this is done by a thermal treatment at high temperatures, leading to the formation of isolated hydroxyl groups on the surface.[7] These isolated OH sites can then react with a molecular complex, leaving behind a grafted organometallic species on the surface of the oxide support. In addition, these surface species can be further treated at high temperature under

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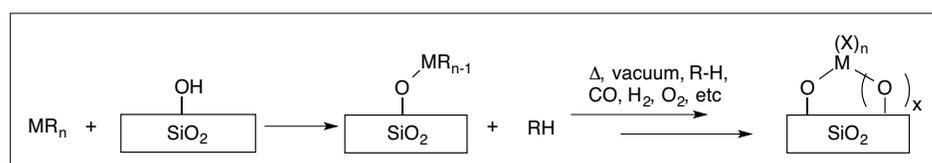
Scheme 2. Formation of surface sites on silica *via* grafting of organometallic compounds and post-treatment steps.

vacuum or hydrogen to generate low coordinated metal sites that would be difficult to obtain in solution.

In contrast to normal industrial catalysts, these species usually have (more) uniform structure (oxidation states and coordination spheres). They also have a high percentage of active sites for catalysis (up to 100%) making them ideal systems to study at a higher level of detail. This is the case for supported high-oxidation early transition metal hydrides or tri-coordinated Cr(III) sites discussed below. Studies of these systems towards C–H bond activation show that the activation step with these systems falls into two important classes: 1) σ–bond metathesis and 2) heterolytic activation, both of which involve proton transfer from a C–H bond.

Activation of Alkanes by Supported Metal Hydrides *via* σ–Bond Metathesis

The σ–bond metathesis reaction is well-established for solution phase organometallic chemistry.[4,8] It involves direct proton transfer from a σ-complex of E–H (where E = H, C, Si, B, and others) to a basic ligand already bound to the metal center. It is commonly cited as an alternate mechanism to the more traditional oxidative addition/reductive elimination scheme (Scheme 3) – the advantage being that σ–bond metathesis avoids a change in oxidation state. It was first proposed for d^0 metal centers but has since been observed for many elements across the transition series.[5]
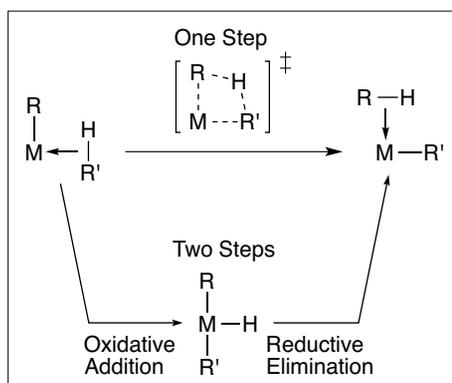
Scheme 3. Oxidative addition/reductive elimination vs. σ-bond metathesis.

σ–Bond metathesis resembles a direct proton transfer from a weak acid (a C–H bond) to a carbanion (M–C). The Lewis acidic metal center is essential to modulate the kinetics of this reaction by changing the pK_a of the E–H bond. For example, the pK_a of H_2 is estimated to be 48 in water,[9] but σ-hydrogen complexes have pK_a's as low as –11.[10] Many examples of σ–bond me-

tathesis are encountered in surface organometallic species, in particular with the d^0 metal hydride complexes. Some of the first examples were silica-supported zirconium hydrides obtained by grafting $Zr(CH_2tBu)_4$ on silica followed by treatment with H_2 at 60 kPa and 150 °C (Eqn. (5), Scheme 4).[11] Here, Zr is d^0 and no oxidative addition/reductive elimination scheme is possible. Based on reaction stoichiometry, and multiple spectroscopic tools (IR, NMR and EXAFS), it has been shown that this species is a mixture of mono and dihydride (**1** and **2**, respectively).[12] These species likely form through the opening of adjacent siloxane bridges by the putative $SiOZrH_3$ intermediate.

These supported zirconium hydrides react with alkanes to give the corresponding metal alkyls.[11] This is the key step in several catalytic reactions mediated by supported metal hydrides including H/D exchange between CH_4/D_2 or CH_4/CD_4 (Eqn. (6), Scheme 5),[13] hydrogenolysis of alkanes at mild conditions (Eqn. (7)),[14] or even the disproportionation of alkanes (Eqn. (8)).[15]

The kinetics of σ–bond metathesis by hydride **1**, have been probed using isotopic exchange reactions. For example, the rates of H/D exchange between H_2/D_2 and CH_4/D_2 mixtures catalyzed by **1** were measured at a variety of temperatures.[13] H_2/D_2 exchange was found to be extremely fast

(complete exchange occurred in less than 6 s at 77 K). Exchange between CH_4 and D_2 catalyzed by **1** is slow enough to measure between 25 and 150 °C. This process has $\Delta H^‡ = 7$ kcal/mol and $\Delta S^‡ = -27$ cal mol^{-1}K^{-1} indicating that this reaction has a highly ordered transition state. Similar activation parameters were observed for σ–bond metathesis reactions with Cp^*_2ScMe.[16] They also estimated the H/D kinetic isotope effect for CH_4/CD_4 to be 2.5, indicating that the rate determining step of these reactions involves C–H bond breaking. Barriers of isotopic exchange reactions by σ–bond metathesis were calculated to be similar to experimentally obtained activation energies.[17] All of these data are consistent with a σ–bond metathesis mechanism for the C–H bond breaking event.

The hydrogenolysis of neopentane (Eqn. (7), Scheme 5) also begins with a C–H σ-bond metathesis (giving **3**), followed by C–C bond breaking by β–alkyl transfer, giving **4** (Scheme 6). Thus, σ-bond metathesis acts as a prerequisite to breaking C–C bonds during catalysis at low temperatures.

Of the later transition-metal complexes, only tantalum leads to the formation of the corresponding silica-supported Ta hydrides under H_2.[18] The silica-supported metal hydrides are in fact a mixture of tris and mono–hydrido Ta complexes (**5** and **6**, Eqn. (9), Scheme 7). Unlike zirconium hy-
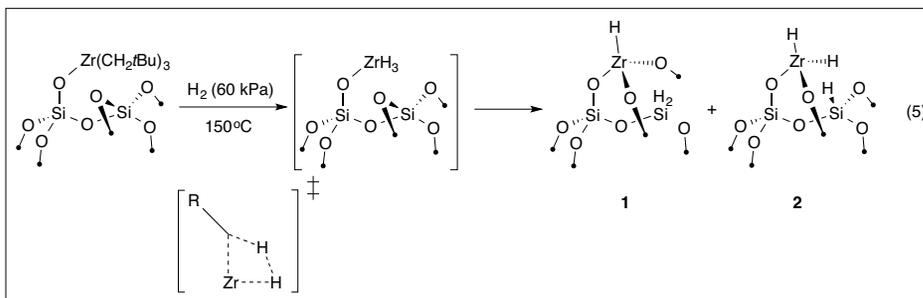
Scheme 4. Formation of Zr hydrides on silica surface.
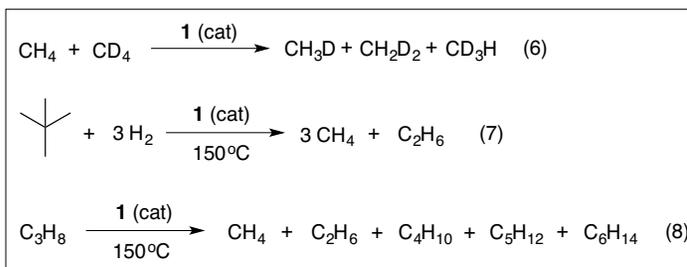
Scheme 5. Transformations of hydrocarbons involving σ-bond metathesis.
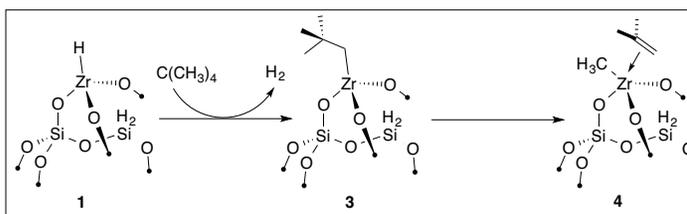
Scheme 6. Hydrogenolysis of neopentane.

drides **1** and **2**, **6** is a Ta(III) center (d^2) and has available electrons for oxidative addition. This system also catalyzes the H/D exchange of CH_4/CD_4 or D_2/CH_4 mixtures[19] and the hydrogenolysis of alkanes.[19] However, the H/D exchange reactions of **5** and **6** are much slower than those of **1**.[13] The characteristics of the C–H bond activations are similar to those with **1** and **2**, and therefore it is still believed that these reactions are true σ-bond metatheses.

The hydrogenolysis of alkanes by silica-supported tantalum hydrides **5** and **6** leads to different product selectivity and allows for the hydrogenolysis of ethane (Scheme 8). While the first step (C–H bond activation) is thought to begin *via* σ–bond metathesis, it has been proposed that the key step of C–C bond cleavage is probably α–Me transfer. The difference in behavior between **5** and **1** could be due to the fact that Ta can change oxidation state, thereby allowing this α-alkyl transfer step.[18]

Tantalum hydrides **5** and **6** led to the discovery of the low temperature disproportionation of alkanes.[20] Detailed mechanistic investigation revealed that direct σ-bond metathesis, involving a four-membered transition state with a carbon in the β-position, was not possible.[17,21] Consistent with what was shown for **1** and **2** above, C–H bond activation occurs before C–C activation. During alkane metathesis, the alkane is first dehydrogenated.[22] The C–C bond formation then occurs by alkene metathesis of the intermediate alkenes (Scheme 9).[23] The reverse of Scheme 8, namely dehydrogenation of methane to give ethane and hydrogen, is catalyzed by **6** above 250 °C.[24] Conversion of methane into chemical feedstocks is of great interest,[25] showing the potential importance of σ–bond metathesis reactions on surfaces.

Surface Species that Activate R–H by a Heterolytic Splitting Mechanism

Other heterogeneous catalysts activate C–H bonds by a heterolytic C–H bond activation process (also called 1,2 addition).[5,26] Heterolytic C–H activation is in many ways similar to σ–bond metathesis. Both processes involve the deprotonation of an incoming C–H bond leaving behind a new alkyl ligand attached to the metal. Also like σ–bond metathesis, the rate of heterolytic C–H bond activation is sensitive to the pK_a of the C–H bond being activated and the basicity of the basic ligand. The main difference between the two processes is that for heterolytic C–H activation, the ligand that acts as the base remains bound to the metal, whereas for σ–bond metathesis the basic ligand is only weakly bound as a σ–complex.
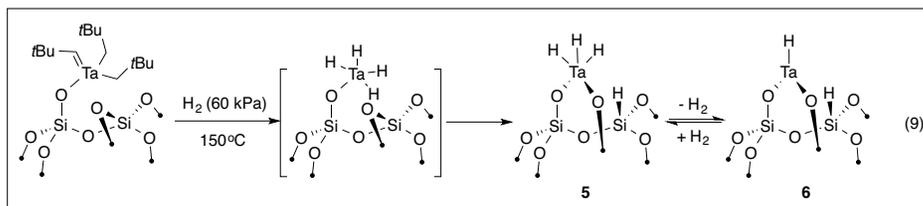
Scheme 7. Formation of Ta hydrides on silica surface.
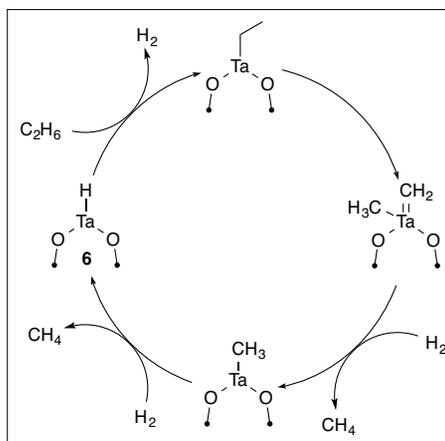
Scheme 8. Hydrogenolysis of ethane.

of C–H bond heterolysis for surface organometallic complexes. For example, $tBuC≡Re(=CHtBu)(CH_2tBu)_2$ grafted onto SiO_2 forms species **7**. Heating the ^{13}C labeled complex **7** showed ^{13}C scrambling into the alkylidene position but not the alkylidyne (Eqn. (11), Scheme 11).[30] This most likely occurs by C–H activation of the methylene group by the alkylidene ligand.

We have recently used SOMC to make a well-defined model system for the Phillips catalyst, used in industrial ethylene polymerization. The Phillips catalyst is made by impregnation of CrO_3 into silica followed by calcination and subsequent reduction under a stream of H_2, CO or eth-

Scheme 9. General mechanism of alkane metathesis.
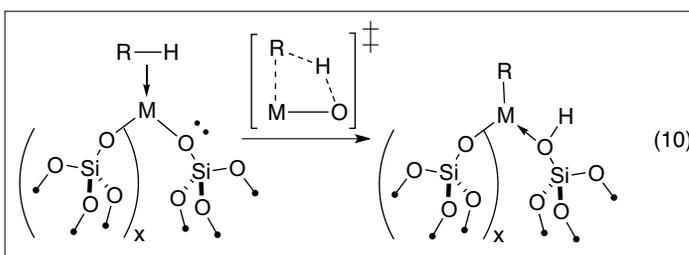
Scheme 10. Mechanism of heterolytic C-H bond activations.
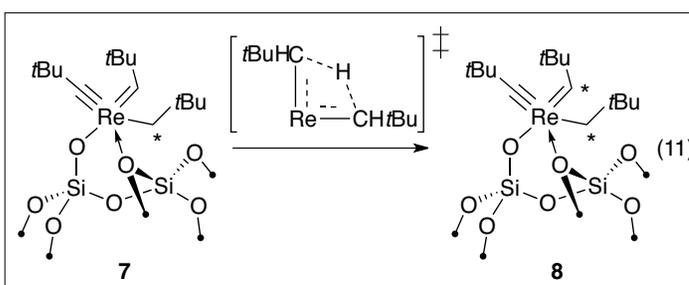
Scheme 11. Proton transfer of a surface Re alkylidene.

Heterolytic splitting of C–H bonds typically occur for either transition metal complexes containing metal ligand multiple bonds such as M=NR[27] or M≡CR[28] or for complexes containing ligands with available π–electrons such as M–OR.[26,29] These π–electrons act as the base to deprotonate the C–H σ–complex, while the π–electrons bind the ligand to the metal (Scheme 10).

There are many examples of this type

ylene.[2] Both the nature of the active site and the mechanism of polymer initiation are a topic of current debate. The active site is thought to either be Cr(II) or Cr(III). However, since less than 10% of Cr ions in the Phillips catalyst are active during polymerization, it is difficult to study the true active site of the catalyst.

Grafting of chromium siloxide **9** onto a uniform silica surface produces the well-defined chromium siloxide surface

species **10** (Scheme 12).[31] We were then able to take advantage of the Thermolytic Molecular Precursor approach espoused by Tilley.[32] Heating **10** under high vacuum (<10^{-5} torr) to 400 °C for 4 h gave **11**, free of hydrocarbons. Using X-ray absorption spectroscopy (XAS), we confirmed that the Cr on the surface was indeed four-coordinate Cr(II) analogous to the starting molecular siloxide complex. However, this species had low activity for the polymerization of ethylene (1.6 kg PE (mol Cr)$^{-1}$h^{-1}).

Treatment of the molecular complex **9** with N$_2$O produced the dimeric Cr(III) species **12** (Scheme 13).[31] Similarly, reaction of surface species **11** with N$_2$O gave an analogous dimeric Cr(III) species **13** on the silica surface (as shown by XAS). Species **13** is much more active during the polymerization of ethylene with an activity of 19 kg PE (mol Cr)$^{-1}$h^{-1}. This suggests that Cr(III) centers are the active sites of the Phillips catalyst. The modest activity of **11** could be caused by trace amounts of Cr(III), observed by EPR.

Additionally, we grafted the mononuclear Cr(III) siloxide **14** onto silica to give **15** (Scheme 14). Species **15** was then thermolyzed at 400 °C under high vacuum (< 10^{-5} torr) to give monomeric Cr(III) surface species **16**, which we also characterized by XAS.[33] Species **16** is an active ethylene polymerization catalyst, giving initial polymerization activity of 15 kg PE (mol Cr)$^{-1}$h^{-1}. The polymer produced with this catalyst has high molecular weight (M_w = 415.1 kg/mol) and high dispersity ($Đ$ = 12.3) presumably due to the amorphous nature of the surface. This also supports monomeric Cr(III) as being the active site for the Phillips catalyst.

The mechanism of polymer chain initiation for the Phillips catalyst is a topic of debate. Olefin polymerization requires that the active site has both an open coordination site and a M–C bond.[5] The active site of Phillips catalyst has open sites but no M–C bond. The question is how does the first M–C bond form? There have been several proposals in the literature for different activation mechansims involving both Cr(II) and Cr(III) centers.[2] A few proposed active polymerization species are shown in Scheme 15.

One mechanism for a Cr(III) active site involves C–H bond activation of an sp^2 C–H bond of ethylene to produce a chromium vinyl species on the surface (Scheme 16). In order to test this hypothesis, we characterized the end groups of the polymer chains produced by our catalyst and by the Phillips catalyst.[33,34] In both cases the polymer contained both vinyl and methyl end groups as measured by ^{1}H and ^{13}C NMR. Additionally, NMR analysis of the polymer showed that it is highly lin-
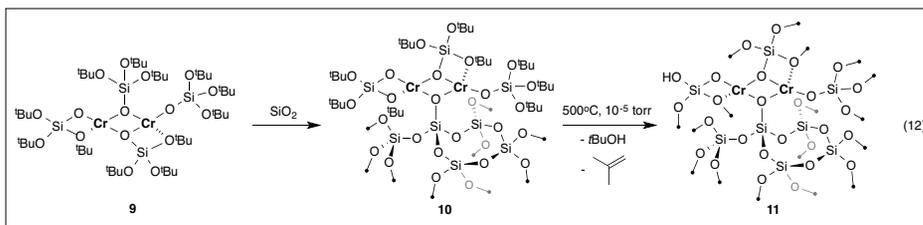
Scheme 12. Synthesis of unsaturated Cr(II) sites on silica.
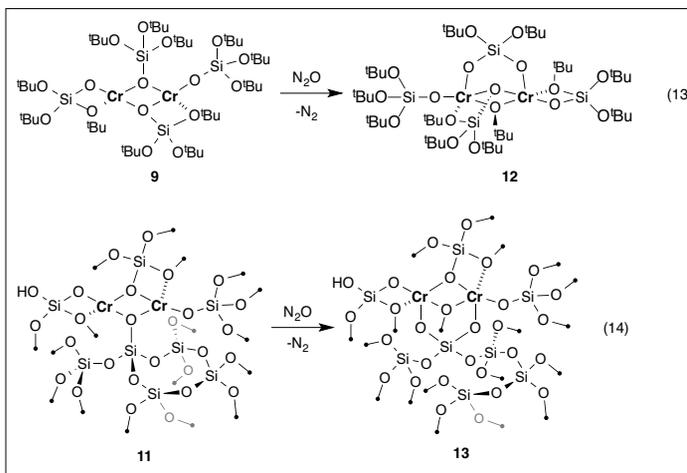
Scheme 13. Synthesis of unsaturated Cr(III) species using N$_2$O.
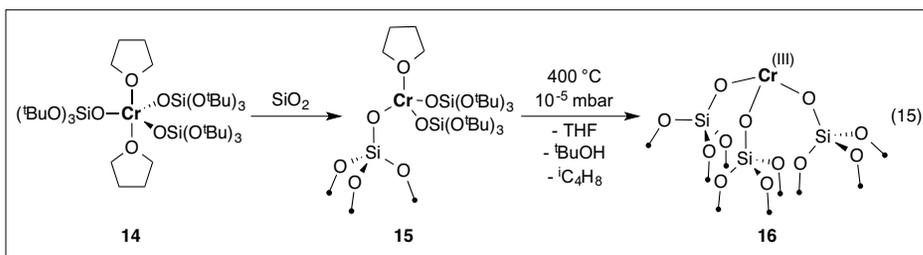
Scheme 14. Synthesis of monomeric Cr(III) species on silica.
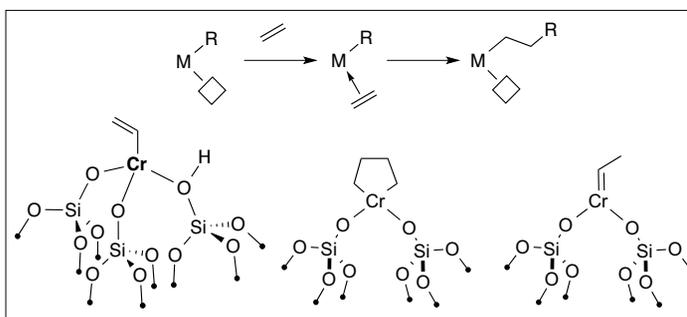
Scheme 15. Possible intermediates during the polymerization of ethylene by isolated Cr(III) sites.

ear, suggesting that β–hydride elimination is slow compared to chain propagation. Additionally XAS measurements indicated that the oxidation state of the active site does not change during catalysis. All these data are consistent with an initiation mechanism where heterolytic C–H activation by Cr(III) sites produces a chromium vinyl species which then polymerizes by a traditional Cossee–Arlman insertion mechanism. DFT calculations showed that this initiation mechanism had the lowest activation energy of all the proposed initiation steps involving a Cr(III) active site.

In fact, species **16** also catalyzes the dehydrogenation of propane to propene. Exposure of **16** to propane in a fixed bed reactor at 550 °C produces propylene and hydrogen along with cracking products methane, ethylene, and ethane.[35] Catalyst **16** forms propene with 72% selectivity at an initial rate of 10.3 mol C$_3$H$_6$ (mol Cr)$^{-1}$h^{-1}. The reaction conditions used in this reaction make mechanistic studies difficult. Thus, we used DFT calculations to investigate the mechanism.[35] The most favored mechanism, shown in Eqn. (16) (Scheme 17), consists of a heterolytic C–H activation to produce a Cr–C$_3$H$_7$ species followed by β–H transfer giving propylene. This is
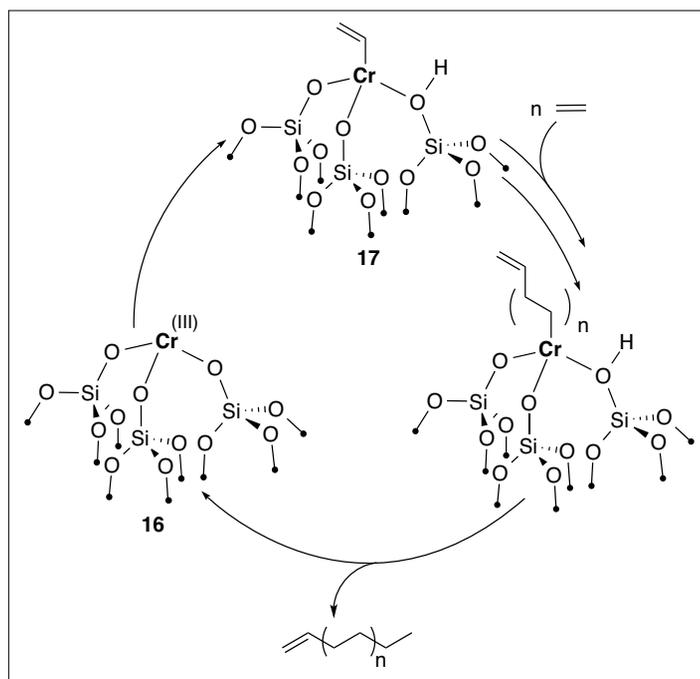
Scheme 16. Possible mechanism of ethylene polymerization by isolated Cr(III) sites.
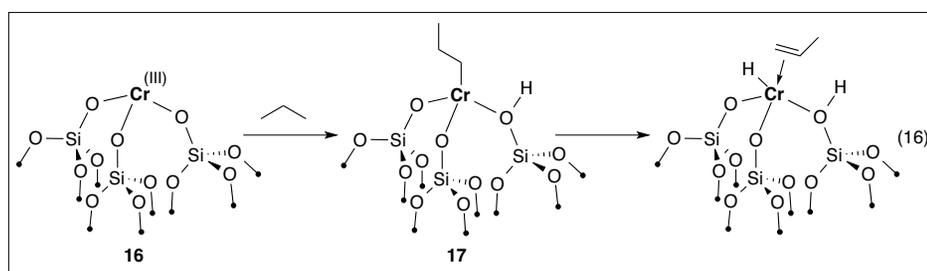
Scheme 17. Possible mechanism of propane dehydrogenation by isolated Cr(III) sites.

similar to the initiation mechanism of ethylene polymerization shown in Scheme 16.

Heterolytic C–H bond activation appears to be general for a variety of metal ions supported on silica. For example Hock and coworkers made a single site Co catalyst by impregnation of $Co(NH_3)_6Cl_3$ into silica at high pH.[36] Subsequent calcination above 150 °C caused reduction of the Co from Co(III) to Co(II) confirmed by XAS and EPR. This catalyst dehydrogenates propane with 91% selectivity and initial activity of 0.66 mol C_3H_6 (mol Cr)$^{-1}$h^{-1}. The activity and selectivity steadily increase over the course of 20 h to 1.76 mol C_3H_6 (mol Cr)$^{-1}$h^{-1} and 95%.

Hock and coworkers also prepared a single site Zn^{2+} on silica by impregnation of $Zn(NO_3)_2$ at high pH and subsequent calcination.[37] This catalyst dehydrogenated propane with an initial activity and selectivity of 0.77 mol C_3H_6 (mol Cr)$^{-1}$h^{-1} and 95%. The catalyst slowly deactivates over 12 h to an activity of 0.39 mol C_3H_6 (mol Cr)$^{-1}$h^{-1}. In both of these cases DFT calculations supported a mechanism in which heterolytic C–H activation was the rate-determining step.

We can draw a few general trends from these observations. Firstly, for many processes catalyzed by metal oxide catalysts the rate-determining step appears to be heterolytic C–H bond activation. This was shown above for both ethylene polymerization and propene dehydrogenation. Secondly, since the rate of these reactions is proportional to the pK_a of the C–H bond, more acidic C–H bonds will react faster. Furthermore, since the metal center can modulate the pK_a of a C–H bond the rate of the reactions appears to increase for metal centers that are more Lewis acidic. In the examples shown above, the rate of propane dehydrogenation increases over an order of magnitude just by going from Zn^{2+} for Cr^{3+}. This shows the importance of proton transfers during heterogeneous catalysis.

Conclusions and Perspectives on Heterogeneous Catalysis

Typically, conversion of alkanes into more useful chemicals must be done at very high temperatures using heterogeneous catalysts. One reason for this is that the first transformation that must take place when converting hydrocarbons is the activation of a strong C–H bond. While

there are many ways this *could* happen, the above examples from SOMC show that proton transfers often play a key role in the homologation of hydrocarbons.

These proton transfers fall into two key categories: σ–bond metathesis and heterolytic C–H bond cleavage. While they both involve proton transfer as a key element, they typically play different roles in catalysis. In the examples above, heterolytic C–H bond activation takes place for metal oxides on silica. However, σ–bond metathesis occurs for metals which already contain a very basic ligand (*i.e.* hydride or alkyl group). Thus during catalysis, heterolytic cleavage often serves to initiate catalysis and produce a M–C bond while propagation of this species to produce other metal alkyl species would take place *via* σ–bond metathesis. Understanding these reactions opens the potential for the development of new catalytic transformations. Optimizing the potential of a particular catalyst for both of these reactions could produce a catalyst that does new and exciting chemistry.

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