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# Olefin Metathesis by Supported Metal Oxide Catalysts

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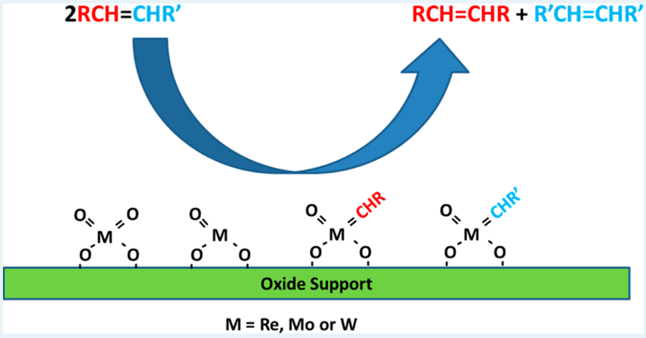

**ABSTRACT:** The literature of olefin metathesis by heterogeneous supported catalysts, both industrial-type supported metal oxides ($ReO_x/Al_2O_3$, $ReO_x/(SiO_2-Al_2O_3)$, $MoO_x/SiO_2$, $MoO_x/Al_2O_3$, $MoO_x/(SiO_2-Al_2O_3)$, $WO_x/SiO_2$, and $WO_x/(SiO_2-Al_2O_3)$) and supported organometallic complexes, is comprehensively reviewed. The focus of this Review is supported metal oxide catalysts, but the well-defined supported organometallic catalyst literature is also covered because such model catalysts have the potential to bridge heterogeneous and homogeneous olefin metathesis catalysis. The recent world shortage of small olefin feedstocks has created renewed interest in olefin metathesis as a route to synthesizing small olefins and is reflected in the recent growth of the patent literature. Despite the extensive application of supported metal oxides in industry for metathesis of small and large olefins, the molecular structures and oxidation states of the catalytic active sites, surface reaction intermediates, and reaction mechanisms of this important catalytic reaction have still not been resolved. The absence of reported in situ and operando spectroscopic studies from the olefin metathesis catalysis literature has hampered progress in this area. It appears from this literature review that the topic of olefin metathesis by heterogeneous supported metal oxide catalysts is still a relatively undeveloped research area and is poised for significant progress in understanding of the fundamental molecular details of these important catalytic systems in the coming years.

**KEYWORDS:** *metathesis, olefins, catalysts, supported, rhenia, molybdena, tungsta, organometallic*

## ■ INTRODUCTION

The olefin metathesis reaction was discovered by Anderson and Merckling at Dupont in 1955 when norbornene was polymerized to polynorbornene using lithium aluminum tetraheptyl and titanium tetrachloride catalysts[1] and would later be known as ring-opening metathesis polymerization.[2] Another Dupont researcher, Eleuterio, found in 1956 that ethylene, propylene, and butenes were produced when propylene was passed over an alumina-supported molybdena catalyst.[2] Natta independently discovered the ring-opening metathesis polymerization of cyclopentene with a molybdenum chloride catalyst.[3] Banks and Bailey of Philips Petroleum discovered that silica-supported tungsten oxide catalysts efficiently perform olefin metathesis of small olefins[4] and in 1964 pioneered the first large-scale olefin metathesis industrial process, called "Phillips Triolefin Process", that converted propylene to ethylene and 2-butene.[4,5] That same year, a patent was awarded to British Petroleum (BP) for disproportionation of short- and long-chain olefins using supported $Re_2O_7/Al_2O_3$ catalysts.[6] Scientists at Shell discovered the formation of liner $\alpha$-olefins via ethylene oligomerization and olefin metathesis in 1968, which subsequently led to commercialization of the Shell Higher Olefin Process (SHOP) in 1977 by supported molybdenum oxide on alumina catalysts.[7] Calderon and coworkers at Goodyear introduced the term "olefin metathesis" from the Greek words "meta" (change) and "thesis" (position)[8] after observing production of 3-hexene and 2-butene from the self-reaction of 2-pentene in the presence of a homogeneous tungsten hexachloride catalyst. There is much renewed interest in olefin metathesis to meet the world's shortage of propylene via metathesis of ethylene and 2-butene and production of sustainable, green products.[5,7,9−12]

The fascinating olefin metathesis reaction interconverts C═C bonds in hydrocarbons and can be tailored to produce a hydrocarbon of any length. It can be summarized as[9]

$$2RCH{=}CHR' \leftrightharpoons RCH{=}CHR + R'CH{=}CHR'$$

in which R and R′ are (functionalized) alkyls or hydrogen atoms.

The three most common types of olefin metathesis reactions are (1) cross-metathesis (exchange of double bonds between linear olefins), (2) ring-opening metathesis polymerization (opening of a closed olefin ring followed by polymerization), and (3) ring-closing metathesis (opposite of ring-opening metathesis).[9,10] The versatility of this novel reaction opened up new chemical routes that resulted in industrial applications of important petrochemicals, oleochemicals, polymers, and specialty chemicals.[5,10−12] These commercial applications

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have sparked a tremendous growth in basic research in this field over the past few decades that culminated in the 2005 Nobel Prize in Chemistry to Chauvin, Grubbs, and Schrock for their fundamental contributions to the development of catalytic olefin metathesis in organic synthesis.[12]

The initial olefin metathesis catalysts developed in the early years were poorly defined multicomponent homogeneous and heterogeneous systems. To address this issue, extensive basic organometallic chemistry research was performed to obtain better fundamental insights into the olefin metathesis reaction.[2,4,11] Employing homogeneous well-defined, single-component organometallic catalysts, it was elegantly shown that olefin metathesis proceeds via metal carbene complexes.[13] More recently, surface organometallic chemistry was also successfully employed to synthesize well-defined heterogeneous model supported tungsten, molybdenum, and rhenium organometallic catalytic active sites that exhibit high catalytic activity.[14] Density functional theory (DFT) calculations have been performed on the model catalyst systems to understand the nature of the catalytic active sites and reaction mechanism at the molecular level.[15−19] In contrast to the progress achieved with well-defined organometallic catalysts, there has been only limited progress for heterogeneous metathesis catalysts because the nature of the catalytic active sites typically has not been identified. The major industrial olefin metathesis processes, however, employ heterogeneous supported metal oxide catalysts (supported rhenia, molybdena and tungsta on $Al_2O_3$, $SiO_2$, and $SiO_2{-}Al_2O_3$ catalyst systems).[2,4,7,9−11] This literature review will focus on olefin metathesis by heterogeneous catalysts to highlight what is currently known and what more needs to be done to fully understand the heterogeneous olefin metathesis catalytic systems.

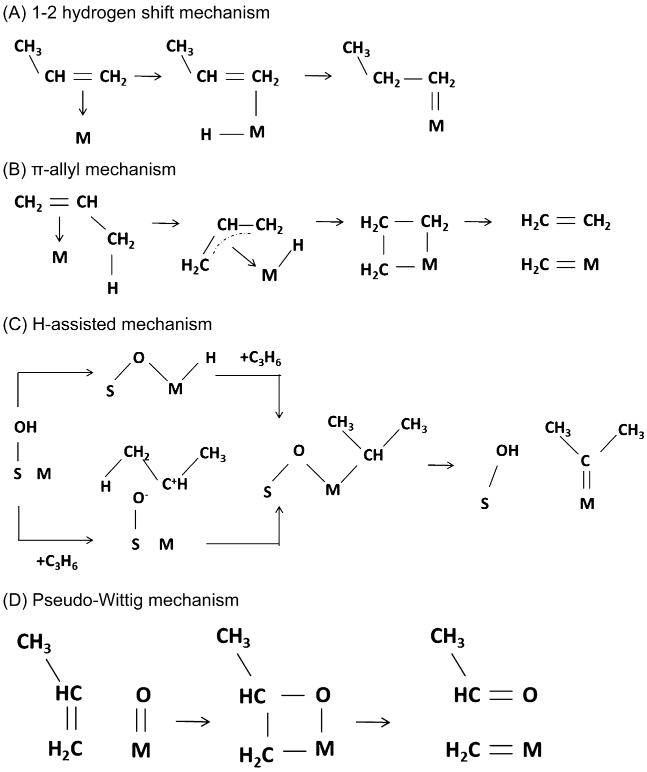
Supported metal oxide catalysts consist of an active metal oxide component dispersed on an inactive oxide support.[20,21] The dispersed metal oxide, the active component, can be present as isolated surface species, oligomeric surface species, clusters (<1 nm), or crystalline nanoparticles on a high surface area oxide support (~100−500 $m^2/g$).[21]

**Initiation Mechanisms.** Formation of the initial metal carbene species during olefin metathesis is claimed to proceed through one or more of the four initiation mechanisms, as shown in Scheme 1, for supported metal oxide catalysts.[22−24]

All of the olefin metathesis initiation pathways except the pseudo-Wittig mechanism involve an oxidative addition reaction in which the catalytic active center is oxidized by losing two electrons.

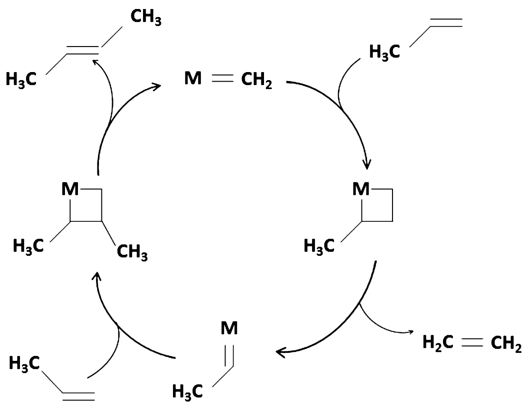
**Reaction Mechanism.** The reaction mechanism for propylene metathesis was proposed by Chauvin on the basis of the results of homogeneous catalysis.[13,25] It was subsequently supported by olefin titration results with supported rhenia/alumna catalysts. In these experiments, the supported rhenia/alumina catalyst was first activated with propylene or 2-butene. The surface intermediates were subsequently titrated with a second olefin (ethylene, propylene, or 2-butene) to form mixed olefin reaction products with deuterated olefins, confirming the mixed products. For example, 2-butene adsorption followed by ethylene adsorption produced propylene and some 2-butene reaction. The same number of sites was obtained by reacting either propylene or 2-butene with ethylene and would not have been the case if metal carbenes and metallacyclobutanes were not reaction intermediates, as shown in Scheme 2.[25]

Scheme 1. Proposed Olefin Metathesis Activation Mechanisms[a]



[a] M represents the catalytic active site and S represents the oxide support[22−24].

Scheme 2. Chauvin's Reaction Mechanism for Olefin Metathesis[13] for the Self-Metathesis of Propylene to Ethylene and 2-Butene



## SUPPORTED REO$_X$/AL$_2$O$_3$

**ReO$_x$ in Initial Oxidized Catalyst.** Supported $ReO_x/Al_2O_3$ heterogeneous catalysts are prepared by impregnation of an aqueous rhenia precursor ($HReO_4$, $(NH_4)ReO_4$, etc.) on the alumina support, then dried and calcined at elevated temperatures in an oxidizing environment. The crystalline $Re_2O_7$ low melting temperature of 297 °C assures that rhenium oxide becomes homogeneously dispersed on the alumina support during calcination at ~500 °C. The supported rhenia/alumina catalyst system has been studied in its initial oxidized state under oxidizing dehydrated conditions prior to activation and exposure to the olefin metathesis reaction conditions, but there is still not complete agreement about the structure of surface rhenium oxide species and oxidation states.

Early characterization with electron microscopy did not detect crystalline $Re_2O_7$ nanoparticles and concluded that if crystallites were present, they would have to be less than 2 nm.[26] Initial in situ Raman and IR studies of supported $ReO_x/Al_2O_3$ catalysts determined that crystalline $Re_2O_7$ nanoparticles were not present and assigned the detected vibrations to dimeric surface $(O{=})_3{-}Re{-}O{-}Re({=}O)_3$ species.[27,28] Subsequent in situ Raman and IR studies demonstrated that the vibrations correspond to two distinct isolated surface $(O{=})_3Re{-}O{-}Al$ trioxo sites on the alumina support, with the relative concentration of the second species increasing with surface rhenia coverage.[29,30] In situ IR spectroscopy measurements also revealed that at low rhenia loadings, surface $ReO_x$ reacts first by consuming the most basic surface, OH groups and at higher loadings, the surface $ReO_x$ consumes moderate and more acidic surface hydroxyls.[29,31,32]

The different anchoring sites on the alumina surface account for the presence of two distinct surface $ReO_x$ species on alumina.[29] As a consequence of the volatilization of rhenia oligomers,[29−31] rhenia is completely dispersed as isolated species on the surface of oxide supports. The molecularly dispersed nature of supported rhenia sites on high-surface-area oxide supports assures that all characterization techniques, surface as well as bulk, provide only surface information about the supported $ReO_x$ sites. In situ X-ray absorption near edge spectroscopy (XANES) studies concluded that surface rhenia on alumina under dehydrated, oxidizing conditions is present as $Re^{7+}$ with trioxo $(O{=})_3ReO$ coordination[33,34] as shown in Figure 1a.

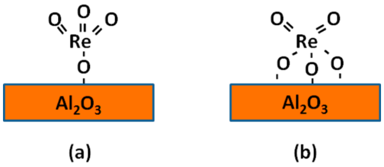


**Figure 1.** Proposed molecular structures of surface $ReO_x$ species with (a) trioxo $ReO_4$ and (b) dioxo $ReO_5$ coordination on $Al_2O_3$.

More recent in situ XANES/EXAFS and DFT calculations concluded that the fully oxidized surface rhenia species may possess dioxo $(O{=})_2Re({-}O{-}support)_3$ penta coordination[35] on $Al_2O_3$, as shown in Figure 1b. The fitting of EXAFS data with only one surface $ReO_x$ structure when in situ Raman and IR spectroscopy show that there are two distinct surface $ReO_x$ species is problematic because XAS provides only an average molecular structure. Additional studies are clearly required to resolve this molecular structural issue surrounding the fully oxidized surface rhenia species. In a recent review, Okal and Kepinski concluded that "even though significant progress has been made in the understanding of the chemistry of supported rhenium oxide catalysts a detailed description of the [rhenia] species is still lacking and requires further study".[36]

**Activated $ReO_x$ in Reducing Environments.** Much less information is currently available about the partially reduced surface rhenia species on alumina. Both Shpiro et al.[37] and Yide et al.[38] studied the oxidation states of supported rhenia/$\gamma$-$Al_2O_3$ catalysts by XPS under vacuum conditions and concluded that after hydrogen reduction, the initial $Re^{7+}$ is transformed to a mixture of Re oxidation states. Balcar et al. concluded that activation of the catalyst in an inert environment results in a mixture of $Re^{7+}$ and reduced surface rhenia species.[39] Fung et al. reduced a low loaded supported rhenia/$Al_2O_3$ catalyst with $H_2$ at elevated temperatures and monitored the changes with in situ EXAFS and XANES and concluded that both oxidized and reduced rhenia species coexisted after the reduction treatment.[40] The Re $L_3$ XANES edge feature suggested that the oxidized rhenia resembled the $Re^{4+}$ present in bulk $ReO_2$. Ronning et al. also concluded from in situ EXAFS analysis after $H_2$ reduction of low loaded supported rhenia/$Al_2O_3$ catalysts that both reduced and oxidized rhenia species were present with the former accounting for ~80% of total $ReO_x$.[41] Similar conclusions were reached by Bare et al. from in situ XANES Re $L_3$ and EXAFS measurements of low loaded supported rhenia/$Al_2O_3$ catalysts after reduction by $H_2$ at 500−700 °C.[34] In situ FT-IR spectra with CO as the probe molecule also demonstrated that the surface rhenia species were partially reduced ($Re^{n+}$, with $0 < n < 7$) upon exposure to olefins.[42−45] Stoyanova et al. reported the presence of $Re^{6+}$ species from ex situ UV−vis spectra of used catalysts.[46] The presence of reduced surface rhenia species during olefin metathesis by supported rhenia/$Al_2O_3$ is consistent with the known activation of supported rhenia/$Al_2O_3$ catalysts in reducing environments of $H_2$,[31] CO,[42] hydrocarbons,[44] and photoreduction.[47]

**Surface Reaction Intermediates during Olefin Metathesis.** Only limited information has appeared in the heterogeneous catalysis literature about the nature of the hydrocarbon surface reaction intermediates during the olefin metathesis reaction by supported rhenia/alumina catalysts. Exposure of supported rhenia/$Al_2O_3$ catalysts to isobutene[42] and *n*-butene[48] at around room temperature and after evacuation gave rise to hydrocarbon fragments with $CH_3$ vibrations in the FT-IR spectra. The same surface $CH_3$ vibrations, however, were also observed with Re-free $Al_2O_3$, suggesting that the $CH_3$ fragments may be formed by the strong surface Lewis acid sites of the alumina support.[48] Furthermore, the catalyst was evacuated for 1 h before the FT-IR spectra were recorded. Such treatment would be expected to result in reaction and desorption of any reactive surface intermediates. In situ FT-IR under flowing propylene at 60 °C gave rise to vibrations from adsorbed propylene, ethylene, 2-butene, and a band at 1450 $cm^{-1}$ characteristic of aliphatic C−H groups.[48]

**Initiation and Reaction Mechanisms.** The most detailed mechanistic studies of olefin metathesis by supported rhenia/$Al_2O_3$ catalysts with chemical probe reactions have been reported by Coperet and collaborators.[23] The 1−2 hydrogen shift and H-assisted metathesis reaction mechanisms were ruled out by the absence of 3-methyl-2-pentene from the self-metathesis of *cis*-2-butene. The allyl mechanism was ruled out by the metathesis of (*Z*)-stilbene with ethylene to form styrene, a transformation that does not require the participation of allyl H atoms. It was concluded from these chemical probe studies that the pseudo-Wittig metathesis mechanism is the most probable for formation of the necessary initial surface carbene species. Earlier studies by Farona et al., however, did not discard the allylic mechanism.[24] Both Coperet et al.[23] and Farona et al.[24] concluded that ethylene cannot initiate metathesis owing to the absence of $H_2C{=}CD_2$ as a product of the cross metathesis of $C_2H_4$ with $C_2D_4$. This is also in agreement with the IR studies of Boelhouwer et al., who claimed ethylene does not reduce a $ReO_x/Al_2O_3$ catalyst.[48] As mentioned in the previous section, Chauvin proposed carbene and metallacyclobutane reaction intermediates from homogeneous catalysis and titration studies.[13,25] Direct determination of the proposed surface intermediates for this catalytic system still awaits confirmation.

**Number of Catalytic Active Sites.** There is a continued discussion in the metathesis catalysis literature about the number of activated sites present and participating during steady-state olefin metathesis because not all the supported $ReO_x$ sites on alumina are claimed to be active for olefin metathesis.[5,25,31] *Indirect* measurements based on kinetic analysis of the olefin metathesis reaction over supported rhenia/alumina catalysts and quantitative titration with chemical probe molecules (NO, CO and bases) of activated catalysts suggest that only a small number of the supported rhenia sites participate in the metathesis reaction at room temperature.[5,25,31] Chauvin et al. quantitatively counted the number of catalytic active sites present after olefin metathesis at room temperature for supported $ReO_x/Al_2O_3$ catalysts by chemical titration. After initial chemisorption of one olefin, evacuation of the catalyst system for 4−6 h and subsequent titration of the resulting surface reaction intermediates with a second olefin formed the mixed metathesis reaction products.[25] The same number of sites was reported to be involved in the reaction, regardless of whether propylene or 2-butene was used as an activator.[25] The number of sites did not depend on the contact time of the second reactant, ethylene, but on its partial pressure. This titration method is most likely undercounting the number of participating sites because (i) the catalyst is evacuated for 4−6 h, during which metathesis and desorption of the first olefin can take place and (ii) it assumes that the titration with the second olefin consumes all the surface reaction intermediates at rather mild temperatures. Without direct observation of the molecular events that take place during this titration method, it is not known if these assumptions are, indeed, representative of the actual reaction pathway. Yide et al.,[38] however, demonstrated that the number of activated surface $ReO_x$ sites on alumina can be significantly increased by activation with olefins at elevated temperatures, which indicates that the number of activated sites strongly depends on the pretreatment conditions. Using high throughput methods, Stoyanova et al. claimed that the calcination procedure (temperature and time), pretreatment conditions (temperature and gas) and reaction temperatures affect both conversion and selectivity.[46] This indeed suggests that the number of activated sites determined with room temperature activation is only a lower limit and that a much higher number of activated sites can be accessed by activation at elevated temperatures and with inclusion of promoters.

**Kinetics.** Kinetic studies of propylene metathesis by Kapteijn and Mol[49] showed that the reaction is pseudo-first-order in propylene partial pressure and that the reaction rate increases with $ReO_x$ loadings as a result of surface heterogeneity of the alumina support. The olefin metathesis catalytic activity of supported $ReO_x/Al_2O_3$ catalysis is strongly dependent on the rhenia loading on the alumina support.[31] For loadings below ~6% $ReO_x/Al_2O_3$ (0.75 Re/nm$^2$), the activity is very low. Optimal catalytic activity is observed for ~14−18% $ReO_x/Al_2O_3$ (~2.4 Re/nm$^2$), which corresponds to the maximum loading of surface rhenium oxide that can be anchored on an alumina support.[31]

The nonlinear relationship between the surface rhenia loading and olefin metathesis activity is most probably related to the relative abundance of two different surface rhenia species at these loadings, which in turn suggests that the surface rhenia species anchored on the neutral and more acidic surface hydroxyl sites may be more active for metathesis than the surface rhenia species on the basic surface hydroxyls.[31] Propylene metathesis by supported $ReO_x/Al_2O_3$ catalyst exhibited an overall activation energy of 25−40 kJ/mol.[49] The exponential increase in the reaction rate as a function of the rhenia content was claimed to result from a combined increase in the reaction rate and equilibrium constants, $k$ and $K$, respectively.[49] However, as noted above, increasing the reaction temperature also increases the number of activated rhenia sites, which further complicates the temperature dependence of the rate and equilibrium constants.[38,46]

**Surface Acidity.** The roles of surface Brønsted and Lewis acid sites on the alumina support upon olefin metathesis by supported rhenia/alumina catalysts have been studied extensively. Earlier researchers were of the opinion that the presence of surface Brønsted acid sites contributed to the metathesis activity of supported rhenia/$Al_2O_3$ catalysts.[50−54] Subsequently, attention has focused on the presence of neighboring Lewis acidic Al sites that are enhanced by the strength of the Brønsted acidity of silica−alumina.[55,56] This realization caused the metathesis literature to focus on the interaction of surface rhenia species with adjacent surface Lewis acid sites as being responsible for olefin-induced activation of rhenia catalysts.[14,35,57] The entire role of acidity upon olefin metathesis still needs to be resolved.

**Alumina Support Type.** Several researchers have also examined the role of mesoporous $Al_2O_3$ supports for olefin metathesis by supported rhenia/alumina. The Balcar and Onaka research groups have claimed that use of mesoporous alumina supports results in higher activity (as much as 20×) due to a higher concentration of surface Lewis acid sites, a lower concentration of basic surface OH groups, and better stabilization of surface reaction intermediates.[39,58−64] Onaka et al. also reported EXAFS studies, which found similar Re−O bonding for $ReO_x$ supported on both mesoporous and regular alumina. This result suggests that the same surface rhenia species are present on both types of alumina supports and that the enhanced performance derives from use of the mesoporous support.[62] The improvement, however, seems to be more significant in metathesis of functionalized olefins rather than that of linear olefins.[57,62] In contrast to Balcar et al. and Onaka et al., Bregeault et al. reported that mesoporous supports do not have an advantage over conventional alumina supports.[65]

**Promoters.** Promoters are claimed to increase the activity of $ReO_x/Al_2O_3$ catalysts by either maintaining Re in a desirable oxidation state,[66] increasing support acidity,[9] or changing local Re structures.[67] Some of the promoters that have been reported are $SiO_2$,[9] $(CH_3)_4Sn$,[31,67] $P_2O_5$,[68] $B_2O_3$,[69] $V_2O_5$,[45,69] $MoO_3$[45,69] and $WO_3$.[45,52] Although the enhancement of catalytic activity by promoters is accepted, additional fundamental studies are still required to understand the promotion mechanism(s).

**$ReO_x$/($SiO_2$−$Al_2O_3$).** The same surface $ReO_x$ structure is reported to be present on silica−alumina supports as on alumina, but a different structure is present on silica.[35] Studies by Mol et al. found that activity decreases with an increase in $ReO_x$ on $SiO_2$−$Al_2O_3$, contrary to the $Al_2O_3$ support.[31] At low rhenia loadings (<0.5 Re/nm$^2$), supported $ReO_x/(SiO_2-Al_2O_3)$ catalysts are 3−6 times more active than supported $ReO_x/Al_2O_3$ catalysts, and supported $ReO_x/SiO_2$ catalysts are inactive for olefin metathesis.[31,35,70] At low rhenia loadings, $ReO_x$ initially anchors by reacting with Si−(OH)−Al bridging hydroxyls, resulting in electron-poor rhenium sites that are claimed to be highly active sites.[31] With increasing rhenia loading, the additional $ReO_x$ is stabilized at Si−OH hydroxyls that result in inactive ≡Si−O−$ReO_3$ sites.[31] A recent paper by Bouchmella and Debecker et al. used a nonhydrolytic sol−gel (NHSG) method with Cl precursors and diisopropyl ether to prepare mesoporous Re−Si−Al catalysts Bouchmella et al.[71] These catalysts displayed superior activity over catalysts prepared via the incipient wetness impregnation method as a result of their superior properties, such as acidic sites, well dispersed $ReO_x$ species, and high surface areas. Interestingly, the loss of rhenia is claimed to be prevented by adding more alumina. The maximum activity is observed at a Si/Al ratio of 0.3.[71] The simultaneous variation of several experimental parameters complicates determination of the origin of the catalytic enhancement for olefin metathesis, and systematic studies are required to fully understand the catalyst structure−activity relationships for supported $ReO_x/(SiO_2-Al_2O_3)$ catalysts.

**Supported Organometallic Catalysts.** Model $ReO_x$ organometallic catalysts can provide fundamental insights about the reactive intermediates and reaction mechanism of olefin metathesis. Hermann et al. discovered in 1991[72] that methyltrioxorhenium (MTO), $CH_3ReO_3$, supported on silica−alumina is very active for metathesis of functionalized olefins. The same product selectivity is obtained for propylene metathesis by the model supported $MTO/Al_2O_3-SiO_2$ and conventional supported $ReO_x/Al_2O_3$ catalysts. Coperet et al. concluded from solid-state $^{13}C$ CPMAS NMR and DFT calculations for $CH_3ReO_3$ supported on alumina that the surface $Al_sCH_2ReO_3$ intermediate located at octahedral alumina sites represents the catalytic active species rather than the majority surface $Al_sReO_3CH_3$ species.[73,74] The active surface $Al_sCH_2ReO_3$ complex is structurally similar to the Tebbe reagent, which was the first well-defined metathesis catalyst and is used in carbonyl methylenation.[73,74]

A different activated structure of $CH_3ReO_3$ was proposed by Scott et al. on the basis of XAS measurements of $ZnCl_2$-modified $CH_3ReO_3/Al_2O_3$.[75] In this proposal, Lewis acidic Al centers are claimed to be the most favorable sites for $CH_3ReO_3$ chemisorption. The use of a mixed silica−alumina support instead of alumina is claimed to result in elongation of one of the Re═O bonds in $CH_3ReO_3$ via an interaction with an Al site.[76] Coperet et al. also reported that modifying the $Al_2O_3$ support by treatment with $Si(allyl)(CH_3)_3$ prior to impregnation with $CH_3ReO_3$ improves the cis/trans ratio of 2-butenes for propylene metathesis, mainly through an increase in the desorption kinetics.[77,78] Although the supported $CH_3ReO_3/Al_2O_3$ catalyst does not exhibit an induction period and is ∼10 times more active than the conventional supported $ReO_4/Al_2O_3$ catalyst system, it deactivates much more rapidly, a clear indication that supported organometallic catalysts are not identical to traditional supported $ReO_x/Al_2O_3$ catalysts.[79]

As mentioned above, silica supported rhenium complexes, rhenium oxide, and MTO typically do not exhibit olefin metathesis activity.[5,9,11,35,72] The *first* successful synthesis of a highly active silica supported ≡SiO−Re(≡C−Bu-*t*)(═CH−Bu-*t*)($CH_2$Bu-*t*) olefin metathesis catalyst was reported by Coperet and Basset et al. in 2001.[80] Structural knowledge of these grafted rhenium compounds having $d^0$ configurations and alkylidene ligands was drawn from the analogous homogeneous systems.[80] The silica support was partially dehydroxylated at high temperatures (700 °C) before impregnation of the Re complex to both stabilize the ligands and remove surface hydroxyls that promote double-bond isomerization.[80,81] The hydrocarbyl complex Re(≡C−Bu-*t*)(═CH−Bu-*t*)($CH_2$Bu-*t*)$_2$ was used as a catalyst precursor, and characterization with solid-state $^{13}C$ and $^1H$ NMR along with its ability to also metathesize alkynes allowed proposing the molecular structure as ≡SiO−Re(≡C−Bu-*t*)(═CH−Bu-*t*)($CH_2$Bu-*t*) catalyst.[80] Given that these compounds already possess Re═carbenes, the silica-supported Re(≡C−Bu-*t*)(═CH−Bu-*t*)($CH_2$Bu-*t*) catalyst does not require activation because it already contains Re═carbenes and is even compatible with functionalized olefins without coactivator such as $Me_4Sn$ required for $Re_2O_7/Al_2O_3$.

**Patents.** The patent literature for olefin metathesis by supported rhenia/$Al_2O_3$ catalysts has been quite active since 2000.[82−119] Supports of choice are $\gamma$-alumina,[82,84−90,93,97,99,102−104,110] mesoporous alumina,[98,99,101] and silica−alumina.[96,112] The alumina-based supports are sometimes treated with an inorganic halide (such as $FeCl_3$, $CuCl_2$, or $ZnCl_2$.)[90,99,102,113] and promoters that include $B_2O_3$,[96] $SnO_2$,[113] $Bu_4Sn$,[108] $Cs_2O$,[118] $Nb_2O_5$,[106,107] and $Ta_2O_5$.[86] The function of the Cl is most probably to remove the surface hydroxyls that are claimed to have a negative effect on the olefin metathesis reaction.[75,120,121] There is also emphasis on maintaining a very low concentration of heteroatom hydrocarbons in the feed because they negatively impact the olefin metathesis catalytic activity, presumably by site blocking.[84] One patent claimed that cofeeding $H_2$ enhances metathesis catalytic activity and allows operation at lower temperatures. Inclusion of $H_2$ could either minimize coke deposition or increase the number of reduced catalytic active sites.[91] Regeneration of supported rhenia/alumina is achieved by heating in an $O_2$-containing gas to >400 °C[107,122] and treatments with $H_2O_2$, NaOH, KOH, or $NH_4OH$.[122] The above olefin metathesis patent literature reveals the methodology employed by industry in preparing commercial supported rhenia/$Al_2O_3$ catalysts and some of their general concerns about how to optimize performance but does not provide any fundamental insights about the supported rhenia catalytic active sites during the different stages of the catalyst evolution: (i) synthesis (effect of support characteristics, promoters, poisons, and Re precursors), (ii) activation (effect of air, inert, $H_2$, and CO), (iii) olefin metathesis reaction conditions (effect of temperature and feed composition), and (iv) regeneration (effect of air, steam, $H_2$, etc.).

**Summary of $ReO_x/Al_2O_3$ Catalysts.** Although supported $ReO_x/Al_2O_3$ catalysts are currently not employed for large industrial applications because of the high price of rhenium and its volatility, this catalyst system has been studied extensively as a result of its high selectivity and catalytic activity at room temperature. Progress has been made in the understanding of $ReO_x/Al_2O_3$-catalyzed olefin metathesis, but many key details continue to elude catalysis researchers in this field. These include the (i) molecular structure of the initial oxidized isolated surface $ReO_x$ species, (ii) molecular structure(s) and oxidation state(s) of activated surface $ReO_x$ site(s) during olefin metathesis, (iii) number of activated catalytic sites during olefin metathesis, (iv) activation mechanism, (v) surface reaction intermediates, (vi) reaction mechanism, and (vii) promotion mechanism(s). The absence of direct characterization studies of supported $ReO_x/Al_2O_3$ catalysts *during olefin metathesis* has hampered progress in the understanding of this catalytic system. The availability of modern in situ and operando spectroscopy instrumentation (XAS, $^{13}C$ NMR, high field EPR, near atmospheric pressure-XPS, Raman and IR vibrational studies with isotopes) complemented with DFT calculations should allow resolution of the above issues in the near future.

## ■ SUPPORTED MOO$_X$ SYSTEMS

Supported molybdena catalysts are active for olefin metathesis at moderate reaction temperatures (25−200 °C) and are usually prepared from aqueous impregnation of ammonium salts, such as ammonium heptamolybdate, via incipient wetness impregnation.[123,124] Other preparative methods include sol−gel techniques,[125] flame spray pyrolysis,[126] and even spontaneous thermal spreading of crystalline $MoO_3$.[127] The resulting supported molybdena heterogeneous catalyst systems have been well characterized in their initial oxidized states under oxidizing dehydrated conditions prior to activation and exposure to the olefin metathesis reaction conditions. The molecular structures of the fully oxidized surface $MoO_x$ sites have been shown to be independent of synthesis method below the maximum dispersion or monolayer coverage limit.[20,128,129] Nonaqueous impregnation techniques employing molybdenum organometallic complexes have also been used to prepare supported molybdena catalysts with a variety of well-defined surface functionalities that are analogous to those of homogeneous metathesis catalysts.[130−132]

**$MoO_3/SiO_2$.** Supported $MoO_3/SiO_2$ catalysts are about an order of magnitude less active for olefin metathesis than supported $MoO_3/Al_2O_3$ catalysts;[70] however, the dehydrated supported $MoO_3/SiO_2$ system is viewed as a model metathesis catalyst because only isolated surface $MoO_x$ sites are generally thought to be present below the maximum dispersion limit of molybdenum.[133−136]

**Supported $MoO_x/SiO_2$ in Initial Oxidized Catalyst.** The dehydrated, fully oxidized surface $MoO_x$ species on $SiO_2$ have experimentally been characterized with in situ UV−vis,[123,133,136] Raman,[20,123,133,136−139] XAS,[136−139] isotopic $^{18}O-^{16}O$ exchange,[140] and IR spectroscopy[133,136] and have been found to be present as isolated dioxo $(O{=})_2MoO_2$ and mono-oxo $O{=}MoO_4$ species, as depicted in Figure 2. The surface dioxo $(O{=})_2MoO_2$ structure represents the majority species (see Figure 2,b, respectively).[128,129,133−136] Above the maximum dispersion limit, crystalline $MoO_3$ NPs also form (see Figure 2c).[128,133,136] One study has claimed that both isolated and oligomeric surface $MoO_x$ sites are present on $SiO_2$ (SBA-15) from in situ Raman, UV−vis, and XAS measurements.[139] The absence of pronounced Mo−Mo features in the 3.2−4.0 Å range in the EXAFS second coordination sphere, present for crystalline $MoO_3$, does not support the assignment of a significant amount of surface oligomers. A more recent study with a similar $MoO_3/SiO_2$ catalyst employing SBA-15 employed more extensive structural characterization (in situ Raman, IR, UV−vis, XANES, EXAFS, and NEXAFS), however, found no evidence for surface $MoO_x$ oligomers and concluded that the surface $MoO_x$ species on $SiO_2$ are primarily present as isolated surface dioxo $MoO_4$ species.[136] DFT calculations support the presence of two isolated surface $MoO_x$ structures on $SiO_2$ and the greater stability of the isolated surface dioxo $MoO_4$ than the mono-oxo $MoO_5$ sites.[16,134]

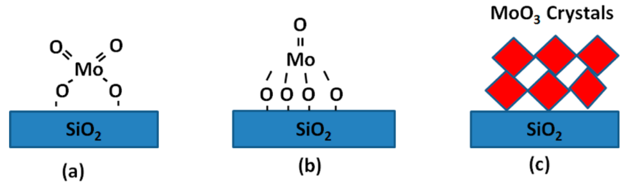


**Figure 2.** Structures of $MoO_x$ species on $SiO_2$. Surface $MoO_x$ dioxo (a) and mono-oxo (b) species coexist with $MoO_3$ crystals (c) at high coverage.

**Activated $MoO_x/SiO_2$ in Reducing Environments.** The nature of surface $MoO_x$ sites during olefin activation and metathesis reaction are still not known because in situ and operando spectroscopy studies during catalyst activation and olefin metathesis reaction conditions have not been reported.[141−146] Yermakov et al. examined a series of organometallic complexes on $SiO_2$, produced from Mo($\pi$-allyl)$_4$ and containing different Mo oxidation states, for self-metathesis of propylene at 90 °C. They concluded that the initial $Mo^{4+}$ complex leads to the highest metathesis activity, whereas initial $Mo^{6+}$ and $Mo^{2+}$ are inactive for the metathesis of propylene at 90 °C, but supporting evidence that the initial oxidation states were unchanged during the metathesis reaction was not provided.[130] Kazansky et al. activated a supported $MoO_3/SiO_2$ catalyst by photoreduction in the presence of CO, which allowed determination of the number of reduced sites by quantifying the $CO_2$ formed, with subsequent cyclopropane adsorption. It was concluded that surface $Mo^{4+}$ species are the active metathesis sites because their concentrations, measured with in situ UV−vis spectroscopy, related relatively well to catalytic activity.[142,143]

Zhang et al. examined the oxidation states of $MoO_x/SiO_2$ catalysts pretreated under $H_2$, $H_2-N_2$ and $H_2$ conditions with ex situ XPS and EPR.[141] A correlation between the room temperature quenched EPR $Mo^{5+}$ signals and propylene conversion suggested that the $Mo^{5+}$ sites are the catalytic active sites. Two distinct $Mo^{5+}$ sites were detected: a distorted $MoO_5$ square pyramidal and a distorted $MoO_6$ coordination, with the former coordination suggested to be the catalytic active site. The optimum $H_2$ pretreatment was found to be 400−450 °C; over-reduction at higher temperatures was proposed to form $Mo^{4+}$, which was thought to be responsible for the reduced activity.[141] DFT calculations have concluded that surface dioxo $MoO_4$, and not the surface mono-oxo $MoO_5$, species are the energetically favored precursors of the catalytic active sites for olefin metathesis.[16]

**Surface Reaction Intermediates during Olefin Metathesis.** No in situ and operando studies during olefin metathesis with supported $MoO_x$ catalysts have been reported. Consequently, surface reaction intermediates have not yet been reported for $MoO_x/SiO_2$ catalysts. Kazansky et al. reported the first in situ IR detection of surface $Mo{=}CH_2$ intermediates from cyclopropane adsorption on photoreduced $MoO_x/SiO_2$ catalysts.[143,144] Adsorption of ethylene on a CO-treated photoreduced $MoO_x/SiO_2$ catalyst resulted in two UV−vis bands at ~480 and ~590 nm, as well as IR bands at 2985, 2955, 2930, and 2870 $cm^{-1}$. These bands were tentatively assigned to molybdenum cyclobutane and $\pi$-bonded propylene complexes, respectively.[144,145] Catalyst deactivation was claimed to result from transformation of the active surface molybdenum cyclobutane intermediates into inactive surface $\pi$-bonded propylene.[145] These very early in situ IR and UV−vis spectroscopy studies, however, were not taken during either catalyst activation with olefins or olefin metathesis reactions. More detailed fundamental insights came from DFT calculations that concluded that the IR bands reported by Kazansky et al. mostly correspond to a stable square-pyramidal (SP)

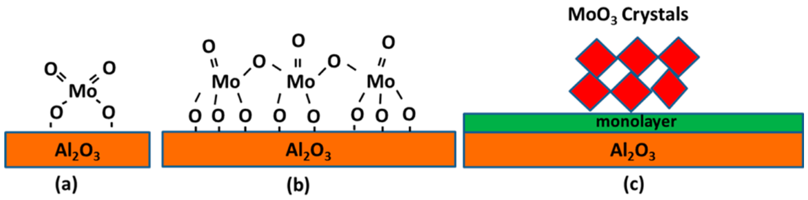


Figure 3. Structures of surface $MoO_x$ species on $Al_2O_3$. (a) Isolated dioxo $MoO_4$, (b) oligomeric mono-oxo $MoO_5$, and (c) crystalline $MoO_3$ NPs on surface $MoO_x$ monolayer.

molybdenum cyclobutane rather than a more reactive trigonal bipyramidal (TBP) molybdenum cyclobutane.[16]

**Initiation and Reaction Mechanisms.** Surface isopropoxide species were recently claimed to be the major surface reaction intermediates during the initial stage of propylene metathesis by supported $MoO_x$/SBA-15 catalysts (activation of surface $Mo^{6+}$ sites by reduction to $Mo^{4+}$ and formation of a $C_3$ oxygenate).[22] This conclusion was based on the similarity of IR bands for the surface intermediates formed by adsorption of propylene and isopropyl alcohol as well as their similar heats of adsorption. The IR vibration for the surface isopropoxide C−O bond, however, was not detected for the photoreduced catalysts described in the previous section, which suggests differences between the photoreduction and initial olefin activation treatments.[143,144] Transient isotopic switching experiments, however, would allow for better discrimination between surface reaction intermediates and possible spectator species. To date, DFT calculations start with a surface $Mo{=}CH_2$ intermediate, do not address the initiation mechanism, and suggest that olefin metathesis occurs via a mechanism that proceeds through a molybdenum cyclobutane intermediate.[16]

**Number of Catalytic Active Sites.** For the $MoO_x$/SBA-15 system, the number of active sites after activation at 50 °C with propylene ($H_2C{=}CHCH_3$) was determined to be <2% of the total surface $MoO_x$ sites. This conclusion was based on perdeuteroethylene titration of the surface intermediates that remained on the catalyst when the reaction was stopped.[22] Bykov et al. investigated the metathesis of $\alpha$-olefins on heterogeneous supported binary ($MoCl_5/SiO_2{-}Me_4Sn$) and ternary ($MoCl_5/SiO_2{-}Me_4Sn{-}ECl_4$, E = Si or Ge) catalysts and concluded that up to 6% of the Mo atoms are active at 50 °C without applying evacuation or desorption steps.[146] Subsequently, these workers reported that 13% of the Mo sites present in ($MoOCl_4/SiO_2$)−$SnMe_4$ catalysts participate in the metathesis reaction.[147] As mentioned above, there are inherent assumptions in the chemical titration approach that may be undercounting the number of activated $MoO_x$ catalytic sites.

**Kinetics.** The propylene metathesis reaction rate, normalized per unit of surface area and expressed as millimoles/(meter$^2$-second), for supported $MoO_x$/SBA-15 catalysts as a function of $MoO_x$ loading exhibited an exponential rise with increasing surface $MoO_x$ coverage until crystalline $MoO_3$ nanoparticles were present at high coverage.[136] This strongly increasing reactivity trend was attributed to increasing distortion of the isolated dioxo surface $MoO_4$ sites with higher surface $MoO_x$ coverage on SBA-15. Such distortion is due to lateral interactions between the $MoO_x$ sites and is also related to the accessibility of anchoring on 6-, 8- or 10-membered rings. The surface $MoO_x$ sites were also proposed to interact with adjacent Brønsted acid sites for activation,[136] but Brønsted acid sites are not significant for siliceous materials, such as SBA-15. The reactivity rapidly decreased with increasing amounts of crystalline $MoO_3$ nanoparticles, which reflects the low activity of $MoO_3$ nanoparticles and probably also agglomeration of a portion of the surface $MoO_x$ catalytic active sites.[128] Earlier studies by Mol et al. observed a similar trend for the $MoO_x/SiO_2$ system, with the catalytic activity reaching a maximum at 1.0 Mo atoms/nm$^2$ and decreasing at higher molybdena loadings.[70,136]

**Supported Organometallic Catalysts.** Coperet and Shrock et al. showed that silica-supported organometallic Mo-based catalysts having the general formula [(Y)M (≡ER)(=CHtBu)(X)] (Y =≡SiO) (X=$CH_2$tBu, OR or NR2; with M = Mo with ER = NR) out-performed their homogeneous analogues.[131] As mentioned in the previous section about supported organometallic $ReO_x$ catalysts, these supported organometallic complexes are grafted by replacing one of the anionic X ligand with a siloxy ligand[131,132] and normally remain intact on the $SiO_2$ support. In situ $^{13}$C CPMAS NMR showed that the Mo-supported organometallic complexes react via the same surface alkylidene and metallacyclobutane intermediates as observed in homogeneous catalysts.[131,132] Although the model silica-supported surface organometallic catalysts have provided many molecular details about olefin metathesis catalytic active sites and surface reaction intermediates, there is still a materials gap between the surface organometallic catalysts and industrial-type heterogeneous supported metal oxide catalysts because of the special ligands used to stabilize the surface organometallic catalysts on $SiO_2$.

**$MoO_3/Al_2O_3$.** Supported $MoO_x/Al_2O_3$ catalysts find industrial application in the SHOP for metathesis of long-chained olefins ($C_2H_4{-}C_{20}H_{40}$).[5,7,9] The supported $MoO_x/Al_2O_3$ catalysts are at least 10 times more active than the supported $MoO_x/SiO_2$ catalysts in the same temperature range, reflecting their easier reduction or activation.[9,70]

**$MoO_x$ in Initial Oxidized Catalyst.** The surface $MoO_x$ structures present for fully oxidized, dehydrated supported $MoO_3/Al_2O_3$ catalysts have been established in the past few years from extensive in situ spectroscopic measurements (Raman,[123,137,148,149] UV−vis,[123] XAS[137,148,149]) and DFT calculations.[150,151] At low surface molybdena coverage (<20% of monolayer), isolated surface dioxo $(O{=})_2MoO_2$ species dominate, and at high surface coverage, both isolated surface dioxo $MoO_4$ and oligomeric mono-oxo $O{=}MoO_4$ species coexist on the alumina support, as indicated in Figure 3. Above monolayer coverage (4.6 Mo atoms/nm$^2$), crystalline $MoO_3$ NPs are also present on top of the surface $MoO_x$ species because there are no anchoring surface Al−OH sites remaining.[152]

**Activated $MoO_x$ in Reducing Environments.** Less is known, however, about the oxidation state and molecular structure of supported $MoO_x/Al_2O_3$ catalysts that have been activated or exposed to olefin metathesis reaction conditions. The earliest reported spectroscopic characterization for supported $MoO_3/Al_2O_3$ involved initially exposing the catalysts to the propylene metathesis reaction at 200 °C and subsequently examining the catalysts with ex situ XPS and EPR spectroscopy.[153,154] It was concluded that activated sites formed only from initial $Mo^{6+}$ and $Mo^{4+}$ species while other oxidation states were inactive, but measurements were performed after metathesis and exposure to air that can oxidize the catalysts. Carbon monoxide reduction of supported $MoO_3/Al_2O_3$ catalysts suggested that surface $MoO_x$ sites anchored at basic surface hydroxyls do not reduce at 500 °C, but surface $MoO_x$ sites anchored at nonbasic surface hydroxyls reduce to approximately $Mo^{4+}$.[155] From ex situ solid-state $^{27}Al$ NMR of molybdena-supported mesoporous $Al_2O_3$, it was proposed that only surface $MoO_x$ sites on surface $AlO_6$ sites are most active for olefin metathesis,[156] but ambient moisture may have affected the coordination of the surface $AlO_x$ sites. The importance of the coordination of the surface alumina sites where the active surface $MoO_x$ species are anchored is supported by DFT calculations.[15−18] The DFT calculations suggest that the most active surface $MoO_x$ sites possess pseudo-$MoO_4$ coordination and are anchored to $AlO_6$ sites on the (100) surface of the $Al_2O_3$ support.

**Surface Reaction Intermediates during Olefin Metathesis.** DFT studies also suggest that the less stable surface Mo-cyclobutane intermediates anchored to the surface $AlO_6$ sites are responsible for their high reactivity.[15] Early in situ studies by Olsthoorn and Moulijn stated that propylene is π-bonded on both oxidized and CO-reduced $MoO_x/Al_2O_3$ catalysts.[157] From the position of the 1600 $cm^{-1}$ C═C bond, which is lower than that (1645 $cm^{-1}$) observed in adsorption of propylene on pure $Al_2O_3$, it was concluded that adsorption is reversible on the $MoO_x/Al_2O_3$ catalyst, and the resulting π-bonded complex could be an intermediate during the reaction.[157] The absence of transient experiments, however, did not allow for discrimination between surface reaction intermediates and possible spectator species.

**Initiation and Reaction Mechanisms.** From isotopic D-labeled studies, it was proposed that olefin metathesis of long chain olefins by supported $MoO_x/Al_2O_3$ catalysts is initiated and proceeds via surface π-allyl species,[158] suggesting that C−H bonds may be involved in metathesis by long-chain olefins. Recent DFT calculations, however, suggest that allylic CH bonds are not required for catalyst activation for small olefins and that the pseudo-Wittig mechanism is the most likely activation mechanism.[159]

**Number of Catalytic Active Sites.** The percentage of catalytic active surface $MoO_x$ sites on alumina that participate in olefin metathesis has received much attention by debates in the literature. Early studies by Burwell et al. for supported $Mo(CO)_6/Al_2O_3$ concluded less than 1% of surface $MoO_x$ sites are involved in the metathesis reaction at 53 °C.[160] This conclusion is in sharp contrast to the findings of Hightower et al., who found from NO poisoning experiments that for cobalt-promoted supported $MoO_3/Al_2O_3$ catalysts, ∼15% of surface $MoO_x$ sites were active at room temperature.[161] Handzlik et al. counted the number of activated surface $MoO_x$ sites present for supported $MoO_x/Al_2O_3$ catalysts during propylene metathesis by either slightly increasing the temperature or switching the flow to argon for tens of minutes. They found that only ∼1% of $MoO_x$ sites were activated at ∼50 °C; however, ∼4.5% of $MoO_x$ sites were activated for a tin-promoted supported $MoO_x/Al_2O_3{-}SnMe_4$ (Mo/Sn = 1.2) catalyst at the same temperature.[162] The lack of consistency in the reported number of catalytic active surface $MoO_x$ sites in each of the above studies is most likely related to the different catalysts and surface $MoO_x$ coverages employed. Furthermore, all the measurements were performed close to room temperature; the influences of activation temperature and olefin partial pressure on the number of activated surface $MoO_x$ sites were not examined. As mentioned above, there are inherent assumptions in the chemical titration approach that may be undercounting the number of activated $MoO_x$ catalytic sites. Direct spectroscopic observations are needed to determine how much these assumptions deviate from the actual situation.

**Kinetics.** The supported $MoO_x/Al_2O_3$ catalysts exhibit a maximum in steady-state activity for metathesis of small olefins at approximately monolayer coverage of surface $MoO_x$ sites.[70,127] This suggested to most investigators that the surface $MoO_x$ sites, either isolated or oligomeric, are probably the precursors to the catalytic active sites and not crystalline $MoO_3$ or $Al_2(MoO_4)_3$ nanoparticles because the latter tend to form above monolayer coverage.[70,124−127,130] The individual contributions of the isolated and oligomeric precursor surface $MoO_x$ sites on alumina in generating activated sites for olefin metathesis, however, is still not known. Grunert and Minachev reported that the reaction order is 0.8 in propylene at 200 °C.[154] The apparent activation energy was reported to be 37−30 kJ/mol and decreased slightly with increasing Mo loadings.[154]

**Promoters.** Some of the promoters added to the $MoO_x/Al_2O_3$ system include $SiO_2$,[124−127] and $ECl_4$ (E = Si or Ge),[147] CoO,[161] and $(CH_3)_4Sn$.[162] $(CH_3)_4Sn$ is claimed to increase the number of Mo active sites.[162] The promotion mechanisms of the other promoters still require further studies for their understanding.

**Patents.** The industrial patent literature for olefin metathesis by supported molybdena catalysts has also seen activity in recent years.[82,84,91,93−97,104,108−112,114,163−188] The support of choice is γ-alumina,[82,163−167,174−183,186−188] but mesoporous alumina[84,98,100,184] and silica−alumina[185] supports have also been claimed. The alumina-based supports are sometimes treated with halides[178] and promoters that include $B_2O_3$,[184] CoO,[189] alkyl-Sn,[190] and alkyl-Pb.[179,190] The patents are about equally divided between metathesis of small olefins ($C_2H_4$-$C_4H_8$)[82,84,165,169−172,174,178,189,191−196] and higher olefins ($C_5H_{10}$−$C_{20}H_{40}$).[94,95,100,108,115,175−177,181−183,186−188,197] The promotion mechanisms have not received attention in the catalysis literature.

**$MoO_x/(SiO_2{-}Al_2O_3)$.** Mixed $Al_2O_3{-}SiO_2$ supports and zeolite supports have been claimed to improve the olefin metathesis activity for supported $MoO_x/(Al_2O_3{-}SiO_2)$ catalysts, but only limited studies have appeared for such catalysts.[124−127,198−205] It was proposed that mixed $SiO_2{-}Al_2O_3$ supports achieve an appropriate level of Brønsted acidity that is crucial for efficient catalytic performance during olefin metathesis with optimal activity achieved at moderate molybdena loadings[126,127,198−201] and that excessive Brønsted acidity may be responsible for side reactions such as cracking and isomerization.[198−200] Surface $Mo^{5+}$ sites, with $MoO_5$ or $MoO_6$ coordination, were detected for supported $MoO_x/(Al_2O_3{-}SiO_2)$ catalysts exposed to propylene metathesis with ex situ EPR after evacuation at 25 and 200 °C.[201] Although surface $Mo^{5+}$ sites were detected after metathesis, no information is provided about other Mo oxidation states that may possibly be more important (e.g., $Mo^{4+}$). The EPR measurements were complemented with ex situ $L_3$-XANES of fresh and used catalysts that indicated that the activated surface

$MoO_x$ sites are present as poorly formed oligomeric species containing some partially reduced Mo cations.[201] The ex situ spectroscopy characterization studies leave much to be desired because they were performed after the reaction was terminated and the samples were evacuated and exposed to ambient conditions containing molecular oxygen and moisture. The spectroscopic findings tend to be dominated by one Mo oxidation state (e.g., EPR is dominated by the $Mo^{5+}$ cations and XANES is dominated by $Mo^{6+}$ cations because a majority of the surface $MoO_x$ sites are not expected to be reduced, especially after exposure to air). Only direct spectroscopic characterization during olefin metathesis will reveal the nature of the actual surface $MoO_x$ cations on alumina present during the reaction.

The metathesis of 2-butene and ethylene on silica, silica−alumina, and alumina-supported $MoO_x$ catalysts was recently reported by Hahn et al.[202] The optimal reactivity is observed around 40 wt % silica. On silica−alumina supports, Brønsted acidity increases with increasing silica and $MoO_x$ loading, whereas an inverse trend is observed for Lewis acidity. This increasing Brønsted acidity is claimed to be responsible for improved metathesis activity of isolated $MoO_4$ and polymeric $MoO_6$ species that were detected from Raman and UV−vis measurements under ambient and dehydrated conditions, respectively. Combining results from ambient (hydrated) and dehydrated conditions is problematic because the molecular structures of surface $MoO_x$ species are strongly dependent on moisture content.[123] When $MoO_3$ crystals are present, the catalytic activity cannot be improved by the Brønsted acidity. Interestingly, in their later paper, butene reactions (self-metathesis of butenes and 2 to 1 isomerization) are reported to be faster on isolated species, where polymeric species catalyze metathesis of 2-butene and ethylene much faster.[203] This is a bit surprising because increasing Brønsted acidity would be expected to contribute more to side reactions, according to earlier studies.[198−200] Debecker et al. earlier claimed from self-metathesis of propylene with flame made $MoO_3/(SiO_2-Al_2O_3)$ that an inverse relationship exists between the number of Mo−O−Mo bonds and specific activity.[126] Therefore, Debecker et al. concluded that isolated $MoO_x$ sites represent the most active sites, which is contrary to the findings of Hahn et al. that polymeric $MoO_x$ sites are the most active sites for olefin metathesis. Debecker et al. also reported an one-pot aerosol synthesis method of $MoO_3-SiO_2-Al_2O_3$ from block copolymer (Brij58), $AlCl_3$, $12MoO_3H_3PO_4\cdot xH_2O$, or $MoCl_5$ with aqueous solution of tetraethyl orthosilicate and ethanol.[204,205] With an average pore size of 1.8−2.0 nm, these catalysts were free of $Al_2(MoO_4)_3$ and $MoO_3$ crystals and displayed activity 2−3 times higher than those prepared by using ammonium heptamolybdate on traditional $SiO_2-Al_2O_3$ supports.[204,205] As indicated above, a more systematic variation of synthesis parameters is needed to fully understand the relationships between synthesis and catalyst performance for olefin metathesis by supported $MoO_3/(SiO_2-Al_2O_3)$ catalysts.

**Summary.** The supported $MoO_x$ olefin metathesis literature has attracted much attention because of the industrial importance of the SHOP olefin metathesis process.[5,7,9] Although the molecular structures of the fully oxidized surface $MoO_x$ sites have been determined for unpromoted supported molybdena catalysts, the nature of the surface MoOx sites and surface reaction intermediates during olefin metathesis still need to be resolved. DFT calculations and model studies with supported organometallic catalysts have been very informative, but *direct* observation of the surface $MoO_x$ sites and surface reaction intermediates during olefin metathesis of both small and long-chain olefins still awaits further in situ and operando spectroscopy studies (e.g., XAS, $^{13}C$ NMR, high field EPR, near atmospheric pressure XPS, Raman, and vibrational IR studies with isotopes). Such studies are expected to resolve many of the key fundamental issues that surround supported $MoO_x$ catalysts.

## ■ SUPPORTED $WO_X/SIO_2$

The supported $WO_x/SiO_2$ catalyst has received much less attention in the olefin metathesis literature than either supported $ReO_x$ and $MoO_x$ catalysts, which is quite surprising because it is the major industrial olefin metathesis catalyst for the "Triolefin Process" that converts two propylene molecules to ethylene and 2-butene molecules.[4,5] The reverse process is called "Olefin Conversion Technology" and is now licensed by ABB Lummus.[5,11] One of the reasons for this relative inattention may be the need to employ higher temperatures (~350−450 °C) for activation of supported $WO_x/SiO_2$ catalysts. Use of such high temperatures precludes performing titration reactions because the surface reaction intermediates should have a very short lifetime and will react during the evacuation step. The supported $WO_x/SiO_2$ catalysts are typically prepared by impregnation of the aqueous $(NH_4)_6H_2W_{12}O_{40}$ precursor onto the $SiO_2$ support, followed by drying and calcination under oxidizing conditions at elevated temperatures (~500 °C).[206]

**$WO_x$ in Initial Oxidized Catalyst.** The surface $WO_x$ structures present for fully oxidized, dehydrated supported $WO_x/SiO_2$ catalysts have been established in the past few years from detailed in situ spectroscopic measurements (Raman[133,140,206] and UV−vis[133,140,206]). Both isolated surface dioxo, $(O{=})_2W(-O)_2$, and mono-oxo $O{=}W(-O)_4$ species coexist on silica (depicted in Figure 4), with the dioxo species being the dominant site. Above the maximum dispersion limit, crystalline $WO_3$ nanoparticles are also present, as shown in Figure 4. The oxidized supported $WO_x/SiO_2$ catalysts have structures that are analogous to the supported $MoO_x/SiO_2$ catalysts, which reflects the similar structural inorganic chemistry of both oxides.[140]

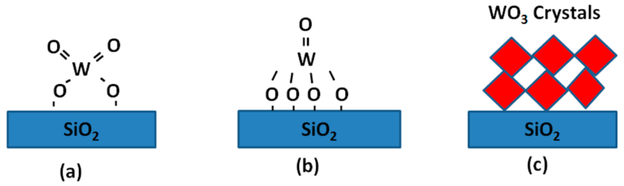


Figure 4. Structures of $WO_x$ species on $SiO_2$. Surface $WO_x$ species coexist with $WO_3$ crystals at high coverage. (a) Dioxo $WO_4$, (b) mono-oxo $WO_5$, and (c) crystalline $WO_3$ nanoparticles.

**Activated $WO_x$ in Reducing Environments.** The nature of the tungsten oxide structures present for supported $WO_3/SiO_2$ catalysts after catalyst activation and under olefin metathesis reaction conditions has not received any attention; no in situ or operando spectroscopy studies have been reported. Consequently, there is no agreement concerning knowledge about the nature of the tungsten oxide active site(s) responsible for olefin metathesis by supported $WO_x/SiO_2$ catalysts.[207−227]

**Initiation and Reaction Mechanisms.** There is no direct characterization study of the initiation and reaction mechanisms for olefin metathesis by $WO_x/SiO_2$ catalysts. Basrur et al. reported formation of traces of acetone and acetaldehyde during the induction period and claimed involvement of lattice oxygen in the mechanism.[224] The pseudo-Wittig mechanism could be implied from their studies. Basrur et al. also claimed detection of nonstoichiometric oxidation states, such as $WO_{2.9}$ from ex situ ESR studies,[224] but provided no information about the nature of the surface $WO_x$ sites. A recent DFT study of olefin metathesis employed the crystalline $WO_3(001)$ plane as the model for its catalytic active sites.[225] However, the oxidation states of $WO_x$ species were not mentioned. The crystalline $WO_3(001)$ plane is the most thermally stable plane and consists of polymeric $WO_5$ and $WO_6$ sites. This model, however, is not representative of the surface $WO_x$ sites anchored on $SiO_2$ (isolated $WO_4$ and $WO_5$ sites and $WO_3$ nanoparticles) in the heterogeneous supported $WO_3/SiO_2$ catalysts. Consequently, DFT studies with more realistic catalyst models still need to be performed.

**Number of Catalytic Active Sites.** No attempt to count the number of sites involved in olefin metathesis by supported $WO_x/SiO_2$ catalysts has been reported. As indicated above, it is highly unlikely that the short-lived surface reaction intermediates could be titrated at the high activation temperatures of 300−500 °C. Direct spectroscopic measurements during activation and olefin metathesis should be able to address the issue of number of participating catalytic active sites.

**Kinetics.** Detailed kinetic studies of olefin metathesis by supported $WO_x/SiO_2$ have not appeared in the literature, but several researchers have attempted to relate the nature of the $WO_x$ structures present on $SiO_2$ to the catalytic activity. Davazoglou et al. observed similar catalytic olefin metathesis performance for well-dispersed tungsten oxide at low loadings and on high loaded supported $WO_3/SiO_2$ catalysts. They concluded that the well dispersed tungsten oxide phase on $SiO_2$ is the catalytic active site because excess crystalline $WO_3$ did not influence the overall catalyst performance.[226] Wang et al. examined 1-butene isomerization and metathesis over two different supported $WO_3/SiO_2$ catalysts prepared with different silica supports.[227] Raman analysis[227] showed that the tungsten oxide was better dispersed on the lower surface area $SiO_2$ support, which is quite surprising because the opposite behavior would generally be expected. Whereas the lower surface area W-free $SiO_2$ support was not active for 1-butene isomerization, the higher surface area W-free $SiO_2$ support almost completely isomerized 1-butene, suggesting that the higher surface area support contained significant amounts of acidic surface impurities. The catalyst with higher surface area exhibited greater olefin metathesis activity, suggesting that the surface impurities were also acting as promoters. Unfortunately, no surface analysis was performed to determine the nature of the surface impurities present on the high surface area silica support.

For the cleaner supported $WO_3/SiO_2$ catalyst, the optimum metathesis performance was obtained at intermediate tungsten oxide loadings, where both dispersed surface $WO_x$ and crystalline $WO_3$ nanoparticles coexist. This observation suggests that $WO_3$ nanoparticles may also be responsible for 1-butene metathesis. Hua et al. investigated 1-butene self-metathesis with supported $WO_x$/MTS-9 (a titano-silica molecular sieve) and found that the metathesis performance was comparable over a wide range of tungsten oxide loadings, which suggests that both dispersed surface $WO_x$ species and $WO_3$ nanoparticles contribute to the olefin metathesis reaction.[215,216]

Chemechuen et al. investigated the influence of calcination temperature on the metathesis of ethylene and 2-butene to propylene over supported $WO_x/SiO_2$ catalysts. They concluded that the surface $WO_x$ species were the catalytic active sites for olefin metathesis, even though both surface $WO_x$ species and crystalline $WO_3$ nanoparticles were always simultaneously present in their catalysts.[213] Most recently, the metathesis of 1-butene was studied over supported $WO_x/SiO_2$ catalysts with moderate dispersions of tungsten oxide, where both surface $WO_x$ species and $WO_3$ nanoparticles coexist and yield the optimum metathesis performance.[218] The contributions of the surface $WO_x$ sites and $WO_3$ nanoparticles on silica to the olefin metathesis reaction appear to be unresolved. Studies with well-defined supported $WO_x/SiO_2$ catalysts are required to determine the catalytic contributions of the different $WO_x$ sites present in supported $WO_x/SiO_2$ catalysts.

**Surface Acidity.** Selectivity is claimed to be related to surface acidity in the $WO_x/SiO_2$ system.[207] Isomerization is claimed to occur through either alkoxide or allylic intermediates.[228] Sources of alkali metal ions such as $Na_2O$ and $K_2O$ can be added to suppress the Brønsted acidity, which is claimed to be responsible for undesired isomerization products.[228] However, large amounts of alkali ions may adversely affect conversion because they can also reduce the Lewis acidity, which is thought to be beneficial for metathesis activity.[208,209,228] The role of surface acidity on olefin metathesis by supported $WO_x/SiO_2$ still awaits resolution with well-defined catalysts.

**$WO_x/(SiO_2-Al_2O_3)$.** Supported $WO_x/Al_2O_3$ catalysts have received less attention in the literature than supported $ReO_x/Al_2O_3$ and $MoO_3/Al_2O_3$ catalysts because of their lower olefin metathesis activity.[9] This lower activity is related to its low ability to form a reduced active site, as seen in $H_2$-TPR spectra studies by Moulijn et al.[229] The olefin metathesis activity of supported $WO_x/SiO_2$ catalysts is reported to be higher than that of supported $WO_x/Al_2O_3$,[218,230] but other researchers found the opposite effect.[231] Andreini and Mol claimed that supported $WO_x/Al_2O_3$ catalysts deactivate above 397 °C, whereas supported $WO_x/SiO_2$ catalysts are stable at such temperatures.[230] For the supported $WO_x/(SiO_2-Al_2O_3)$ system, the optimal $SiO_2$ loading is reported to be 20−30 wt %.[218] Liu et al. claimed to only achieve moderate dispersion of surface $WO_x$ species by impregnation of 3-aminopropyltriethoxylsilane on the $Al_2O_3$ support from Raman and UV−vis experiments under ambient conditions.[218] These researchers concluded that the most active species are polymeric surface $WO_x$ species, not isolated $WO_x$ sites or $WO_3$ nanocrystallites.[218] Huang et al. attributed the improved self-metathesis activity of 1-butene to addition of 30% $\gamma$-$Al_2O_3$ to HY-zeolite (Si/$Al_2$ = 10), which was enhanced relative to either $\gamma$-$Al_2O_3$ and HY-zeolite.[232] The improved performance was related to the Raman band for the surface $WO_x$ species.[232] Debecker et al. reported W−Si−Al catalysts synthesized by an aerosol method outperformed traditional supported $WO_x/(SiO_2-Al_2O_3)$ by a factor of 1.5 at 250 °C, which was attributed to an improved well-balanced acidity, pore size, and better dispersion of $WO_x$ species in the former samples.[231] As already mentioned earlier, simultaneous variation of the catalyst parameters prevents determining the origin of the catalyst structure−activity relationships for olefin metathesis, and more systematic studies are required to really understand the fundamentals of supported $WO_x/(SiO_2{-}Al_2O_3)$ catalysts.

**Supported Organometallic Catalysts.** Several model silica-supported surface $WO_x$-organometallic catalysts have been reported. Verpoort et al. anchored aryloxy tungsten complexes on an $Nb_2O_5/SiO_2$ support and subsequently converted the aryloxy ligands to phenoxy ligands by refluxing with phenol in *n*-hexane.[213] The resulting catalysts were extremely active for 2-pentene metathesis and also much more active than their corresponding homogeneous analogues. The enhanced activity was assigned to the anchoring of the tungsten complexes to the acidic dispersed $NbO_x$ species on the silica support. Characterization of the supported complexes, however, was not performed, and thus, a molecular level understanding of such novel supported organometallic metathesis catalysts is lacking. Le Roux et al. successfully synthesized and molecularly characterized a well-defined surface tungsten hydride organometallic catalyst on $SiO_2$ that was active for alkane metathesis.[221]

Gauvin et al. synthesized and extensively characterized a well-defined silica supported surface dinuclear tungsten amido organometallic catalyst, which was not active for alkyne metathesis but became active after it was reacted with *tert*-butyl alcohol to introduce *tert*-butoxide ligands.[222] The presence of alkylidene and metallacyclobutane surface reaction intermediates was detected with in situ solid state NMR by Schrock and Coperet et al. on a silica supported $[W(\equiv NAr)(=CH\textit{t}\text{-}Bu)(2,5\text{-}Me_2NC_4H_2)_2]$ catalyst.[132]

Mazoyer et al. synthesized and extensively characterized the first well-defined surface tungsten oxide oxo (W=O) alkyl organometallic catalysts on $SiO_2$, that were quite active for propylene metathesis.[223] It was hypothesized that metathesis catalytic active sites require W=O oxo bonds.[223] Recently, Schrock and Coperet et al. grafted $(ArO)_2W(=O)(=CH\textit{t}\text{-}Bu)$ (ArO = 2,6-mesitylphenoxide) on silica that had been partially dehydroxylated at 700 °C and was found to be one of the most active olefin metathesis catalysts to date.[233] IR and NMR analysis revealed the formation of $[(\equiv SiO)W(=O)(=CH\textit{t}\text{-}Bu)(OAr)]$ (80%) and $[(\equiv SiO)W(=O)(CH_2\textit{t}\text{-}Bu){-}(OAr)_2]$ (20%) surface complexes.[233]

Unlike the industrial supported $WO_3/SiO_2$ catalysts that require high temperatures and are inactive for metathesis of functionalized olefins, the silica-supported $[(\equiv SiO)W(=O)(=CHtBu)(OAr)]$ catalyst is able to perform metathesis of olefins containing oxygenated groups such as oleic acid esters.[233] The surface organometallic catalysts have an advantage in metathesis of functionalized olefins because these complexes better stabilize bulky compounds.[80,233] The significantly enhanced activity of the silica-supported W organometallic complexes over industrial type supported $WO_3/SiO_2$ catalysts indicates that the structures and ease of activation of the catalytic active sites are different for these two catalyst systems.

**Patents.** Since 2000, the industrial patent literature for olefin metathesis by supported $WO_x/SiO_2$ catalysts has been receiving much attention, both worldwide and in the U.S.[83,84,86,97,103,104,109,114,115,163,169,172,191,193,194,234−243] Although most of the patented metathesis processes are devoted to the use of ethylene and 2-butene feedstocks to make propylene, some of the processes also employ unconventional feeds, such as butenes (partially converted to ethylene),[109,114,165,168,238] isobutyl alcohol (dehydrated to butene),[172,191] and ethylene (partially dimerized to butene).[82,115] Some of the metathesis patents focus on the nature of the $SiO_2$ support (amorphous $SiO_2$, MCM-22, or MCM-48),[106,197,235,236] and there is also emphasis on the purity of the $SiO_2$ support.[109] It has also been claimed that metathesis catalytic activity can be enhanced by initially acid-washing the silica support to reduce levels of impurities (e.g., Mg, Ca, Na, Al, and Fe, which must be maintained below several hundred parts per million),[234,235] and that the metathesis activity can be increased by the addition of promoters such as $Nb_2O_5$ (0.01−10%).[171] Impregnation of the active tungsten oxide component on the silica support is always performed with the aqueous $(NH_4)_6H_2W_{12}O_{40}$ precursor, followed by drying at ∼120 °C to remove the water and subsequent treatment at elevated temperatures.[104] The standard elevated temperature treatment involves calcination in air, but some patents also report heating in inert environments ($N_2$) or olefins.[104,106,239,243] Patents on regeneration of coked catalysts describe regeneration with air and steam.[168,193]

**Summary.** Although the molecular structures of the multiple $WO_x$ sites present on silica for the initially oxidized supported $WO_x/SiO_2$ catalysts are known, there is no information about the nature of these $WO_x$ sites during catalyst activation and olefin metathesis. The absence of direct characterization during catalyst activation and olefin metathesis prevents accessing fundamental information about the surface reaction intermediates and reaction mechanism. Relevant DFT calculations for olefin metathesis by supported $WO_x/SiO_2$ catalysts that relate the specific reactivity of each of the $WO_x$ sites have to be performed. In comparison with the other supported metal oxide olefin metathesis catalysts, the supported $WO_x/SiO_2$ catalyst system has received minimal attention in the catalysis literature, which is surprising, given the industrial importance of this olefin metathesis catalytic system.

## ■ SUMMARY OF OLEFIN METATHESIS BY SUPPORTED METAL OXIDE CATALYSTS

The absence of direct observation measurements of the catalytic active sites and surface reaction intermediates during olefin metathesis is one of the primary reasons for the lack of scientific progress in this important field of heterogeneous catalysis. Systematic time-resolved in situ and operando molecular spectroscopy studies of supported rhenium, molybdenum, and tungsten oxide catalysts during catalyst activation and olefin metathesis should significantly advance our fundamental understanding of the nature of the catalytic active sites, surface reaction intermediates, reaction mechanisms, and structure−reactivity relationships of these important heterogeneous catalysts for olefin metathesis. A recent critical review of heterogeneous olefin metathesis by Coperet concluded that future research should be focused on (i) synthesis of well-defined supported catalysts, (ii) control of the surface structure of the oxide supports as a way to control the coordination sphere of the surface active species, (iii) development of advanced in situ and operando spectroscopic characterization methods to better understand the evolution of supported active sites and surface reaction intermediates under working conditions, (iv) correlation of the spectroscopic findings with kinetic studies (structure−activity relationships) and (v) elucidation of deactivation phenomena to prepare more robust catalysts and to provide novel methods of catalyst regeneration.[79] It appears from this literature review that the topic of olefin metathesis by heterogeneous supported metal oxide catalysts is still a relatively undeveloped research area and is poised for significant progress in understanding of the fundamental molecular details of these important catalytic systems in the coming years.

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### Notes

The authors declare no competing financial interest.

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