Low Temperature Activation of Supported Metathesis Catalysts by Organosilicon Reducing Agents

Victor Mougel,†‡⊥ Ka-Wing Chan,†‡§ Georges Siddiqi,† Kento Kawakita,∥ Haruki Nagae,∥ Hayato Tsurugi,∥ Kazushi Mashima,*∥‡ Olga Safonova,⊥ and Christophe Copéret†§

†Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir Prelog Weg 1-5, 8093 Zürich, Switzerland
∥Department of Chemistry, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan
⊥Paul Scherrer Institute, CH-5232 Villigen, Switzerland

Supporting Information

ABSTRACT: Alkene metathesis is a widely and increasingly used reaction in academia and industry because of its efficiency in terms of atom economy and its wide applicability. This reaction is notably responsible for the production of several million tons of propene annually. Such industrial processes rely on inexpensive silica-supported tungsten oxide catalysts, which operate at high temperatures (>350 °C), in contrast with the mild room temperature reaction conditions typically used with the corresponding molecular alkene metathesis homogeneous catalysts. This large difference in the temperature requirements is generally thought to arise from the difficulty in generating active sites (carbenes or metallacyclobutanes) in the classical metal oxide catalysts and prevents broader applicability, notably with functionalized substrates. We report here a low temperature activation process of well-defined metal oxo surface species using organosilicon reductants, which generate a large amount of active species at only 70 °C (0.6 active sites/W). This high activity at low temperature broadens the scope of these catalysts to functionalized substrates. This activation process can also be applied to classical industrial catalysts. We provide evidence for the formation of a metallacyclopentane intermediate and propose how the active species are formed.

INTRODUCTION

Olefins metathesis has had a critical industrial impact, being used in applications ranging from petrochemicals and polymers to fine chemicals.1,2 Despite the growing industrial use of homogeneous well-defined metal alkylidene catalysts, the largest alkene metathesis processes, notably for the production of propene (over 1.5 billion lb of propene produced per year by OCT process), are based on WO3/SiO2 and related catalysts. However, these catalysts show limitations because of their intolerance to functional groups, selectivity issues due to double bond isomerization, and the need of high temperatures for activation and operation. Understanding the initiation and reaction mechanisms is critical to rationally tackle these issues. The mechanism of alkene metathesis, proposed by Hérisson and Chauvin3 in the 1970s, is based on a cycloaddition step of an olefin to a metal alkylidene, affording a metallacyclobutane intermediate, which then undergoes cycloreversion to afford new metal alkylidene and alkene, leading to an overall exchange of alkylidene ligands in olefin mixtures (Figure 1A). This mechanism has been supported by the detailed investigations of the catalytic cycle from molecular metal alkylidene complexes, and it is generally assumed that the industrial supported metal oxide (Mo, W, Re) alkene metathesis catalysts have similar active sites and reaction mechanism.4 For supported metal oxide and in particular WO3/SiO2 catalysts, the active sites have been proposed to correspond to isolated metal oxo alkylidene moieties in their highest oxidation state, formed under the harsh operating conditions of ca. 400 °C (Figure 1B).5,6 Major research efforts have been conducted in the past 40 years to generate the corresponding well-defined molecular and surface mimics.1,7,8 Such catalysts display very high activity at room temperature (>100 turnover number (TON)/min)9,10 in contrast to industrial catalysts, showing that the low activity of the industrial WO3/SiO2 catalysts is presumably due to the difficulty to generate the active oxo alkylidene from the oxo surface species rather than an intrinsic low activity of tungsten oxo alkylidene moieties.

Most activation strategies for industrial catalysts involve high temperature treatments under gas atmospheres (alkenes, inert gases, air, H2) or the use of alkylating agents such as R4Sn.11,12 However, the performance of these activated industrial catalysts is still far from that of the well-defined molecular and surface mimics. Proposed to involve either redox or nonredox mechanisms,4,13 these activation processes are still largely

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debated and hinder the rational development of activation strategies for these industrial catalysts.

Here, we disclose a practical, low temperature activation of molecularly defined silica-supported tungsten oxo catalysts using organosilicon reducing agents, generating highly active alkene metathesis heterogeneous catalysts compatible with functionalized olefins (Figure 1E). We show that this activation process is also applicable to the classical supported group 6 metal oxide industrial catalysts. We demonstrate that the generation of the active propagating species (alkylidenes and metallacyclobutanes) results from the formation of metal-lacyclopentane intermediates via oxidative coupling of the olefin reduced metal sites followed by ring contraction.

**RESULTS AND DISCUSSION**

**Synthesis of Well-Defined Silica Supported Tungsten Dioxo Complexes.** The complex mixture of surface species in classical supported tungsten catalysts such as WO3/SiO2 limits the understanding of the molecular transformations occurring at the catalytic active sites. To overcome these limitations, we have first investigated the synthesis of molecularly defined isolated tungsten(VI) oxo surface sites on silica through a thermolytic precursor approach. This approach consists of grafting a molecular complex containing (tBuO)3SiO− ligands followed by a thermolysis step, under oxidative (e.g., air) or nonoxidative conditions (e.g., vacuum/inert gas). We grafted [W(O)2(OSi(OtBu)3)2(DME)]19,20 on silica partially dehydroxylated at 700 °C (SiO2-700, Figure 1D), followed by a thermal treatment under vacuum—as recently reported for Cr21—affording the material 1 (Figure 2A). A tungsten loading of 3.15%wt was determined by elemental analysis, corresponding to a site density of ca. 0.5 W/nm2 and indicating a partial reaction of the molecular complex with the surface silanols, which was corroborated by IR spectroscopy (Figure 2B, see the Supporting Information for details).

The material 1 presents a W LIII-edge XANES white line energy of 10210.9 eV, very similar to the white line energy value of the molecular precursors [W(O)(OSi(OtBu)3)4] and [W(O)2(OSi(OtBu)3)2(DME)] (10211.0 and 10210.9 eV respectively), confirming that the tungsten centers are present in the +VI oxidation state. The W LIII-edge EXAFS spectra of material 1 is shown in Figure 2C. Fitting this spectrum with scattering paths from the nearest oxygen neighbors shows that the presence of a single surface species like the dioxo [(SiO)2WO2] or the monooxo [(SiO)4WO] is not possible. The best fit shows that the number of O atoms at 1.70 and 1.89 Å is 1.5 and 2.9 respectively (Table S7), in agreement with a ca. 1:1 mixture of [(SiO)2WO2] and [(SiO)4WO] species, as shown in Figure 2. In addition, the absence of intense peaks at high R values indicates the isolated nature of the tungsten centers in our material (W–W scattering path being typically observed at ca. 3.7 Å for bulk crystalline WO3 reference, Figure S21). The absence of crystalline WO3 in our sample was confirmed by powder X-ray diffraction of the material (Figure 1).
To overcome the low activity and need of elevated temperatures, we explored the use of organic reducing agents for low temperature activation. Reduction of supported metal complexes is complicated by the fact that most of the typically used reducing agents in molecular inorganic/organometallic chemistry (e.g., alkali metals, organometallic reagents) generate salts or metallic coproducts upon reduction. These byproducts stay adsorbed on the surface, which hinders both the understanding of the activity of the surface sites and the efficient recycling/reactivation of the catalyst. In that context, reduction of surface complexes with (metal/salt-free) organosilicon reagents has emerged as a promising alternative to classical reducing agents. We thus examined the activation of 1 using 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (Me₄BTDP).

The addition of 1 equiv of Me₄BTDP to a suspension of 1 in benzene at 70 °C afforded a dark purple solid. Based on proton NMR spectra of the filtrate, Me₄BTDP reacted quantitatively; 0.5 equiv of 2,3,5,6-tetramethylpyrazine and 0.03 equiv of HMDSO were released in solution, and reduction of the material was confirmed by a shift of the XANES white line to lower energy. The activity of this material in alkene metathesis was investigated using cis-4-nonene as a prototypical substrate. In contrast to 1, inactive in similar conditions, the catalysts activated with Me₄BTDP converted 1000 equiv of cis-4-nonene to thermodynamic conversion at 70 °C in 6 h. Note that no significant activity was observed at room temperature.

Analysis of the reduced materials by IR spectroscopy revealed that upon addition of Me₄BTDP new C−H stretches were formed and remaining isolated silanols were consumed, likely indicating a passivation of the surface upon exposure to the organosilicon reducing agent. As the passivation of surface silanols by Me₄BTDP—observed even on neat SiO₂₇₀₀ (see the Supporting Information for details)—could prevent full use of the reductant for the reduction of the W centers, we investigated the optimal amount of reductant required for quantitative reduction of the tungsten sites. Reductions in similar conditions as described above with x = 0.5, 0.8, 1, 2, 3, and 4 equiv of Me₄BTDP per W site were evaluated by NMR spectroscopy of the filtrate and XANES spectroscopy of the materials, thereafter coined 1-(Red)ₓ (Figure 3C).
Proton NMR of the filtrate after addition of Me₄-BTDP revealed that Me₄-BTDP is fully consumed when 1 equiv or less are used, while increasing amount of unreacted Me₄-BTDP is observed when more than 1 equiv is used. In all the conditions investigated, only small amounts of HMDSO (less than 0.1 equiv) were released in solution. This relatively small amount correlates with the passivation of the surface with TMS groups and the oxo functionalization of tungsten moieties with TMS groups (see below for details), as established by both solid state NMR and IR.

The activated materials were analyzed by XANES, monitoring the variation of the tungsten LIII white line energy. The latter gradually decreases with addition of reductant from 10210.9 eV for 1 to 10209.1 eV for 1-(Red)₂ (see the Supporting Information), this value remaining similar for materials activated with 2 equiv or more of Me₄-BTDP. This, combined with the presence of unreacted reductant when more than 2 equiv is used, indicates that the use of a larger amount of the reductant is not necessary to fully reduce the material. For this reason, we choose to characterize and focus our further studies on 1 reduced with 2 equiv of Me₄-BTDP, 1-(Red)₂.

Characterization of 1-(Red)₂. Clear information on the oxidation state of the sample is difficult, as very few similar low valent W references are available. We could however observe...
that the W LIII white line energy of the most reduced sample (10209.1 eV for 1-(Red)3, Figure 3B) is lower in energy than W(VI) and W(V) reference materials (10211.0 eV for [W(O)(OSi(OtBu)3)4(DME)] and 10210.9 eV for [W(O)(OSi(OtBu)3)]2(DME), and 10209.5 eV for W(OEt)2(SiO2)29 respectively), indicating that the main oxidation state of the material is likely to be lower than +V. In particular, the XANES spectra of 1 and 1-(Red)2 are very close to the spectra of Na2WO4 and WO2 reference materials respectively, consistent with their proposed oxidation state (Figure S24).

To confirm the oxidation state assignment in 1-(Red)2, chemical titration of the reduced material using an excess [(Cp2Fe)(PF6)] in chemical titration of the reduced material using an excess shift above 400 nm being typical for d transition of W(V) and W(VI) species according to spin counting (see the Supporting Information for details). Hence, W(V) species probably account for 75% of the surface species, together with 15% of W(VI) species and 10% of nonreduced W(VI) species, in agreement with the XANES shift described above. As both the dioxo [(≡SiO)2WO2] and monooxo [(≡SiO)WO] surface sites are present in a 1:1 ratio in 1, this indicates that both species can be reduced by Me4-BTDP. UV-DRS of 1-(Red)2 shows strong absorbance in all the 200–800 nm region, similar to what is observed for H2 treated tungsten oxides, the shifts above 400 nm being typical for d–d transition of W(V) species, but may also arise from other reduced W species. EXAFS studies of 1-(Red)2 show that the numbers of oxygen atoms at ca. 1.7 Å decreased together with an increase in the numbers of oxygen neighbors at ca. 1.9 Å with respect to 1, which is in agreement with an average of fewer W≡O double bonds and more W–O single bonds. From the quantitative analysis, the number of W≡O bonds before and after reaction drops from 1.5 to 0.8 while the number of W–O bonds increases from 2.9 to 3.1 (see Figure S22 and Tables S7 and S9). This is consistent with the reduction of the tungsten sites and the TMS functionalization of the oxo moieties upon reaction with the organosilicon reducing agent. This information is consistent with the C, H, N, and W elemental analysis of 1-(Red)2, indicating the presence of ca. 0.5 equiv of 2,3,5,6-tetramethylpyrazine and ca. 2.9 equiv of TMS moieties per surface tungsten center (13 C, 1 N, and 33 H atoms per W center), the latter accounting also for the presence of at least 1.4 (≡SiOTMS) moieties per W center resulting from silica passivation. This passivation can result from the reaction of residual surface silanols with Me4-BTDP ut also with HMDMSO.

At this stage, however, it is not possible to propose a defined structure after reduction, as the reduced material is likely composed of several surface species with tungsten in +IV (75%), +V (15%), and +VI (10%) oxidation states.

**Catalytic Activity.** In order to evaluate the potential of the most reduced catalyst 1-(Red)2, alkene metathesis of liquid olefins in batch conditions, we evaluated its activity with cis-4-norbornene. The reduced catalyst showed good activity in the metathesis of cis-4-norbornene, converting 1000 equiv of cis-4-norbornene to thermodynamic conversion at 70 °C in less than 12 h. However, as shown in Figure 3E, dark blue diamonds, an induction period of 3 h took place before metathesis started. Interestingly, we noticed that this induction period was affected by the amount of Me4-BTDP used, as shorter induction periods were observed for 1-(Red)1 and 1-(Red)3 (Figure 3E, light blue squares and purple dots). We reasoned that this induction period might be due to the reversible poisoning of some active sites by 2,3,5,6-tetramethylpyrazine released upon activation of the catalysts with the reducing agent. To test this hypothesis, we looked into directly activating the material under catalytic conditions. When 2 equiv of Me4-BTDP was added to the materials in the presence of 1000 equiv of cis-4-norbornene, full conversion was observed in less than 3 h, without observing an induction period (Figure 3E, green triangles). This activity is comparable to that with some well-defined silica-supported tungsten alkylidene catalysts. This high activity prompted us to investigate the catalytic activity with a broader range of substrates, including ethyl oleate, a prototypical functionalized substrate from biomass (Table 1). The catalyst was proven efficient with 1-norbornene, albeit with lower TOF, reaching equilibrium conversion in 24 h using 1 mol % loading. With ethyl oleate, equilibrium conversion is also observed at 1 mol % loading in 24 h. Ring opening metathesis was realized with a TON of 100 with cyclooctene. The molecular dioxo and monooxo analogues of the surface species ([W(O)(OSi(OtBu)3)]2(DME)) and [W(O)(Os(OtBu)3)]2) were found inactive under the same reaction conditions. The good activity displayed by 1 in the presence of 2 equiv of Me4-BTDP at low temperatures, including for functionalized substrates, is unprecedented for supported tungsten oxide catalysts.

**Catalyst Recycling, Poisoning, and Reactivation.** After initial activation of 1 with 2 equiv of Me4-BTDP in the presence of 1000 equiv of cis-4-norbornene and observation of thermodynamic conversion, the catalyst can be recovered by filtration. A new portion of 1000 equiv can be converted to thermodynamic conversion with this recycled catalyst, however at the expense of much slower TOF, equilibrium conversion being reached in about 24 h (vs 3 h for the initial cycle, Figure S32). This highlights the potential of the reducant to reactivate the deactivated sites (see the Supporting Information for details). We thus investigated the reactivation of poisoned catalyst with dioxygen, water, and alcohol. After poisoning the catalyst with dioxygen, and alcohol, Metathesis of cis-4-norbornene was initiated using 1 at 0.1 mol % loading in the presence of 2 equiv of Me4-BTDP; after 1.5 h, and ensuring that the catalytic reaction took place, H2O, dry air, or ethanol (1 equiv, excess, and 1 equiv respectively)
was added to the reaction mixtures (see the Supporting Information for details). After 1.5 h, the deactivated catalysts were separated from the solution phase to remove the contaminants and exposed to a new portion of 1000 equiv of cis-4-nonene. No catalytic activity was observed with these poisoned catalysts, confirming their complete deactivation. These poisoned catalysts were then reactivated with 2 equiv of Me₂-BTDP and display full conversions in all three cases (observed after 100 h for O₂ poisoned catalyst and 48 h for H₂O and ethanol). This unprecedented reactivation of poisoned catalysts paves the way toward continuous regeneration of the catalyst in flow conditions.

Extension to Classical MoO₃/SiO₂ Catalysts. Assuming that the MoO₃/SiO₂ (M = Mo, W) analogues of industrial catalysts have similar surface sites as our well-defined model 1, we applied the same strategy to activate these industrial catalysts. We observed that, in the presence of 2 equiv of Me₂-BTDP, 7.1% MoO₃/SiO₂ and 2.5% WO₃/SiO₂ become active for the metathesis of cis-4-nonene at low temperature, converting 1000 equiv of cis-4-nonene in less than 24 h at 70 °C at a maximum rate of 2 and 0.6 min⁻¹, respectively (see the Supporting Information for details). Similarly, while WO₃/SiO₂ catalysts are almost inactive at 100 °C in propene metathesis in flow conditions, upon reduction with 1 equiv of Me₂-BTDP it turned active, reaching a maximum TOF of 0.3 min⁻¹ and yielding a TON of 190 after 24 h.

Characterization of the Active Sites and Mechanism. In order to investigate the changes occurring at the metal sites in catalytic conditions, we investigated the changes in the XANES of 1-(Red)₂ before and after catalytic tests with cis-4-nonene in the conditions described above (1000 equiv of cis-4-nonene in toluene at 70 °C for 24 h). The XANES white line energy of the catalyst 1-(Red)₂ before and after exposure to the olefin increased from 10209.1 to 10209.4 eV, this increase in the white line energy being consistent with the partial reoxidation of the material upon exposure to alkenes.

Moreover, EPR studies of 1-(Red)₂ before and after exposure to cis-4-nonene in catalytic conditions show that the signal attributed to W(VI) sites is barely affected in terms of shape and intensity (Figure S26), indicating that these are likely spectator species in the catalytic reaction. The presence of these remaining W(V) sites after exposure to olefins probably explains why the value of the tungsten white line energy after exposure is still lower than that of the parent W(VI) precursor 1 (10209.4 eV for 1-(Red)₂ after exposure to 1000 equiv of cis-4-nonene vs 10210.9 eV for 1).

These observations tend to favor the formation of active species from the W(VI) sites, probably via an oxidative pathway. To further probe this hypothesis, 1-(Red)₂ was exposed to 1 equiv of ethylene at 100 °C for 12 h. GC-MS characterization of the gas phase after reaction revealed the release of ca. 0.5 equiv of propene and 0.03 quiv of but-2-enes. ¹³C cross-polarization magic angle spinning (CP MAS) and HETCOR NMR spectrum of a sample prepared analogously with ¹³C dilabeled ethylene revealed the appearance of peaks at 74, 38, 34, and 21 ppm correlating to ¹H signals at 3.2, 3.5, 2.0, and 2.6 ppm respectively (Figures S11–S13). The set of signals at 34 and 21 ppm are reminiscent from SP metallocyclobutane units while the signals at 74 and 38 ppm can be tentatively assigned to a metallocyclopentane moiety. To confirm this hypothesis, a suspension of this sample in CH₃Br₂ was contacted with Br₂; GC-MS analysis of the product solution revealed the presence of 1,4-dibromobutane, in agreement with the presence of the proposed metallocyclopentane complex (see the Supporting Information for details).

The formation of propene byproducts and the observation of a metallocyclopentane intermediate is reminiscent of the well documented (for molecular complexes) formation of metallocyclopentane intermediates from M(IV) olefin adducts (M = Ta, Mo, W)³⁹–⁴⁴ and their ring contraction to form carbene species (Figure 3F).⁴⁶ This suggests that the formation of the carbene active sites in our material occurs by a similar mechanism.

Quantification of the number of active sites in 1-(Red)₂ was carried out by exposing the material successively to nonlabeled ethylene and ¹³C dilabeled ethylene, evacuating the gas phase under high vacuum between the two steps. Analysis of the gas phase after second exposure by GC–MS revealed the presence of ca. 0.6 equiv of monolabeled ethylene, indicating the presence of ca. 60% of active sites in the reduced catalyst, in agreement with the amount of propene observed after initial exposure to ethylene. In addition, no significant amount of metallocyclopentane moietiy can be observed in the ¹³C CP MAS spectrum of the material (Figure S16), indicating that some of the metallocyclopentane moieties—previously observed by CP MAS and HETCOR—are mostly inactive in alkene metathesis. Assuming that all W(IV) sites react through 2 + 2 addition of ethylene, we can conclude that, among all the metallocyclopentane initially formed after ethylene addition, about 80% of them ring contract and give rise to metathesis active sites (metallocyclobutanes or alkylidenes) while 20% are inactive and remain as metallocyclopentane.

■ CONCLUSION

Using a molecularly defined tungsten oxo model of the surface species existing in WO₃/SiO₂ catalysts, we have identified a simple activation process via the reduction of the surface sites with organosilicon reductants at low temperatures. This process allows the generation of highly active catalysts, notably through the in situ reduction of the catalyst in the presence of the substrate and the formation of a large amount of active sites (0.6/W). This strategy also applies to the classical industrial MoO₃/SiO₂ catalysts (M = Mo, W), affording highly active alkene metathesis catalysts at low temperatures (70 °C in place of 150 and 400 °C for Mo and W, respectively). By showing evidence for the generation of metathesis active sites from W(IV) centers, this approach builds bridges between molecular and classical heterogeneous metal oxide metathesis catalysts. This activation process paves the way toward simple improvement of existing alkene metathesis processes by allowing lower temperature operation and improved selectivity.

■ ASSOCIATED CONTENT

$\text{Supporting Information}$

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.6b00176.

Synthesis and characterization, IR and solid-state NMR spectra, catalytic data, and XRD and XAS details (PDF)

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: ccoperet@ethz.ch.
*E-mail: mashima@chem.es.osaka-u.ac.jp.
Present Address
Laboratoire de Chimie des Processus Biologiques, CNRS UMR 8229, Collège de France, Université Pierre et Marie Curie, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05, France.

Author Contributions
V.M. and K.-W.C. contributed equally.

Notes
The authors declare no competing financial interest.

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