www.czasopisma.pan.pl PAN www.journals.pan.pl

Chemical and Process Engineering: New Frontiers, 2025, 46(3), e104
DOI: 10.24425/cpe.2025.155542

CRITICAL REVIEW

Olefin metathesis catalyst activation: Recent advances and the promise of integrated olefin synthesis

Mariya Myradova*, Piotr Michorczyk

Cracow University of Technology, Department of Organic Chemistry and Technology, Warszawska 24, 31-155 Kraków, Poland

*** Corresponding author, e-mail:**
mariya.myradova@pk.edu.pl

Article info:
Received: 30 April 2025
Revised: 07 July 2025
Accepted: 12 August 2025

Abstract

Olefin metathesis represents a key process in selective olefin production. Despite being relatively new compared to light paraffin dehydrogenation, its history spans from accidental discovery through Nobel Prize-winning catalyst development that significantly advanced catalysis science. A longstanding challenge in heterogeneous catalysis has been the limited number of carbene centers (active sites), in many cases, only a small fraction of the surface metal forms active sites. While photoreduction methods using CO with molybdenum catalysts emerged in the 1970s–90s to generate more active centers, the past decade has witnessed the development of simpler activation approaches. This review examines contemporary methods for activating heterogeneous metathesis catalysts, particularly focusing on activation in methane and olefin atmospheres. The potential use of paraffins introduces promising catalytic synergies. Furthermore, if paraffins prove effective in activating olefin metathesis catalysts, this could enable the integration of dehydrogenation reactions and facilitate scaling from laboratory to industrial applications.

Keywords
propylene metathesis, oxide-based catalysts, carbene sites, catalysis, generation of active sites

1. INTRODUCTION

Metathesis is widely regarded as one of the most important on-purpose technologies for olefin production. These compounds serve as crucial intermediates in the synthesis of a wide range of industrial products, including polymers (polyethylene, polypropylene, polyesters), oxygenates (ethylene glycol, acetone, propylene oxide), and surfactants. As a selective olefin synthesis process, metathesis offers remarkable flexibility: depending on market demand, the reaction can be directed either toward synthesizing propylene from a mixture of ethylene and butenes, or vice versa, producing ethylene and butenes through propylene metathesis.

Olefin metathesis was first reported in the 1950s by industrial chemists. During his studies on propylene polymerization over a Mo/Al_2O_3 catalyst, Eleuterio observed an unexpected conversion of propylene to ethylene and butene. IR analysis revealed that the resulting polymer was partially a propylene-ethylene copolymer, with ethylene and 1-butene detected in the gaseous product stream. When he extended the experiment to cyclopentene, the results were even more striking: "the polymer I got looked like somebody took a pair of scissors, opened up cyclopentene, and neatly sewed it up again" (Eleuterio, 1991; Rouhi, 2002). R. Banks and G. Bailey of Phillips Petroleum were working on alternative heterogeneous catalysts intended to substitute HF in the isoparaffin alkylation of olefins (e.g. isobutane by C_3-C_5 olefins) (Banks and Bailey, 1964). It was observed that in the presence of the Mo/Al_2O_3 catalyst, paraffin alkylation did not occur. Instead, propylene would cleave and catalytically reform into ethylene and butene. This observation was later implemented by Phillips Petroleum in their industrially relevant Triolefin Process (Heckelsberg, 1965). From 1966 to 1972, Phillips Petroleum produced ethylene and 2-butenes from propylene. The reaction is reversible and depending on current market demands propylene can also be produced by conducting olefin metathesis between ethylene and 2-butenes. In 1967, researchers at Goodyear elucidated the reaction mechanism: unexpected products are formed when the double bonds in olefins undergo cleavage and reformation according to the following equation:

$$2\mathrm{RCH}=\mathrm{CHR}' \rightleftarrows \mathrm{RCH}=\mathrm{CHR}+\mathrm{R}'\mathrm{CH}=\mathrm{CHR}' \qquad (1)$$

where: R and R′ – alkyl groups or hydrogen atom.

The researchers named the reaction "olefin metathesis" (Calderon et al., 1967). The following year, Shell researchers discovered the formation of linear α-olefins through ethylene oligomerization on a molybdenum catalyst, a discovery that later developed into the Shell Higher Olefin Process (SHOP) (Keim, 2013). Nevertheless, the mechanism by which the reaction proceeds was still unknown.

The potential for industrial-scale exploitation of the reaction sparked an increase in basic research in the field, which earned Chauvin, Grubbs, and Schrock the Nobel Prize in Chemistry in 2005 "for the development of the metathesis method in organic synthesis" (The Royal Swedish Academy of Sciences, 2005).

2. OLEFIN METATHESIS MECHANISM DEVELOPMENT

Scientists raced to understand olefin metathesis mechanisms in the late 1960s and early 1970s. Initially, Calderon proposed what became known as the "conventional mechanism" involving a metal-complexed cyclobutane intermediate (Calderon et al., 1968). However, experimental evidence contradicted this hypothesis since cyclobutanes were neither produced during metathesis nor generated alkenes when introduced to metathesis systems.

In 1971, University of Texas professor Roland Pettit suggested an alternative involving a tetramethylene complex with four methylene units bonded to a central metal atom (Lewandos and Pettit, 1971).

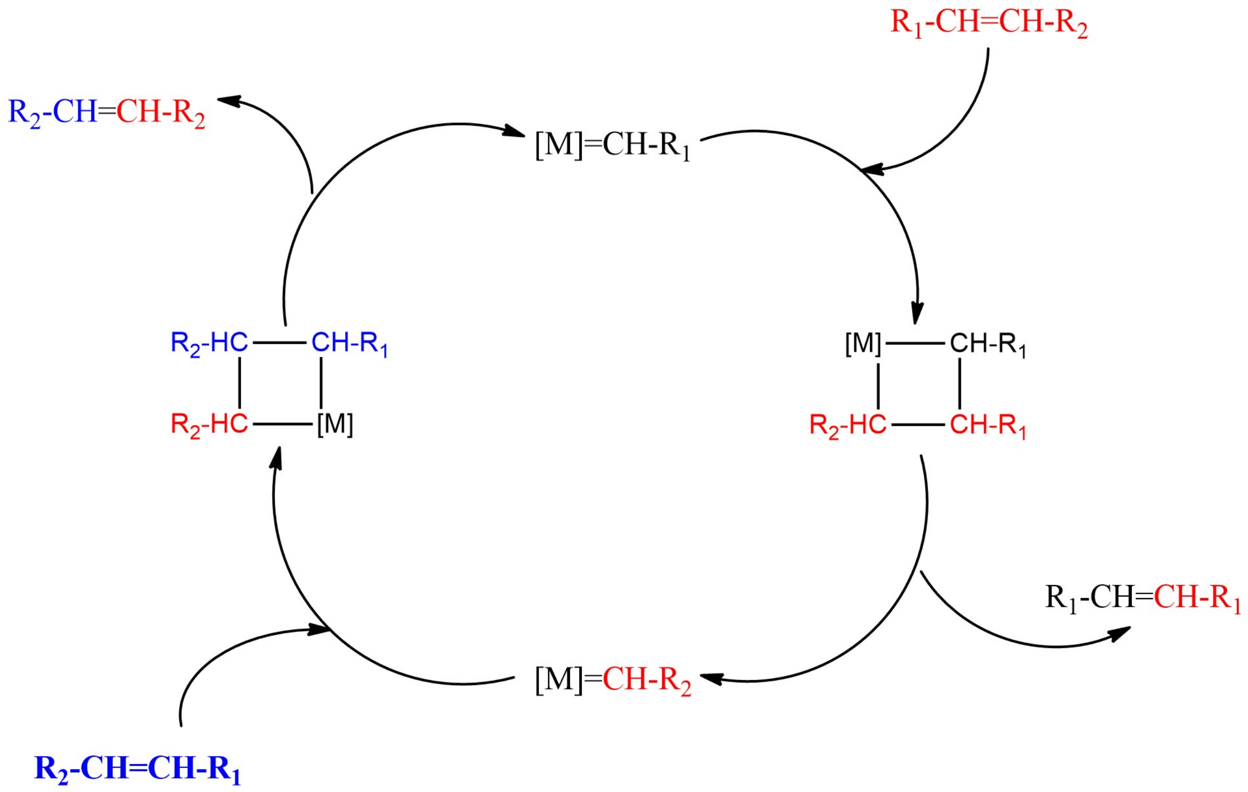
Robert Grubbs, who became interested in olefin metathesis during his Stanford postdoctoral work, proposed a metallacyclopentane intermediate theory at Michigan State University (Grubbs and Brunck, 1972). He later revised his theory to include a metal carbene-complexed cyclobutene (Biefeld et al., 1973).

The breakthrough came from French Petroleum Institute researchers Yves Chauvin and Jean-Louis Hérisson in 1971. Their mechanism, which proved correct, suggested that a metal carbene initiates the reaction by forming a metallacyclobutane intermediate with an olefin. This intermediate then decomposes to yield a new olefin and a new metal carbene that continues the catalytic cycle (Chauvin, 2006; Hérisson and Chauvin, 1971). This work, though published early in the investigation, remained largely overlooked by other researchers during this period.

Chauvin's and Hérisson's publication was later widely acknowledged as the first to correctly identify metal carbenes as key intermediates in olefin metathesis, explaining the mechanism behind group exchange at carbon-carbon double bonds. Three significant 1964 publications influenced Chauvin's hypothesis: Fischer's work from Munich University introducing a novel metal-carbon bond in tungsten carbene complexes $(CO)_5W{=}C(CH_3)(OCH_3)$ (Fischer and Maasböl, 1964), Natta's research from Milan Polytechnic on cyclopentene ring-opening polymerization using aluminium and tungsten catalysts (Natta et al., 1964), and the Phillips Petroleum report by Banks and Bailey detailing propylene disproportionation (Banks and Bailey, 1964). These foundational studies provided Chauvin with the critical insights needed to develop his revolutionary mechanistic proposal.

The crucial step in proposed mechanism involves a $[2+2]$ cycloaddition between an alkene and a metalalkylidene complex. This interaction generates an unstable metalacyclobutane intermediate that subsequently breaks down, yielding either the original substrates or new metathesis products (Scheme 1) (Chauvin and Commereuc, 1992).

Further experimental validation of this mechanism came from sequential titration studies using Re_2O_7/Al_2O_3 catalysts. In these experiments, researchers first titrated the catalyst with



Scheme 1. Carbene mechanism proposed by Chauvin (Hérisson and Chauvin, 1971).

propylene or 2-butene, then followed with deuterated ethylene. The resulting formation of propylene provided strong evidence supporting the carbene mechanism.

These investigations revealed two important insights about the reaction process:

- Carbene complexes are not formed during high-temperature catalyst activation under inert gas conditions, but rather are formed upon contact between the catalyst and the olefin.
- Only a fraction of all surface oxide forms of the catalyst are able to transform into carbene complexes.

3. METATHESIS CATALYSTS, BRIEF OVERVIEW

Olefin metathesis can be catalysed by homogeneous as well as heterogeneous catalytic systems. In recent years, surface organometallic chemistry (SOMC) has proven valuable for developing well-defined heterogeneous catalysts with W, Mo and Re organometallic active sites that demonstrate exceptional catalytic performance (Copéret et al., 2021; Iwasawa et al., 1981; Popoff et al., 2013). Density functional theory (DFT) computational studies on these systems have enhanced molecular-level understanding of active site characteristics and reaction mechanisms (Handzlik, 2005, 2007; Handzlik and Sautet, 2008; Solans-Monfort et al., 2006). Despite these advances in well-defined organometallic catalysis, progress with heterogeneous metathesis catalysts has been comparatively modest, primarily due to difficulties in identifying the precise nature of catalytic active sites. Nevertheless, the most important industrial olefin metathesis processes continue to rely on heterogeneous supported metal oxide catalysts, especially ReO_x, MoO_x and WO_x as active phases on Al_2O_3, SiO_2 and SiO_2–Al_2O_3 supports, as these systems exhibit the highest activity. Rhenium-based catalysts have a higher activity and can be operated at lower temperatures (20–100 °C) compared to other metal systems. However, their industrial application is still limited as they are quickly deactivated when exposed to oxidizing agents and their high cost (Lwin and Wachs, 2014; Mitra et al., 2001). In contrast, MoO_x and WO_x catalysts have found widespread application in industrial olefin metathesis processes. MoO_x catalysts occupy the middle ground in terms of activity – less active than rhenium systems but more active than tungsten counterparts and are mainly used in the Shell Higher Olefin Process (SHOP) (Keim, 2013). A significant advantage of molybdenum-based catalysts is their operational temperature range (20–200 °C), which is considerably lower than that required for tungsten oxide catalysts (350–500 °C) (Lwin and Wachs, 2014).

3.1. ReO_x catalysts

ReO_x dispersed on high-surface-area oxide supports (Al_2O_3 or SiO_2–Al_2O_3) are highly selective and active catalytic systems for olefin metathesis at 20–100 °C. These catalysts are prepared by impregnating Al_2O_3 with aqueous rhenium salts (NH_4ReO_4 or $HReO_4$), followed by calcination at 500–550 °C to form surface rhenium oxide species.

A widely discussed model proposes formation of a highly dispersed Re_2O_7 monolayer as the catalyst precursor. Early electron microscopy studies supported this model by detecting no crystalline Re_2O_7 nanoparticles, suggesting no crystallites were smaller than 2 nm (Olsthoorn and Boelhouwer, 1976). However, the precise structure and oxidation states of surface rhenium oxide species remain under debate despite extensive investigation (Lwin and Wachs, 2014).

Initial in-situ IR and Raman studies identified monomeric ReO_4^- species at low rhenia loadings and dimeric Re–O–Re species at higher loadings (Nakamura et al., 1981; Nakamura and Echigoya, 1982; Wang and Hall, 1983). These are catalyst precursors rather than active species. Subsequent studies revealed that ReO_4^- species first adsorb on Lewis acid Al^{3+} sites and basic surface OH groups. Catalysts with > 6 wt% Re_2O_7 exhibit Brønsted acid sites correlating with rhenium oxide coverage, though Lewis acidity plays the dominant role in metathesis performance.

In-situ XANES studies initially suggested Re^{7+} with trioxo coordination under dehydrated, oxidizing conditions. (Fig. 1a) (Bare et al., 2011; Hardcastle et al., 1988). However, XANES/EXAFS studies and DFT calculations propose dioxo pentacoordinate species (Vicente et al., 2011) (Fig. 1b). The challenge of fitting EXAFS data becomes problematic when spectroscopy reveals multiple distinct surface ReO_x species, as XAS provides only average molecular structures.

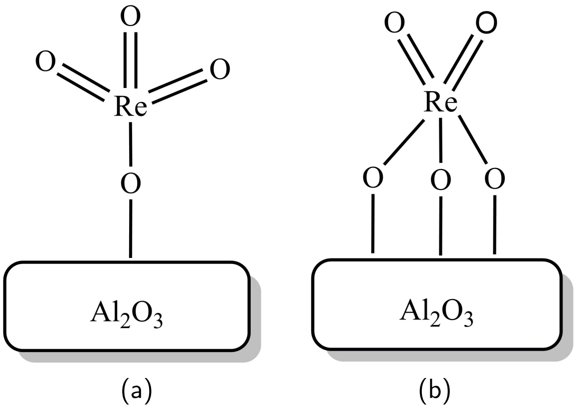


Figure 1. Proposed surface structures of ReO_x on the surface of Al_2O_3 with (a) trioxo and (b) dioxo coordination.

Catalytic activity is low at low rhenium content and increases with ReOx loading. Optimum loading is 14–18 wt% (2.2–3.0 Re atoms/nm^2), corresponding to monolayer coverage.

ReO_x/SiO_2–Al_2O_3 catalysts significantly outperform ReO_x/Al_2O_3 particularly at lower rhenium loadings, being 3–6 times more active. This enhancement correlates with the higher acidity of SiO_2–Al_2O_3 supports compared to γ-Al_2O_3. ReO_x/SiO_2 catalysts are completely inactive in olefin metathesis (Ivin and Mol, 1997; Mol, 1999; Mol and Andreini, 1988; Sibeijn and Mol, 1990; Vicente et al., 2011). The SiO_2–Al_2O_3 support contains two hydroxyl types: bridging Si–OH–Al groups and terminal Si–OH groups.

Studies of mesoporous Re-Si-Al catalysts prepared via nonhydrolytic sol-gel methods showed optimal activity at Si/Al ratios of 0.3 (Bouchmella et al., 2013). Key parameters for high activity include numerous acidic sites, high surface area, and well-dispersed ReO_x species. However, high support acidity promotes alkene isomerization, reducing metathesis selectivity.

Despite exceptional selectivity and ambient-temperature performance, ReO_x/SiO_2–Al_2O_3 catalysts are not yet employed in large industrial processes due to rhenium's high cost, volatility, thermal instability and high purity requirements of feed stream. These systems have nonetheless driven significant advances in understanding supported metal oxide catalysis.

Critical knowledge gaps remain regarding the molecular structure of initial oxidized ReO_x species, active site characteristics during catalysis, activation mechanisms, reaction pathways, and promotion effects. Limited in-situ characterization under actual metathesis conditions has impeded deeper mechanistic understanding of this promising catalytic system. Future research should focus on developing comprehensive in-situ spectroscopic approaches to elucidate the structure-activity relationships governing ReO_x-catalyzed olefin metathesis.

3.2. MoO_x catalysts

Typically, heterogeneous MoO_x catalysts are supported on high surface area materials like SiO_2 or Al_2O_3. The incipient wetness technique is most commonly employed method to prepare the catalyst (Debecker et al., 2011b; Tian et al., 2010), though alternative methods include sol-gel (Debecker et al., 2009), flame pyrolysis (Debecker et al., 2011a), thermal decomposition, and dispersion of crystalline MoO_3 (Debecker et al., 2010). Recent advances in nonhydrolytic sol-gel chemistry and aerosol-assisted sol-gel routes have demonstrated noticeably higher catalytic activity compared to conventional preparation techniques. Molybdenum silicate microspheres prepared via nonhydrolytic sol-gel methods showed up to two orders of magnitude higher activity in propylene metathesis due to homogeneous distribution of highly dispersed MoO_x species and absence of crystalline MoO_3 phases (Skoda et al., 2023). Aerosol-assisted sol-gel synthesis of MoO_3–SiO_2–Al_2O_3 catalysts produces materials with ordered super microporosity and well-dispersed Mo sites, achieving up to 3 times higher activity than conventional systems (Debecker et al., 2012).

Physicochemical analysis of molecular structure of fresh catalysts indicates that preparative method has minimal impact on the surface structure of molybdenum oxide species, provided the support surface saturation threshold is not exceeded (below monolayer coverage). MoO_x species below monolayer coverage predominantly exist in isolated monomeric species: dioxo MoO_2 $=(O)_2$ (dominant form on support surface) and monooxo MoO_4 $=O$, above monolayer coverage crystalline forms of MoO_3 start to emerge, which exhibit no metathesis activity. The catalytic performance of MoO_x systems strongly correlates with the concentration of MoO_x species on the support surface. Turnover frequency (TOF) values increase proportionally with molybdenum content until support surface saturation occurs. Beyond this saturation point, accompanied by the formation of polymerized or crystalline MoO_3 forms, catalytic activity decreases (Ivin and Mol, 1997).

Two studies by Amakawa et al. (2012; 2015) proposed that the transformation of Mo(VI) species into carbene centres occurs via a hydrodioxo-Mo entity, which is connected to the support through a Mo–O–Si single bond and possesses two oxo ligands and one hydroxo ligand (Fig. 2).

MoO_x catalysts supported on SiO_2–Al_2O_3 usually exhibit around 1 order of magnitude enhanced activity in olefin metathesis, compared to those on either SiO_2 or Al_2O_3 (Debecker et al., 2009; 2010; 2011a; 2011b). A critical design consideration for such combined supports is selecting the appropriate SiO_2/Al_2O_3 ratio, as Al_2O_3 addition affects the support's Brønsted acidity. Excessive Brønsted acidity may promote undesired isomerization reactions.

Supported MoO_x catalysts for olefin metathesis have drawn significant attention due to the industrial relevance of the

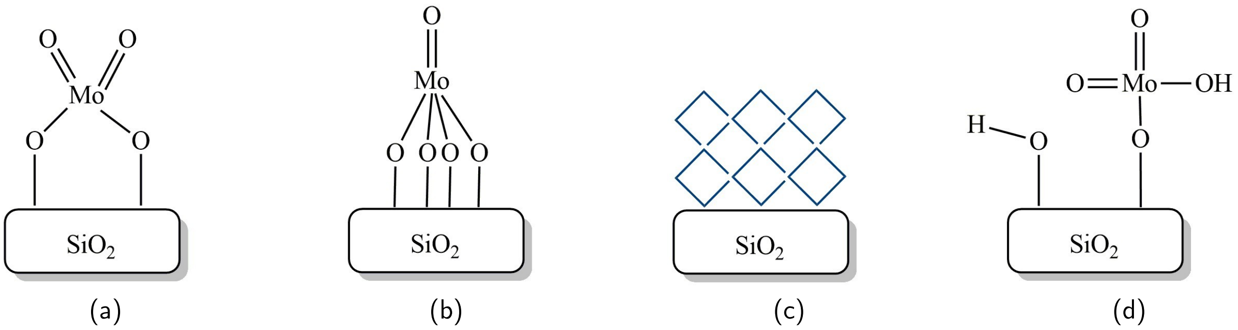


Figure 2. MoO_x structures on the surface of SiO_2, (a) dioxo; (b) monooxo; (c) MoO_3 crystals and (d) hydrodioxo structures.

SHOP olefin metathesis process (Keim, 2013; Mol, 2004) While the molecular structures of fully oxidized surface MoO_x species on unpromoted supported molybdena catalysts have been identified, the exact nature of the active surface MoO_x sites and the surface-bound intermediates involved in olefin metathesis reactions remains unclear.

3.3. WO_x catalysts

Unlike MoO_x systems, tungsten catalysts require significantly higher reaction temperatures. The $WO_3/\gamma\text{-}Al_2O_3$ system exhibits activity comparable to $MoO_3/\gamma\text{-}Al_2O_3$, but requires temperatures approximately 200 °C higher (Mol, 1990). WO_3/SiO_2 demonstrates larger potential for practical application in metathesis processes due to its reduced sensitivity to poisoning, e.g. it is a catalyst for "Triolefin Process" which converts propylene to ethylene and 2-butenes. A study on 8%WO_3/SiO_2 suggested that optimal reaction temperature was 500 °C (Rodríguez-Ramos et al., 1995). WO_x supported on SiO_2 in contrast to Al_2O_3 supports does not promote undesirable side reaction. Similarly to MoO_x/SiO_2 systems on the surface of WO_x/SiO_2 isolated dioxo and mono-oxo species exist, with dioxo species being the predominant form (Lee and Wachs, 2007; 2008; Ross-Medgaarden and Wachs, 2007). When coverage exceeds monolayer capacity, catalytically inactive crystalline WO_3 forms develop (Fig. 3).

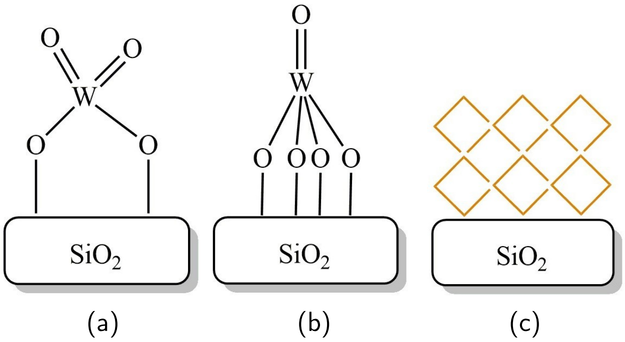


Figure 3. WO_x structures on the surface of SiO_2, (a) dioxo; (b) monooxo structures and (c) MoO_3 crystal form.

Recent work by Gani et al. (2023) has highlighted strategies to overcome the high-temperature limitations of WO_x-based catalysts and demonstrated that co-feeding specific olefins, such as 2,3-dimethyl-1-butene, can promote a dynamic cycle of active site renewal and decay, resulting in a 30-fold increase in propylene metathesis rate at 250 °C on WO_x/SiO_2 catalysts, with negligible promoter consumption. This finding suggests the possibility of operating at much lower temperatures than previously possible, providing a promising path forward for improving catalytic efficiency and durability.

Despite the current knowledge of the molecular structures of various WO_x species on silica in freshly oxidized WO_x/SiO_2 catalysts, a significant knowledge gap exists regarding the behaviour and transformation of these sites during both catalyst activation and the olefin metathesis reaction. This lack of in-situ characterization techniques limits understanding of crucial surface reaction intermediates and mechanistic pathways. Several computational studies emerged in recent years (Handzlik et al., 2024; Kurleto et al., 2020; Le et al., 2023). Most of them agree that dioxo species $(\equiv SiO)_2WO_2$ (Fig. 3a) most probably are precursors to active sites and that surface silanol groups have influence on stability and activity of WO_x species.

While WO_x catalysts hold considerable industrial importance, they have been underexplored in academic research compared to ReO_x and MoO_x systems. Recent studies (Maksasithorn et al., 2014; Wu et al., 2016) offer valuable perspectives on structure-activity relationship and mechanistic insights.

4. PROPOSED MECHANISMS FOR ACTIVE SITE GENERATION

In olefin metathesis reactions, carbene complexes are considered as active centres. On conventional oxide catalyst surfaces, these complexes do not exist initially on the surface of the catalyst, but form upon contact of surface metal oxide with olefin. Experimental work by Chauvin and Commereuc demonstrated that merely a small fraction – approximately 1.5–2% – of the catalyst's oxide forms possess the capability to undergo transformation into active carbene complexes (Amakawa et al., 2012; Lwin and Wachs, 2014). The precise mechanistic pathway for this oxide-to-carbene conversion remains unknown, though several routes were proposed in the scientific literature. Notably, the specific route significantly influences the structural characteristics of the resulting carbene complexes, adding complexity to understanding these catalytic systems.

4.1. 1,2-hydrogen shift mechanism

This mechanism assumes that a hydrogen atom from the vinyl position transfers to the metal atom, and subsequently migrates to the allyl carbon of the olefin. This process results in the generation of carbene complexes (Fischer et al., 1976; Iwasawa et al., 1985).

Recent computational studies on both MoO_x/SiO_2 and WO_x/SiO_2 catalysts suggest that this pathway is moderately plausible (Handzlik et al., 2021; 2024). For Mo systems, it proceeds through agostic or isopropenyl-hydride intermediates, but the high overall activation barriers (above 220 kJ/mol) limit its efficiency. WO_x/SiO_2 shows slightly lower barriers ($\sim$ 196 kJ/mol), particularly favouring isopropylidene formation, suggesting this route may be more relevant for tungsten catalysts under specific structural conditions. Nevertheless, it remains less favourable than silanol-assisted routes.

4.2. $\pi-$allyl mechanism (or allylic C–H activation)

The π-allyl mechanism involves the transfer of hydrogen from the olefin to the metal, forming a π-allyl complex. This is followed by migration of the coordinated hydrogen to the allylic carbon of the π-allyl ligand, resulting in a metalacyclobutane complex. The metalacyclobutane complex then breaks down into an olefin and a carbene complex (Grubbs and Swetnick, 1980; McCoy and Farona, 1991; Sherman and Schreiner, 1978). Computational studies showed that π-allyl mechanism results in higher energy barriers ($>$ 210 kJ/mol for WO_x and $>$ 220 kJ/mol for MoO_x), often proceeding via η^1- or η^3-allyl metal hydride intermediates. The pathway is mechanistically fascinating, though compared to others is less favoured kinetically and thermodynamically, and therefore is unlikely to be considered the dominant mechanism for metathetically active site generation (Handzlik et al., 2021; 2024).

4.3. H-assisted mechanism (α-elimination mechanism)

This mechanism is only valid for catalysts supported on materials containing Brønsted acid centres (Laverty et al., 1976; Lwin and Wachs, 2014). It proposes that the metal forms an unstable hydride through interaction with a surface hydroxyl group. This metal hydride then coordinates with the olefin to generate a metal-alkylidene bond. Subsequently, α-elimination occurs, leading to the formation of a carbene complex.

This mechanism is strongly supported by recent theoretical (Handzlik et al., 2021; 2024) and experimental evidence (Amakawa et al., 2019), particularly for silica-supported systems containing surface silanol groups. Studies demonstrate that silanol-assisted activation, whether via reduction (Mo(VI) or W(VI)→M(IV)) or direct formation of alkylidenes, proceeds with significantly lower activation barriers compared to non-assisted pathways. It is now regarded as the most thermodynamically and kinetically favoured route for both Mo and W catalysts. Surface silanol groups not only assist in hydride formation but also stabilize key intermediates, enabling efficient carbene complex generation.

4.4. Pseudo-Witting mechanism

The pseudo-Wittig mechanism, proposed based on mechanistic calculations (Rappe and Goddard, 1982), does not require a change in the oxidation state of the catalyst's metal center during the initiation stage. According to this mechanism, the oxide form of the metal, upon contact with the olefin, forms an oxometalbutane complex. This complex subsequently decomposes into two products: a compound containing a carbonyl group and a carbene complex. The carbene complex then participates in the Chauvin–Herrison mechanism in the following stages (Goldwasser et al., 1981; Rappe and Goddard, 1982) (Scheme 2).

The pseudo-Wittig mechanism, both in experimental (Ding et al., 2016; Grünert et al., 1989; Lwin and Wachs, 2014; Van Schalkwyk et al., 2003) and theoretical works (Griffe et al., 2001; Guan et al., 2008) is the most frequently proposed generation mechanism of metathetically active sites due to its simplicity and experimental detection of aldehyde byproducts. However, modern computational studies show that it is both kinetically and thermodynamically unfavourable. Activation barriers for this pathway typically exceed 260 kJ/mol, and the reactions are strongly endergonic. These energetic requirements make the *pseudo*-Wittig mechanism unlikely to operate efficiently under standard catalytic conditions, especially when more favourable silanol-assisted processes are available (Handzlik et al., 2021; 2024).

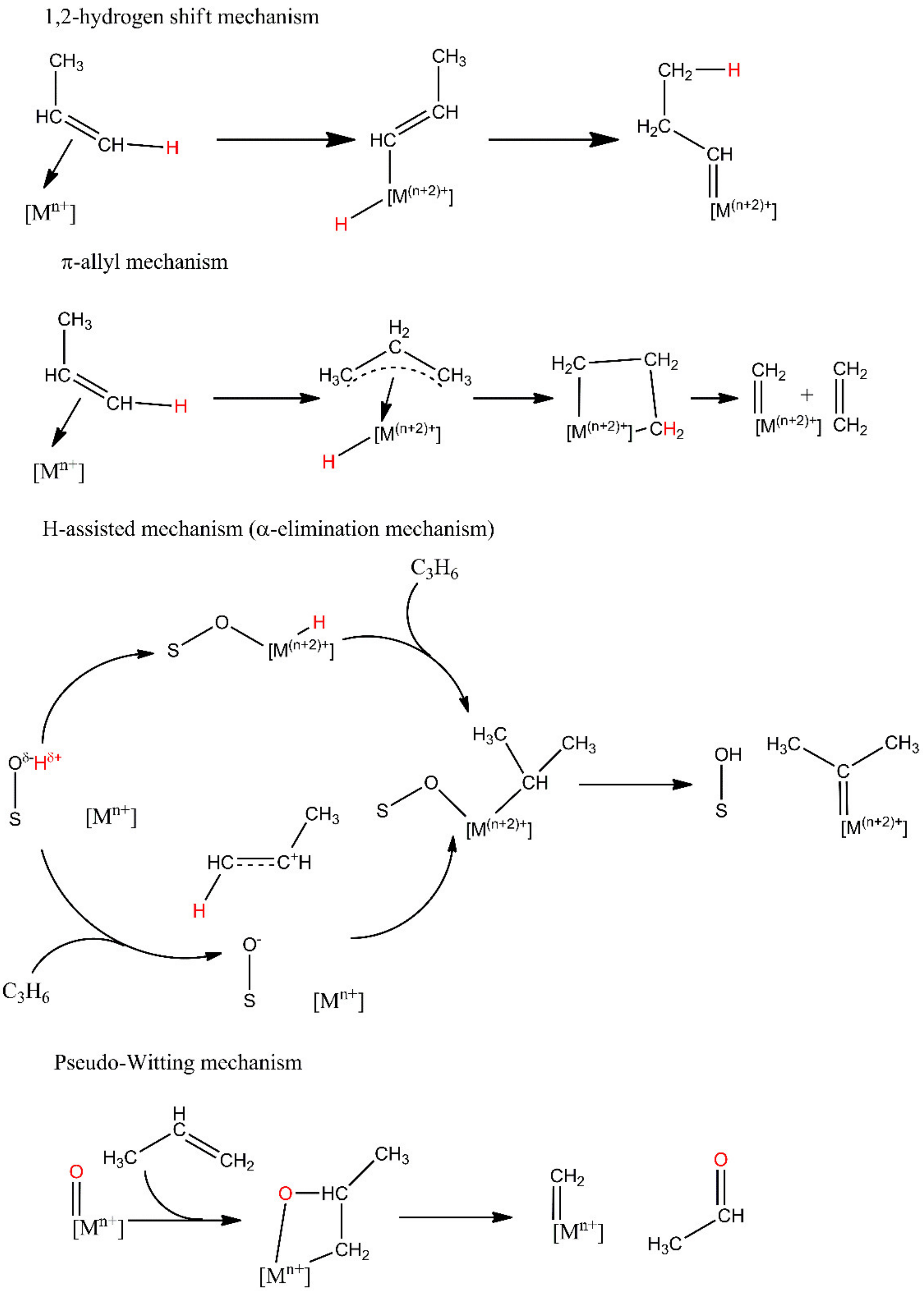
5. METHODS OF GENERATING CARBON CENTERS

The olefin metathesis reaction carried out in heterogeneous systems may exhibit an induction period – the time required to establish the steady state of catalyst operation. The presence of this induction period suggests that Mo/W is reduced by the olefin, with active metal carbene centres forming only as a result of the reaction between the olefin and these reduced Mo/W species (Andreini and Mol, 1981; Basrur et al., 1991). Unreduced oxide forms of molybdenum(VI) and tungsten(VI) catalysts supported on silica show only weak catalytic activity, and only at high temperatures (400–500 °C) (Thomas et al., 1980; Vaghi et al., 1976). Reduction can help decrease the reaction temperature and enhance catalytic activity through the generation of carbene sites. The scientific literature describes several methods for generating active sites by activating oxide-based catalysts prior to the metathesis reaction.

5.1. Activation in inert gas atmosphere

Activation in an inert gas atmosphere has become the most conventional method for the activation of classical olefin metathesis oxide catalysts. Studies have shown that high-temperature activation of classical heterogeneous catalysts in an inert gas atmosphere leads to shorter induction period and higher substrate conversion compared to catalysts activated in air. For example, when WO_3/SiO_2 catalyst was activated at temperatures of 550, 600, 640, and 680 °C and then used in propylene metathesis at 400 °C, a linear relationship emerged between activation temperature and metathesis activity. The catalyst activated at 680 °C exhibited no induction period, with conversion approaching equilibrium values. This behaviour was attributed to the desorption of oxygen and hydroxyl groups from the catalyst support, which exposes tungsten ions – some of which are reduced – favouring carbene center generation (Andreini and Mol, 1981).

In another study, 20 wt.% WO_3/SiO_2 activated in nitrogen at temperatures ranging from 500–650 °C was tested in propylene



1,2-hydrogen shift mechanism

π-allyl mechanism

H-assisted mechanism (α-elimination mechanism)

Pseudo-Witting mechanism

Scheme 2. Proposed mechanism for active site generation (Goldwasser et al., 1981; Grubbs and Swetnick, 1980; McCoy and Farona, 1991; Rappe and Goddard, 1982; Sherman and Schreiner, 1978).

metathesis at 500 °C (Basrur et al., 1991). Catalytic activity improved with activation temperatures up to 600 °C, with no further improvement at higher temperatures. EPR spectra of the unreduced catalyst showed a narrow intense signal originating from non-stoichiometric WO_x form.

To determine whether WO_3 reduces to non-stoichiometric $WO_{2.9}$ during the induction period (Gangwal et al., 1977; Luckner and Wills, 1973), researchers conducted comparative experiments with catalyst activation at 600 °C in both air flow and hydrogen flow. The subsequent metathesis reaction was carried out at 550 °C. IR studies during the induction period revealed bands characteristic of acetone and acetaldehyde, with significantly lower acetone band intensity in the hydrogen-reduced catalyst. When regenerated (600 °C in N_2 and 3% O_2, followed by air), the catalyst regained activity with a shorter induction period. Additionally, the more intense EPR band of WO_2 indicated that some reduced WO_x remained stable, resisting oxidation during regeneration.

High-temperature activation of tungsten catalysts was further investigated using tungsten oxide deposited on ordered mesoporous SBA-15 silica via two methods: incipient wetness (IWI) and ion exchange (IE) (Howell et al., 2016). After activation in either air or helium (600 °C), propylene metathesis activity was evaluated at 420 °C. Regardless of the deposition method, catalysts activated in air reached steady state more slowly and showed approximately half the activity of helium-activated catalysts. The induction period for air-activated catalysts featured acetone formation, with production rates highest at the beginning and lowest near the point of increased metathesis activity. The authors attributed acetone formation to the reduction of di-oxo W^{6+} to mono-oxo W^{4+}. Based on XANES spectra, the researchers proposed that during high-temperature activation, mono-oxo structures transform to di-oxo structures, which are then reduced to W^{4+} upon contact with propylene (for air-activated catalysts), forming acetone. With continued propylene exposure, these reduced structures eventually form carbene complexes – the active sites for propylene metathesis (Fig. 4).

In a series of studies, researchers investigated the effect of activation temperature on $nMoO_3/\gamma\text{-}Al_2O_3$ and $nWO_3/\gamma\text{-}Al_2O_3$ catalysts (Grünert et al., 1989; 1992a; 1992b). Activation in argon was conducted across a temperature range of 600–900 °C. XPS and EPR spectra confirmed partial reduction of Mo from 6+ to 4+ oxidation state during activation at 700 °C, as well as to 5+, 2+ and 0 forms, with the latter not participating in propylene metathesis reactions. Based on EPR studies, researchers estimated that Mo^{5+} comprised $\geq$ 10% in activated samples. (Grünert et al., 1992b) Similarly, tungsten catalysts showed reduction from 6+ oxidation state to 4+ and 5+ (Grünert et al., 1992a).

Metathesis reactions were conducted at 200 °C for $MoO_3/\gamma\text{-}Al_2O_3$ and 300 °C for $WO_3/\gamma\text{-}Al_2O_3$. The studies revealed an optimal activation temperature in argon between 650–870 °C, with reaction rates decreasing as concentrations of MoO_3 or WO_3 on the support increased. While no induction period was observed, catalysts with high Mo and W contents showed activity loss over time. The initially high catalyst activity may be attributed to extreme activation temperatures, which caused sublimation of deposited Mo and W and degradation of $\gamma\text{-}Al_2O_3$ supports. Hydrogen reduction enhanced catalyst activity, but only for those activated at temperatures up to 627 °C. Current literature generally recommends activation temperatures not exceeding 600 °C (Lwin and Wachs, 2014; Mol, 1990).

The support properties significantly influence catalytic activity in high-temperature activated olefin metathesis reactions. One study examined how the acidity of molybdenum catalyst supports affected metathesis activity (Handzlik et al., 2006). Molybdenum preparations were deposited on $\gamma\text{–}Al_2O_3$, SiO_2, and $SiO_2\text{–}Al_2O_3$ surfaces, with acidity increasing in the series: $SiO2 < \gamma\text{–}Al_2O_3 < SiO_2\text{–}Al_2O_3$. After two hours of activation in argon at 600 °C, propylene metathesis was conducted at 30 °C. Catalysts on Al_2O_3 and $SiO_2\text{–}Al_2O_3$ demonstrated high selectivity, producing only ethylene, trans-2-butene, and cis-2-butene. $MoO_3/SiO_2\text{–}Al_2O_3$ achieved the highest initial propylene conversion, but like MoO_3/SiO_2, rapidly deactivated. These systems showed

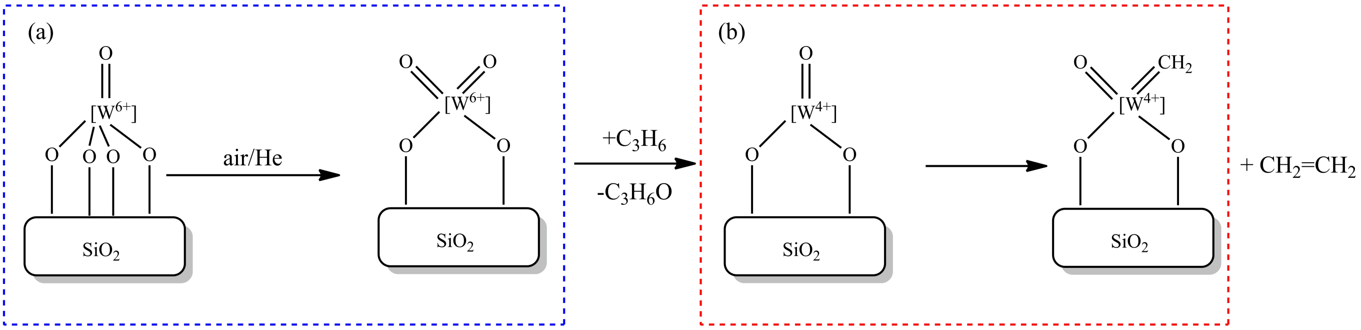


Figure 4. The transformation mechanism of monooxo structures into dioxo structures during high-temperature activation in a stream of air/helium and their reduction (a) and the formation of carbene centers upon contact of reduced W^{4+} forms with propylene (b). Based on (Howell et al., 2016).

greater deactivation tendencies as Mo content increased. In contrast, MoO_3/Al_2O_3 deactivated more slowly and demonstrated the highest activity at ≥ 0.6Mo/nm²content among the tested catalysts. This effect may relate to Al_2O_3's higher surface capacity compared to SiO_2.

Rhenium catalysts exhibited similar activity patterns. At lower Re_2O_7 contents (approximately 3 wt.% (Spronk et al., 1991)), Re_2O_7/SiO_2–Al_2O_3 showed greater metathesis activity than corresponding Re_2O_7/Al_2O_3 catalysts (Mol, 1990; 1999). This enhanced activity can be attributed to SiO_2–Al_2O_3's higher acidity compared to Al_2O_3. The SiO_2–Al_2O_3 support surface contains two types of –OH groups (Nakamura and Echigoya, 1982), including bridging groups connecting Si–Al, while lacking basic centers (Andreini, 1991). This suggests that as Re content increases on the surface, rhenium substitutes the acidic –OH groups, forming highly electron-deficient rhenium ions that serve as precursors for metathesis active centers (Mol, 1999; Sibeijn and Mol, 1990).

Although molybdenum catalysts are more complex than rhenium catalysts, the activity differences between MoO_3/SiO_2–Al_2O_3 and MoO_3/Al_2O_3 systems can be explained similarly to their rhenium counterparts. Both the local structure of molybdenum centers and the acid-base properties of the support significantly influence molybdenum catalyst activity.

5.2. In-situ generation of active sites with generation of isopropoxide

An in-situ mechanism for generating carbene centers on the MoOx/SBA-15 catalyst was proposed by Amakawa et al. (2012) MoOx was deposited on the SBA-15 surface by the ion exchange method. During the adsorption of propylene on the catalyst surface, the formation of acetone was observed, which can be explained by the pseudo-Wittig mechanism. However, based on calorimetric and spectroscopic studies, the authors proposed a different, two-step mechanism (Fig. 5).

During the initial adsorption of C_3H_6 on Mo-OH, Mo^{6+} is reduced to Mo^{4+} with the formation of a transitional molybdenum-oxygen-isopropylene complex, which subsequently undergoes oxidative dehydrogenation to acetone. This step was later confirmed by DFT calculations (Handzlik et al., 2021). The above mentioned mechanism was found to be more plausible at moderate to high temperatures and even may compete with commonly accepted pseudo-Witting mechanism. The exergonic formation of Mo(VI)-isopropylene complex can occur under mild conditions, while the alternative formation of Mo(VI) n-propoxy species, that lead to the formation of propionaldehyde, is less kinetically favoured.

A second propylene molecule, adsorbing on Mo^{4+}, generates a catalytically active molybdenum-carbene center via a 1,2-hydrogen shift. The predicted surface structure of this metalalkylidene complex resembles highly active Schrock-type catalysts.

5.3. Photoreduction of MoO_3/SiO_2

The method of obtaining active Mo=R carbene complexes on the surface of MoO_3/SiO_2 catalyst through photoreduction was first described in a patent (Elev et al., 1968). This method utilized a MoO_3/SiO_2 catalyst containing 1 wt.% Mo, prepared by impregnation, as a precursor. After appropriate thermal treatment, the surface forms of MoO_3 developed

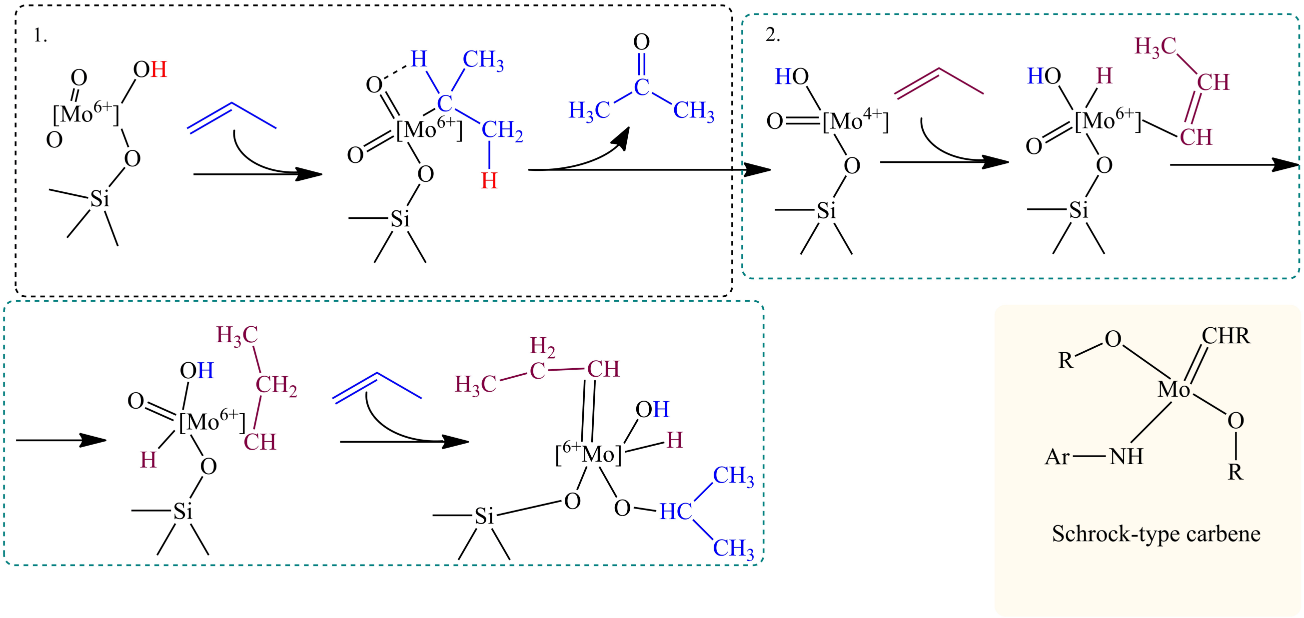


Figure 5. Proposed mechanism of generating Mo=carbene sites through reduction of Mo^{6+} by propylene and subsequent 1,2 hydrogen shift. Based on (Amakawa et al., 2012).

a dioxo structure. The catalyst was then reduced at room temperature using CO under ultraviolet radiation. This reduction process yielded a monooxo structure.

The oxidation states of molybdenum ions were determined by measuring CO_2 formation during photoreduction. Most Mo atoms were reduced from the 6+ oxidation state to 4+, with up to 3% of ions forming in the 5+ oxidation state (inactive Mo forms-according to the authors). When comparing the activity of the photoreduced catalyst with catalysts thermally reduced in H_2 and CO, the thermally CO-reduced catalyst exhibited almost 20 times greater activity than the H_2-reduced version (Shelimov et al., 1986).

The tested activation procedures improved catalytic activity in the following order:
Thermal reduction in H_2 < thermal reduction in CO < photoreduction in CO

Adsorption of small amounts of oxidizing agents (O_2, N_2O, or NO) at room temperature on photoreduced catalysts led to irreversible deactivation of active centers. Prior to adsorption experiments, researchers determined the number of active Mo^{4+} centers formed after catalyst photoreduction. Complete loss of catalytic activity corresponded precisely to the amount of oxidizing compounds adsorbed on the catalyst surface matching the number of determined Mo^{4+} centers. This correlation indicates that the formed Mo^{4+} centers exhibit good homogeneity across the catalyst surface (Fig. 6).

Subsequent research presented studies on the chemisorption of cyclopropane and methylcyclopropane on photoreduced Mo^{4+}/SiO_2 catalysts (Kazansky and Shelimov, 1991; Shelimov et al., 1988; Vikulov et al., 1989; 1991). These studies demonstrated that reduced Mo^{4+} centers interacted with cyclopropane or methylcyclopropane at 20 °C, forming molybdenumcyclobutane centers that transformed into stable active carbene centers – $Mo{=}CH_2$ and $Mo{=}CH{-}CH_3$ (in the case of methylcyclopropane chemisorption). Experimental measurements revealed that the formation of such complexes increased catalytic activity by one to two orders of magnitude compared to catalysts synthesized with immobilization methods (Kazansky and Shelimov, 1991; Vikulov et al., 1989; 1991).

IR and UV-Vis analyses indicated that approximately 90% of Mo^{4+} ions formed during photoreduction successfully adsorbed cyclopropane (Vikulov et al., 1989), while methylcyclopropane adsorption occurred on only 55% of these ions (Vikulov et al., 1991). In follow-up studies (Vikulov et al., 1992), researchers investigated the chemisorption of 1,3,5-cycloheptatriene (CHT) under similar conditions. CHT chemisorption at room temperature resulted in the formation of surface carbenes $Mo{=}CH_2$ and benzene. However, catalytic tests showed no increase in activity or gaseous decomposition products of CHT. The researchers proposed that CHT sorbs less selectively on Mo^{4+} ions, forming a stable π complex ((η-1,6-C_7H_8)Mo) that decomposes into by-products only at elevated temperatures (300 °C) (Vikulov et al., 1992).

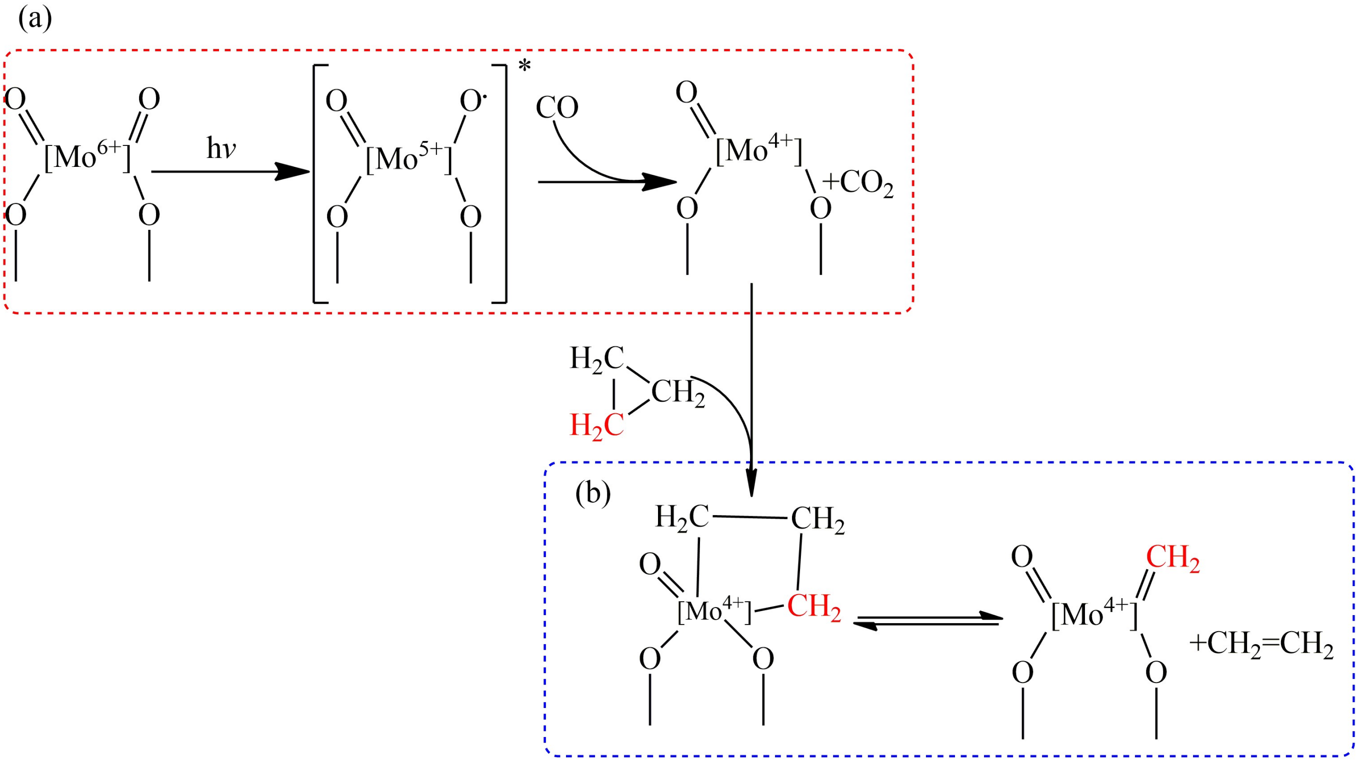


Figure 6. Photoreduction mechanism of MoO_3/SiO_2 with CO (a), formation of carbene centers after chemisorption of cyclopropane (b). Based on (Shelimov et al., 1986; Vikulov et al., 1991).

The photoreduction method for molybdenum catalysts enables the formation of a high concentration of active carbene centres $Mo{=}CH_2$ sites under laboratory conditions, allowing detailed studies of olefin metathesis mechanisms. This approach leads to highly homogeneous catalytic surfaces, offering high activity. In laboratory-scale research, photoreduction also allows precise control over the degree of metal reduction and facilitates spectroscopic characterization. However, in industrial applications, this method is impractical as it requires specialized UV irradiation equipment that would be difficult and expensive to scale up for large catalyst volumes. Additionally, the process involves controlled light exposure under specific CO atmosphere conditions, which poses safety challenges when handling carbon monoxide at industrial scales. The photoreduction method also appears to require careful control of radiation intensity and exposure time to achieve optimal Mo^{6+} to Mo^{4+} conversion, making it more suitable for laboratory research than for the consistent, high-throughput catalyst activation needed in commercial operations.

5.4. Activation in hydrocarbon atmosphere

Even though thermal pre-treatment in inert gas improves initial activity by shortening the break-in period, the general activity remains modest. Recently, several experimental works appeared showing that simply substituting inert gas by hydrocarbon enhances catalytic activity of heterogeneous catalysts by 2–3 orders of magnitude in low-temperature propylene metathesis.

Ding et al. (2016) presented a method for activating MoO_3/SiO_2 and WO_3/SiO_2 catalysts prepared by the "incipient wetness" technique using a propylene atmosphere at elevated temperatures. For the molybdenum catalyst, activation lasted for 30 minutes in a diluted propylene stream (4/96 vol. % C_3H_6/N_2) at 550 °C. The tungsten catalyst underwent a two-step process: initial activation at 550 °C in propylene, followed by temperature elevation to 700 °C in the same atmosphere for an additional 30 minutes. After activation catalysts were purged in nitrogen for 10 minutes before cooling to the appropriate temperature for propylene metathesis reactions (20 °C for MoO_3/SiO_2 and 250 °C for WO_3/SiO_2). This activation protocol achieved near-equilibrium propylene conversion rates (approximately 42% at 20 °C, according to the authors). During the reaction, only ethylene and 2-butenes were detected at an approximately 1:1 molar ratio, with isomerization products comprising less than 0.5% of the yield. The turnover numbers (TON) were 2–3 orders of magnitude higher compared to catalysts activated in inert gases, with values comparable to the most active heterogeneous catalysts with defined SOMC derived structures (Iwasawa et al., 1981; Popoff et al., 2013). Importantly, deactivated catalysts could regain their initial activity after regeneration in inert gas (550 °C for MoO_3 and 700 °C for WO_3) over several cycles.

To investigate the activation procedure's effect on alkylidene center formation mechanisms, the researchers employed temperature-programmed surface reaction (TPRS). These studies revealed that during temperature increases in propylene atmosphere, CO, CH_4, and H_2 began forming at approximately 500 °C on MoO_3 and 600 °C on WO_3. These observations support a pseudo-Wittig mechanism, wherein an unstable carbonyl compound forms and subsequently decomposes into the above-mentioned compounds at high temperatures. Further temperature increases led to benzene and ethylene formation, similar to the induction period observed in methane aromatization reactions (Rahman et al., 2018).

To quantify the number of active Mo centers formed on activated MoO_3/SiO_2 surfaces, the authors utilized isotope labelling methods similar to the Chauvin and Commereuc experiment (Chauvin and Commereuc, 1992). MoO_3/SiO_2 samples with varying MoO_3 content were activated in propylene until steady-state propylene metathesis was established, thoroughly purged with N_2, and then titrated with $^{13}CH_2{=}^{13}CH_2$. GC-MS analysis detected $^{13}CH_2{=}CH_2$ and $^{13}CH_2{=}CH\text{-}CH_3$ products. Experimental series determined that the most active Mo formed in samples with the lowest MoO_3 content on the support surface, while samples not activated by propylene showed zero active Mo content on their surfaces (Table 1).

An effective activation method for MoO_3/SBA-1 catalysts is presented in another publication (Michorczyk et al., 2019). The researchers prepared a series of catalysts with varying MoO_3 content ($n = 1, 3, 5, 10,$ and 20 wt.%) on meso-

Table 1. Results of active site counting by $^{13}CH_2{=}^{13}CH_2$ tracing MoO_3 (Ding et al., 2016).

MoO_3 [%wt.]	Mo coverage [per nm^2]	$^{13}CH_2{=}CH_2$ [mmol]	$^{13}CH_2{=}CH{-}CH_3$ [mmol]	Fraction of active Mo [%]
1.4	0.06	6.7×10^{-4}	2.6×10^{-3}	10.9
2.8	0.1	1.1×10^{-3}	2.3×10^{-3}	8.6
6.7	0.4	1.4×10^{-3}	2.5×10^{-3}	4.2
12.6	0.8	1.7×10^{-3}	3.8×10^{-3}	3.2
20.1	2.6	1.8×10^{-3}	3.4×10^{-3}	1.9
30.2	8.5	1.1×10^{-3}	1.8×10^{-3}	0.7
6.7[a]	0.4	0.0	0.0	0.0

[a] catalyst pretreated by 550 °C calcination in N_2 flow without high-temperature activation in propylene flow

porous SBA-1 silica support and activated in CH_4 atmosphere for 30 minutes at 700 °C. Among the tested materials, the $20MoO_3/SBA-1$ sample exhibited the highest specific activity. However, TOF values calculated for total Mo content decreased with increasing MoO_3 concentrations, confirming that dispersed Mo species serve as precursors for active sites in the metathesis reaction.

The effects of activation temperature (550–700 °C) and various activating gases (argon, methane, ethylene, propylene, and hydrogen) on the $20MoO_3/SBA-1$ sample was also investigated. Hydrogen activation at 550–650 °C showed no improvement compared to argon activation. In contrast, hydrocarbon activation significantly enhanced the catalytic activity of $20MoO_3/SBA-1$ in propylene metathesis reactions at 50 °C, achieving propylene conversion rates comparable to those observed with propylene-activated MoO_3/SiO_2 (Ding et al., 2016).

The influence of CH_4 on $20MoO_3/SBA-1$ activity in propylene metathesis was studied using TPRS technique. The catalyst was heated in a CH_4 atmosphere to 800 °C, with GC analysis revealing that initial catalyst-CH_4 interactions began around 400 °C, producing only CO_2 up to 600 °C. Between 600–700 °CC, additional CO and H_2 formation was observed, with maximum production occurring near 700 °C, coinciding with the complete disappearance of CO_2. From 700 to 800 °C, H_2 and CO generation decreased while benzene and ethylene gradually appeared – behaviour similar to the induction period of methane aromatization, analogous to previous studies (Ding et al., 2016).

During methane aromatization's induction period, the first stage involves reduction of Mo^{6+} with methane followed by carburization to MoC_x carbides and MoC_xO_y oxycarbides (Schwach et al., 2017). Subsequently, CO, H_2, and C_2H_4 form. Based on these observations, the authors suggest that the initial stage of the $20MoO_3/SBA-1$ TPRS experiment involves Mo^{6+} reduction by methane, with H_2 and CO generation associated with the formation of MoC_x carbides and MoC_xO_y oxycarbides. These forms contribute to the *in-situ* formation of ethylene, which can generate metal-carbene centers according to the proposed mechanism (Ding et al., 2016). The only discrepancy is the absence of carbonyl compounds that could decompose into CO and H_2, as they are unstable at high temperatures.

The observed interaction between methane and $20MoO_3/SBA-1$ during TPRS suggests that metal-carbene centers might also form through hydrogenation of MoC_x and MoC_xO_y species.

The comparison of initial activity of the abovementioned methods of activation with some examples for SOMC catalysts is presented in Table 2.

The catalyst activation methods described in this part of discussion offer not only effective activation methods but also potential for industrial application. As demonstrated in another publication (Myradova et al., 2022), molybdenum catalysts on SiO_2 can be successfully activated in alkane atmosphere (ethane or propane), achieving activities in olefin metathesis comparable to catalysts activated in methane (Michorczyk et al., 2019) or propylene (Ding et al., 2016) and as well those that were synthesized by SOMC (Merle et al., 2017). A brief pretreatment lasting 2–15 minutes using light alkanes (C_1–C_3) at 650 °C improves catalytic activity for propylene metathesis conducted at 50 °C. Brief exposure to ethane or propane during pretreatment produces comparable results to previously reported pretreatments using ethylene, propylene, or methane. Compared to direct activation using alkenes, effective alkane pretreatment requires temperatures that are 100–150 °C higher (600–700 °C). This temperature requirement likely comes from the need for alkenes to generate active sites, where these alkenes are formed

Table 2. Comparison of initial activities of molybdenum catalysts activated by various methods and synthesized by SOMC.

Catalyst/ precatalyst	Activation conditions (atmosphere, temperature, time)	Reaction conditions	TOF (h^{-1})	Conversion of propylene (%)	Ref.
$5MoO_3/SiSBA-1$	C_3H_8, 650 °C, 10 min	50 °C, C_3H_6	301.9	28.6	(Myradova et al., 2022)
	C_3H_8, 650 °C, 2 min	50 °C, C_3H_6	343.5	35.1	
	C_2H_6, 650 °C, 15 min	50 °C, C_3H_6	147.3	13.9	
$6.7MoO_3/SiO_2$	C_3H_6/N_2, 550 °C, 30 min	20 °C, C_3H_6	640.0	34.5	(Ding et al., 2016)
	C_2H_4/N_2, 550 °C, 30 min	20 °C, C_3H_6	–	28.7	
$5MoO_3/SBA-1$	CH_4, 650 °C, 30 min	50 °C, C_3H_6	162	38.9	(Michorczyk et al., 2019)
$1.5MoO_3/SiO_2$	CO (photoreduction), 27 °C	20 °C, C_3H_6	1512	–	(Shelimov et al., 1986)
$Mo(NAr)(CH^tBu)(CH_2^tBu)_2/SiO_{2-700}$	–	60 °C, C_3H_6	1572.0	10.0	(Merle et al., 2017)
$MoO(CH_2^tBu)_3Cl/SiO_{2-700}$	–	60 °C, C_3H_6	6126.0	30.0	(Merle et al., 2017)

in situ through dehydrogenation reactions during alkane pretreatment of the catalyst. The dehydrogenation of ethane and propane occurs efficiently at temperatures above 600 °C.

Recent findings by the Roman-Leshkov group (Gani et al., 2023) revealed that, in addition to the classical Chauvin cycle, active site formation in SOMC-derived metathesis catalysts may proceed via a reversible Brønsted acid-catalysed renewal mechanism. Surface silanol groups on silica supports can protonate olefins to form alkoxides, which regenerate active alkylidene species. This dynamic pathway explains induction periods and rate limitations tied to site renewal rather than metathesis itself. Notably, co-feeding non-metathesis-active alkenes (e.g., 2,3-dimethyl-1-butene) enhanced site regeneration and catalytic performance. DFT calculations confirmed that silanol-assisted mechanisms are kinetically accessible, highlighting the crucial role of support acidity in catalyst design and activity enhancement.

6. CONCLUTIONS AND PERSPECTIVES

In the current hydrocarbon market, paraffins are cheaper than olefins, making their use for catalyst activation potentially more justified. Notably, these activation temperatures are close to the temperatures required for dehydrogenation of short-chain alkanes (550–650 °C). For instance, propane dehydrogenation is an efficient and selective propylene synthesis technology that has attracted increasing interest over the past decade due to the existing "propylene gap" in the market. This temperature compatibility suggests an interesting possibility: the potential combination of two industrial processes-dehydrogenation of short-chain paraffins and olefin metathesis-to create an integrated approach for olefin production. The dehydrogenation product composition-rich in light paraffins and olefins-can contribute to the *in-situ* regeneration and sustained activation of the metathesis function.

An important challenge in the dehydrogenation reaction is catalyst coking, which can block the newly generated active sites for the subsequent metathesis reaction. When designing an integration of paraffin dehydrogenation with olefin metathesis, it is necessary to rationally plan an activation protocol, consider methods for catalyst regeneration and the possibility of restoring its metathesis activity. Ding et al. (2016) reported that purging the catalyst with an inert gas can partially restore catalytic activity, highlighting the importance of regeneration strategies in integrated processes.

In summary, the prospect of combining paraffin dehydrogenation with metathesis represents a promising dual opportunity: generating new carbene sites while integrating selective olefin synthesis processes. This approach may offer an efficient and industrially attractive pathway for the production of next-generation olefins.

ACKNOWLEDGEMENTS

The work was supported by the National Science Centre, Poland, under the research project "Combination of dehydrogenation with metathesis as an approach to raw material integration and an efficient method of metathetic active site formation", no. 2022/45/B/ST8/01798.

REFERENCES

Amakawa K., Kröhnert J., Wrabetz S., Frank B., Hemmann F., Jäger C., Schlögl R., Trunschke A., 2015. Active sites in olefin metathesis over supported molybdena catalysts. *ChemCatChem*, 7, 4059–4065. DOI: 10.1002/cctc.201500725.

Amakawa K., Wang Y., Kröhnert J., Schlögl R., Trunschke A., 2019. Acid sites on silica-supported molybdenum oxides probed by ammonia adsorption: Experiment and theory. *Mol. Catal.*, 478, 110580. DOI: 10.1016/j.mcat.2019.110580

Amakawa K., Wrabetz S., Kröhnert J., Tzolova-Müller G., Schlögl R., Trunschke A., 2012. In situ generation of active sites in olefin metathesis. *J. Am. Chem. Soc.*, 134, 11462–11473. DOI: 10.1021/ja3011989.

Andreini A., 1991. Re-oxide-silica-alumina metathesis catalysts: role of genesis and modification of precursor structures, and lack of activity of the low-loading Re-oxide-alumina catalyst. *J. Mol. Catal.*, 65, 359–376. DOI: 10.1016/0304-5102(91)85071-9.

Andreini A., Mol J.C., 1981. Activity of supported tungsten oxide catalysts for the metathesis of propene. *J. Colloid Interface Sci.*, 84, 57–65. DOI: 10.1016/0021-9797(81)90259-9.

Banks R.L., Bailey G.C., 1964. Olefin disproportionation. A New Catalytic Process. *Ind. Eng. Chem. Prod. Res. Dev.*, 3, 170–173. DOI: 10.1021/i360011a002.

Bare S.R., Kelly S.D., D.vila F., Boldingh E., Karapetrova E., Kas J., Mickelson G.E., Modica F.S., Yang N., Rehr J.J., 2011. Experimental (XAS, STEM, TPR, and XPS) and theoretical (DFT) characterization of supported rhenium catalysts. *J. Phys. Chem. C*, 115, 5740–5755. DOI: 10.1021/jp1105218.

Basrur A.G., Patwardhan S.R., Was S.N., 1991. Propene metathesis over silica-supported tungsten oxide catalyst – Catalyst induction mechanism. *J. Catal.*, 127, 86–95. DOI: 10.1016/0021-9517(91)90211-L.

Biefeld C.G., Eick H.A., Grubbs R.H., 1973. Crystal structure of bis(triphenylphosphine)tetramethyleneplatinum(II). *Inorg. Chem.*, 12, 2166–2170. DOI: 10.1021/ic50127a046.

Bouchmella K., Mutin P.H., Stoyanova M., Poleunis C., Eloy P., Rodemerck U., Gaigneaux E.M., Debecker D.P., 2013. Olefin metathesis with mesoporous rhenium-silicium-aluminum mixed oxides obtained via a one-step non-hydrolytic sol-gel route. *J. Catal.*, 301, 233–241. DOI: 10.1016/j.jcat.2013.02.016.

Calderon N., Chen H.Y., Scott K.W., 1967. Olefin metathesis – A novel reaction for skeletal transformations of unsaturated hydrocarbons. *Tetrahedron Lett.*, 8, 3327–3329. DOI: 10.1016/S0040-4039(01)89881-6.

Calderon N., Ofstead E.A., Ward J.P., Allen Judy W., Scott K.W., 1968. Olefin metathesis. I. Acyclic vinylenic hydrocarbons. *J. Am. Chem. Soc.*, 90, 4133–4140. DOI: 10.1021/ja01017a039.

Chauvin Y., 2006. Olefin metathesis: The early days (Nobel lecture). *Angew. Chem. Int. Ed.*, 45, 3740–3747. DOI: 10.1002/anie.200601234.

Chauvin Y., Commereuc D., 1992. Chemical counting and characterization of the active sites in the rhenium oxide/alumina metathesis catalyst. *J. Chem. Soc. Chem. Commun.*, 462–464. DOI: 10.1039/C39920000462.

Copéret C., Berkson Z.J., Chan K.W., Jordan J.S., Gordon C.P., Pucino M., Zhizhko P.A., 2021. Olefin metathesis: what have we learned about homogeneous and heterogeneous catalysts from surface organometallic chemistry? *Chem. Sci.* 12, 3092–3115. DOI: 10.1039/d0sc06880b.

Debecker D.P., Bouchmella K., Poleunis C., Eloy P., Bertrand P., Gaigneaux E.M., Mutin P.H., 2009. Design of SiO_2–Al_2O_3-MoO_3 metathesis catalysts by nonhydrolytic sol-gel. *Chem. Mater.*, 21, 2817–2824. DOI: 10.1021/cm900490t.

Debecker D.P., Schimmoeller B., Stoyanova M., Poleunis C., Bertrand P., Rodemerck U., Gaigneaux E.M., 2011a. Flame-made MoO_3/SiO_2–Al_2O_3 metathesis catalysts with highly dispersed and highly active molybdate species. *J. Catal.*, 277, 154–163. DOI: 10.1016/j.jcat.2010.11.003.

Debecker D.P., Stoyanova M., Colbeau-Justin F., Rodemerck U., Boissière C., Gaigneaux E.M., Sanchez C., 2012. One-pot aerosol route to MoO_3/SiO_2–Al_2O_3 catalysts with ordered super microporosity and high olefin metathesis activity. *Angew. Chemie Int. Ed.*, 51, 2129–2131. DOI: 10.1002/anie.201106277.

Debecker D.P., Stoyanova M., Rodemerck U., Eloy P., Léonard A., Su B.-L., Gaigneaux E.M., 2010. Thermal spreading as an alternative for the wet impregnation method: Advantages and downsides in the preparation of $MoO_3/SiO_2-Al_2O_3$ metathesis catalysts. *J. Phys. Chem. C*, 114, 18664–18673. DOI: 10.1021/jp1074994.

Debecker D.P., Stoyanova M., Rodemerck U., Gaigneaux E.M., 2011b. Preparation of MoO3/SiO2-Al2O3 metathesis catalysts via wet impregnation with different Mo precursors. *J. Mol. Catal. A: Chem.*, 340, 65–76. DOI: 10.1016/j.molcata.2011.03.011.

Ding K., Gulec A., Johnson A.M., Drake T.L., Wu W., Lin Y., Weitz E., Marks L.D., Stair P.C., 2016. Highly efficient activation, regeneration, and active site identification of oxide-based olefin metathesis catalysts. *ACS Catal.*, 6, 5740–5746. DOI: 10.1021/acscatal.6b00098.

Eleuterio H.S., 1991. Olefin metathesis: chance favors those minds that are best prepared. *J. Mol. Catal.*, 65, 55–61. DOI: 10.1016/0304-5102(91)85082-D.

Elev I.V., Shelimov B.N., Kazansky V.B., 1968. *Method of preparing catalyst for disproportioning olefins.* SU1286273.

Fischer E.O., Hollfelder H., Kreissl F.R., Uedelhoven W., 1976. Übergangsmetall-carben-komplexe: XCII. Triphenyl silyläth oxycarben-pentacarbonyl-chrom und triphenylsilyldimethylamino carben-pentacarbonylchrom, zwei neuartige carben-komplexe. *J. Organomet. Chem.*, 113, C31–C34. DOI: 10.1016/s0022-328x(00)87339-8.

Fischer E.O., Maasböl A., 1964. On the existence of a tungsten carbonyl carbene complex. *Angew. Chemie*, 3, 580–581. DOI: 10.1002/anie.196405801.

Gangwal S.K., Fathi-kalajahl J., Wills G.B., 1977. Break-in behavior of a tungsten oxide on silica catalyst in propylene disproportionation. *Ind. Eng. Chem. Prod. Res. Dev.*, 16, 237–241. DOI: 10.1021/i360063a009.

Gani T.Z.H., Berkson Z.J., Zhu R., Kang J.H., Di Iorio J.R., Chan K.W., Consoli D.F., Shaikh S.K., Copéret C., Román-Leshkov Y., 2023. Promoting active site renewal in heterogeneous olefin metathesis catalysts. *Nature*, 617, 524–528. DOI: 10.1038/s41586-023-05897-w.

Goldwasser J., Engelhardt J., Hall W.K., 1981. The isomerization and metathesis of *n*-butenes. I. Unreduced molybdena-alumina catalysts. *J. Catal.*, 70, 275–286. DOI: 10.1016/0021-9517(81)90340-7.

Griffe B., Sierraalta A., Ruette F., Brito J.L., 2001. Parametric calculations of Mo-allyl complexes anchored on silica. *J. Mol. Catal. A: Chem.*, 168, 265–277. DOI: 10.1016/S1381-1169(00)00543-4.

Grubbs R.H., Brunck T.K., 1972. Possible intermediate in the tungsten-catalyzed olefin metathesis reaction. *J. Am. Chem. Soc.*, 94, 2538–2540. DOI: 10.1021/ja00762a073.

Grubbs R.H., Swetnick S.J., 1980. Mechanism of olefin metathesis over a supported molybdenum catalyst. *J. Mol. Catal.*, 8, 25–36. DOI: 10.1016/0304-5102(80)87003-9.

Grünert W., Feldhaus R., Anders K., Shpiro E.S., Minachev K.M., 1989. eduction behavior and metathesis activity of $WO_3Al_2O_3$ catalysts: III. The activation of $WO_3Al_2O_3$ catalysts. *J. Catal.*, 120, 444–456. DOI: 10.1016/0021-9517(89)90284-4.

Grünert W., Stakheev A.Y., Feldhaus R., Anders K., Shpiro E.S., Minachev K.M., 1992a. Reduction and metathesis activity of MoO_3/Al_2O_3 catalysts II. The activation of MoO_3/Al_2O_3 catalysts. *J. Catal.*, 135, 287–299. DOI: 10.1016/0021-9517(92)90286-Q.

Grünert W., Stakheev A.Y., Mörke W., Feldhaus R., Anders K., Shpiro E.S., Minachev K.M., 1992b. Reduction and metathesis activity of MoO_3/Al_2O_3 catalysts: I. An XPS investigation of MoO_3/Al_2O_3 catalysts. *J. Catal.*, 135, 269–286. DOI: 10.1016/0021-9517(92)90285-P.

Guan J., Yang G., Zhou D., Zhang W., Liu X., Han X., Bao X., 2008. Formation of Mo-carbene active sites in Mo/Beta zeolite catalysts with different olefins: Theoretical exploration of possible reaction pathways and substituent effects. *Catal. Commun.*, 9, 2213–2216. DOI: 10.1016/j.catcom.2008.05.020.

Handzlik J., 2005. Metathesis activity and properties of Mo-alkylidene sites differently located on silica. A density functional theory study. *J. Phys. Chem. B*, 109, 20794–20804. DOI: 10.1021/jp053517b.

Handzlik J., 2007. Properties and metathesis activity of monomeric and dimeric Mo centres variously located on γ-alumina – A DFT study. *Surf. Sci.*, 601, 2054–2065. DOI: 10.1016/j.susc.2007.03.002.

Handzlik J., Gierada M., Kurleto K., 2024. Role of surface silanols in active site formation during olefin metathesis over a WO_x/SiO_2 catalyst: A computational perspective. *J. Phys. Chem. C*, 128, 5934–5946. DOI: 10.1021/acs.jpcc.4c01305.

Handzlik J., Kurleto K., Gierada M., 2021. Computational insights into active site formation during alkene metathesis over a MoO_x/SiO_2 catalyst: The role of surface silanols. *ACS Catal.*, 11, 13575–13590. DOI: 10.1021/acscatal.1c03912.

Handzlik J., Ogonowski J., Stoch J., Mikołajczyk M., Michorczyk P., 2006. Properties and metathesis activity of molybdena-alumina, molybdena-silica-alumina and molybdena-silica catalysts – a comparative study. *Appl. Catal., A*, 312, 213–219. DOI: 10.1016/j.apcata.2006.07.002.

Handzlik J., Sautet P., 2008. Active sites of olefin metathesis on molybdena-alumina system: A periodic DFT study. *J. Catal.*, 256, 1–14. DOI: 10.1016/j.jcat.2008.02.016.

Hardcastle F.D., Wachs I.E., Horsley J.A., Via G.H., 1988. The structure of surface rhenium oxide on alumina from laser raman spectroscopy and x-ray absorption near-edge spectroscopy. *J. Mol. Catal.*, 46, 15–36. DOI: 10.1016/0304-5102(88)85081-8.

Heckelsberg L.F., 1965. *Conversion of olefins*. US3365513.

Hérisson J.-L.P., Chauvin Y., 1971. Catalyse de transformation des oléfines par les complexes du tungstène. II. Télomérisation des oléfines cycliques en présence d'oléfines acycliques. *Makromol. Chem.*, 141, 161–176. DOI: 10.1002/macp.1971.021410112.

Howell J.G., Li Y.P., Bell A.T., 2016. Propene metathesis over supported tungsten oxide catalysts: A study of active site formation. *ACS Catal.*, 6, 7728–7738. DOI: 10.1021/acscatal.6b01842.

Ivin K.C., Mol J.C., 1997. *Olefin metathesis and metathesis polymerization*. Academic Press, London.

Iwasawa Y., Ichinose H., Ogasawara S., Soma M., 1981. Olefin metathesis over well-defined active fixed molybdenum catalysts. Structure and oxidation state of the active site and reaction mechanism. *J. Chem. Soc. Faraday Trans. 1*, 77, 1763. DOI: 10.1039/f19817701763.

Iwasawa Y., Kubo H., Hamamura H., 1985. Olefin metathesis over Al_2O_3 or SiO_2-attached molybdenum catalysts: active structures and mechanism for initial carbene formation. *J. Mol. Catal.*, 28, 191–208. DOI: 10.1016/0304-5102(85)87028-0.

Kazansky V.B., Shelimov B.N., 1991. Supported silica-molybdena catalysts for olefin metathesis activated by photoreduction. *Res. Chem. Intermed.*, 15, 1–16. DOI: 10.1163/156856791X00084.

Keim W., 2013. Oligomerization of ethylene to α-olefins: Discovery and development of the shell higher olefin process (SHOP). *Angew. Chem. Int. Ed.*, 52, 12492–12496. DOI: 10.1002/anie.201305308.

Kurleto K., Tielens F., Handzlik J., 2020. Isolated molybdenum(VI) and tungsten(VI) oxide species on partly dehydroxylated silica: A computational perspective. *J. Phys. Chem. C*, 124, 3002–3013. DOI: 10.1021/acs.jpcc.9b09586.

Laverty D., Rooney J.J., Stewart A., 1976. Possible role of hydrido-metal complexes in metathesis, isomerization, dimerization, and polymerization of alkenes. *J. Catal.*, 45, 110–113. DOI: 10.1016/0021-9517(76)90061-0.

Le A.V., Rajbanshi B., Lobo R.F., Bai P., 2023. Mechanistic study of heterogeneous propene metathesis on WO_x/SiO_2 catalysts. *J. Catal.*, 427, 115117. DOI: 10.1016/j.jcat.2023.115117.

Lee E.L., Wachs I.E., 2007. In situ spectroscopic investigation of the molecular and electronic structures of SiO_2 supported surface metal oxides. *J. Phys. Chem. C*, 111, 14410–14425. DOI: 10.1021/jp0735482.

Lee E.L., Wachs I.E., 2008. In situ raman spectroscopy of SiO_2-supported transition metal oxide catalysts: An isotopic $^{18}O-^{16}O$ exchange study. *J. Phys. Chem. C*, 112, 6487–6498. DOI: 10.1021/jp076485w.

Lewandos G.S., Pettit R., 1971. Mechanism of the metal-catalyzed disproportionation of olefins. *J. Am. Chem. Soc.*, 93, 7087–7088. DOI: 10.1021/ja00754a067.

Luckner R.C., Wills G.B., 1973. Transient kinetics of the disproportionation of propylene over a tungsten oxide on silica catalyst. *J. Catal.*, 28, 83–91. DOI: 10.1016/0021-9517(73)90182-6.

Lwin S., Wachs I.E., 2014. Olefin metathesis by supported metal oxide catalysts. *ACS Catal.*, 4, 2505–2520. DOI: 10.1021/cs500528h.

Maksasithorn S., Praserthdam P., Suriye K., Devillers M., Debecker D.P., 2014. WO_3-based catalysts prepared by non-hydrolytic sol-gel for the production of propene by cross-metathesis of ethene and 2-butene. *Appl. Catal., A*, 488, 200–207. DOI: 10.1016/j.apcata.2014.09.030.

McCoy J.R., Farona M.F., 1991. Olefin metathesis over a $Re_20_7/A1_20_3$ metathesis catalyst: Mechanism for initial metallacarbene formation. *J. Mol. Catal.*, 66, 51–58. DOI: 10.1016/0304-5102(91)85020-3.

Merle N., Le Queìmeìner F., Bouhoute Y., Szeto K.C., De Mallmann A., Barman S., Samantaray M.K., Delevoye L., Gauvin R.M., Taoufik M., Basset J.M., 2017. Well-defined molybdenum oxo alkyl complex supported on silica by surface organometallic chemistry: A highly active olefin metathesis precatalyst. *J. Am. Chem. Soc.*, 139, 2144–2147. DOI: 10.1021/jacs.6b11220.

Michorczyk P., Węgrzyniak A., Węgrzynowicz A., Handzlik J., 2019. Simple and efficient way of molybdenum oxide-based catalyst activation for olefins metathesis by methane pretreatment. *ACS Catal.*, 9, 11461–11467. DOI: 10.1021/acscatal.9b03714.

Mitra B., Gao X., Wachs I.E., Hirt A.M., Deo G., 2001. Characterization of supported rhenium oxide catalysts: Effect of loading, support and additives. *Phys. Chem. Chem. Phys.*, 3, 1144–1152. DOI: 10.1039/B007381O.

Mol J.C., 1990. General properties of supported metathesis catalysts, In: İmamoğlu Y., Zümreoğlu-Karan B., Amass A.J. (Eds.), *Olefin metathesis and polymerization catalysts*. Springer Dordrecht, 247–269. DOI: 10.1007/978-94-011-3328-9.

Mol J.C., 1999. Olefin metathesis over supported rhenium oxide catalysts. *Catal. Today*, 51, 289–299. DOI: 10.1016/S0920-5861(99)00051-6.

Mol J.C., 2004. Industrial applications of olefin metathesis. *J. Mol. Catal. A: Chem.*, 213, 39–45. DOI: 10.1016/j.molcata.2003.10.049.

Mol J.C., Andreini A., 1988. Activity and selectivity of rhenium-based catalysts for alkene metathesis. *J. Mol. Catal.*, 46, 151–156. DOI: 10.1016/0304-5102(88)85090-9.

Myradova M., Węgrzynowicz A., Węgrzyniak A., Gierada M., Jodłowski P., Łojewska J., Handzlik J., Michorczyk P., 2022. Tuning the metathesis performance of a molybdenum oxide-based catalyst by silica support acidity modulation and high temperature pretreatment. *Catal. Sci. Technol.*, 12, 2134–2145. DOI: 10.1039/D1CY02064A.

Nakamura R., Abe F., Echigoya E., 1981. Structures Of rhenium(VII) oxides on alumina and their catalytic activities for metathesis of olefins. *Chem. Lett.*, 10, 51–54. DOI: 10.1246/cl.1981.51.

Nakamura R., Echigoya E., 1982. Structure and nature of active sites on an O_2^-/Re oxide/alumina metathesis catalyst. *J. Mol. Catal.*, 15, 147–156. DOI: 10.1016/0304-5102(82)80013-8.

Natta G., Dall'Asta G., Mazzanti G., 1964. Stereospecific homompolymerization of cyclopentene. *Angew. Chem. Int. Ed.*, 3, 723–729. DOI: 10.1002/anie.196407231.

Olsthoorn A.A., Boelhouwer C., 1976. An infrared spectroscopic study of the $Re_2O_7Al_2O_3$ metathesis catalyst: I. Physicochemical properties, structure, and synthesis. *J. Catal.*, 44, 197–206. DOI: 10.1016/0021-9517(76)90390-0.

Popoff N., Mazoyer E., Pelletier J., Gauvin R.M., Taoufi M., 2013. Expanding the scope of metathesis: a survey of polyfunctional, single-site supported tungsten systems for hydrocarbon valorization. *Chem. Soc. Rev.*, 42, 9035–9054. DOI: 10.1039/c3cs60115c.

Rahman M., Sridhar A., Khatib S.J., 2018. Impact of the presence of Mo carbide species prepared *ex situ* in Mo/HZSM-5 on the catalytic properties in methane aromatization. *Appl. Catal., A*, 558, 67–80. DOI: 10.1016/j.apcata.2018.03.023.

Rappe A.K., Goddard III W.A., 1982. Olefin metathesis – a mechanistic study of high-valent Group VI catalysts. *J. Am. Chem. Soc.*, 104, 448–456. DOI: 10.1021/ja00366a013.

Rodríguez-Ramos I., Guerrero-Ruiz A., Homs N., Ramírez de la Piscina P., Fierro J.L.G., 1995. Reactions of propene on supported molybdenum and tungsten oxides. *J. Mol. Catal. A: Chem.*, 95, 147–154. DOI: 10.1016/1381-1169(94)00017-4.

Ross-Medgaarden E.I., Wachs I.E., 2007. Structural determination of bulk and surface tungsten oxides with UV−vis diffuse reflectance spectroscopy and Raman spectroscopy. *J. Phys. Chem. C*, 111, 15089–15099. DOI: 10.1021/jp074219c.

Rouhi A.M., 2002. Olefin metathesis: the early days. Recognizing the role of metal carbenes was key in realizing the promise of olefin metathesis. *Chem. Eng. News*, 80, 34–38.

Schwach P., Pan X., Bao X., 2017. Direct conversion of methane to value-added chemicals over heterogeneous catalysts: challenges and prospects. *Chem. Rev.*, 117, 8497–8520. DOI: 10.1021/acs.chemrev.6b00715.

Shelimov B.N., Elev I. V., Kazansky V.B., 1986. Use of photoreduction for activation of silica-molybdena catalysts for propylene metathesis: Comparison with thermal reduction. *J. Catal.*, 98, 70–81. DOI: 10.1016/0021-9517(86)90296-4.

Shelimov B.N., Elev I.V., Kazansky V.B., 1988. Spectroscopic study of formation of active metal-carbene species in photoreduced silica-molybdena catalysts for olefin metathesis. *J. Mol. Catal.*, 46, 187–200. DOI: 10.1016/0304-5102(88)85093-4.

Sherman Jr. E.O., Schreiner P.R., 1978. Oxidative-addition of tertiary phosphine-ruthenium complexes to allylic carbon-hydrogen bonds. *J. Chem. Soc., Chem. Commun.*, 1978, 223–224. DOI: 10.1039/C39780000223.

Sibeijn M., Mol J.C., 1990. Activity of supported Re_2O_7 catalysts for the metathesis of methyl oleate. *Appl. Catal.*, 67, 279–295. DOI: 10.1016/S0166-9834(00)84451-6.

Skoda D., Zhu R., Hanulikova B., Styskalik A., Vykoukal V., Machac P., Simonikova L., Kuritka I., Poleunis C., Debecker D.P., Román-Leshkov Y., 2023. Propylene metathesis over molybdenum silicate microspheres with dispersed active sites. *ACS Catal.*, 13, 12970–12982. DOI: 10.1021/acscatal.3c02045.

Solans-Monfort X., Filhol J.S., Copéret C., Eisenstein O., 2006. Structure, spectroscopic and electronic properties of a well defined silica supported olefin metathesis catalyst, $[(\equiv SiO)Re(\equiv CR)(=CHR)(CH_2R)]$, through DFT periodic calculations: silica is just a large siloxy ligand. *New J. Chem.*, 30, 842–850. DOI: 10.1039/b603426h.

Spronk R., Andreini A., Mol J.C., 1991. Deactivation of rhenium-based catalysts for the metathesis of propene. *J. Mol. Catal.*, 65, 219–235. DOI: 10.1016/0304-5102(91)85099-N.

The Royal Swedish Academy of Sciences, 2005. *The Nobel Prize in Chemistry 2005*. Available at: https://www.nobelprize.org/prizes/chemistry/2005/popular-information/.

Thomas R., Moulijn J.A., De Beer V.H.J., Medema J., 1980. Structure/metathesis activity relations of silica supported molybdenum and tungsten oxide. *J. Mol. Catal.*, 8, 161–174. DOI: 10.1016/0304-5102(80)87015-5.

Tian H., Roberts C.A., Wachs I.E., 2010. Molecular structural determination of molybdena in different environments: Aqueous solutions, bulk mixed oxides, and supported MoO_3 catalysts. *J. Phys. Chem. C*, 114, 14110–14120. DOI: 10.1021/jp103269w.

Vaghi A., Castellan A., Bart J.C.J., Giordano N., Ragaini V., 1976. Structure and catalytic activity of $MoO_3 \cdot SiO_2$ systems: II. Catalytic activity in the oxidation and disproportionation of propylene. *J. Catal.*, 42, 381–387. DOI: 10.1016/0021-9517(76)90113-5.

Van Schalkwyk C., Spamer A., Moodley D.J., Dube T., Reynhardt J., Botha J.M., Vosloo H.C.M., 2003. Factors that could influence the activity of a WO_3/SiO_2 catalyst: Part III. *Appl. Catal., A*, 255, 143–152. DOI: 10.1016/S0926-860X(03)00536-2.

Vicente B.C., Nelson R.C., Moses A.W., Chattopadhyay S., Scott S.L., 2011. Interactions involving lewis acidic aluminum sites in oxide-supported perrhenate catalysts. *J. Phys. Chem. C*, 115, 9010–9024. DOI: 10.1021/jp109929g.

Vikulov K.A., Elev I.V., Shelimov B.N., Kazansky V.B., 1989. Ir and UV-vis spectroscopic studies of the stable Mo CH_2 carbene complexes over photoreduced silica-molybdena catalysts with chemisorbed cyclopropane, and their role in olefin metathesis reactions. *J. Mol. Catal.*, 55, 126–145. DOI: 10.1016/0304-5102(89)80248-2.

Vikulov K.A., Shelimov B.N., Kazansky V.B., 1991. IR and UV-Vis spectroscopic studies of the surface Mo CH_2 and Mo $CH–CH_3$ carbene complexes produced by methylcyclopropane chemisorption over photoreduced silica-molybdena catalysts. *J. Mol. Catal.*, 65, 393–402. DOI: 10.1016/0304-5102(91)85074-C.

Vikulov K.A., Shelimov B.N., Kazansky V.B., 1992. Formation of Mo CH_2 carbene complex on the surface of photoreduced silica-molybdena catalyst treated with 1,3,5-cycloheptatriene. *J. Mol. Catal.*, 72, 117–125. DOI: 10.1016/0304-5102(92)80035-F.

Wang L., Hall W.K., 1983. The preparation and properties of rhenia-alumina catalysts. *J. Catal.*, 82, 177–184. DOI: 10.1016/0021-9517(83)90128-8.

Wu J.-F., Ramanathan A., Snavely W.K., Zhu H., Rokicki A., Subramaniam B., 2016. Enhanced metathesis of ethylene and 2-butene on tungsten incorporated ordered mesoporous silicates. *Appl. Catal., A*, 528, 142–149. DOI: 10.1016/j.apcata.2016.10.004.