

Activation of Surface ReO_x Sites on Al_2O_3 Catalysts for Olefin Metathesis

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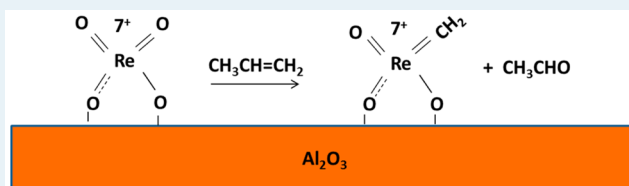
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Supporting Information

ABSTRACT: The nature of activated surface ReO_x sites and surface reaction intermediates for supported $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalysts during propylene self-metathesis were systematically investigated for the first time using in situ spectroscopy (Raman, UV-vis, XAS (XANES/EXAFS) and IR). In situ Raman spectroscopy reveals that olefins selectively interact with the surface dioxo ReO_4 sites anchored at acidic alumina hydroxyls. In situ UV-vis indicates that surface Re^{5+} and some Re^{6+} sites form, and in situ XAS indicates a reduction in the number of $\text{Re}=\text{O}$ bond character in the propylene self-metathesis reaction environment, especially as the temperature is increased. The appearance of oxygenated products during propylene activation supports the conclusion that catalyst activation involves removal of oxygen from the surface rhenia sites (pseudo-Wittig mechanism). Isotopic $\text{CD}_3\text{CD}=\text{CD}_2 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2$ switch experiments demonstrate the presence of surface $\text{Re}=\text{CD}_2$ and $\text{Re}=\text{CDCD}_3$ reaction intermediates, with the surface $\text{Re}=\text{CD}_2$ species being the most abundant reaction intermediate. In situ IR spectroscopy indicates the presence of significant surface propylene π complexes on alumina and rhenia sites of the catalyst, which complicates analysis of surface reaction intermediates during propylene self-metathesis.

KEYWORDS: catalyst, rhenia, Al_2O_3 , metathesis, olefin, spectroscopy, in situ, Raman, IR, UV-vis, XAS, TPSR, titration



1. INTRODUCTION

The oxidation states of surface rhenia sites on Al_2O_3 catalysts under different environmental conditions have received much attention, but the activation process and nature of the activated surface rhenia sites on Al_2O_3 present during olefin metathesis are still not known.^{1–6} Balcar et al.³ and Yide et al.⁴ detected the presence of Re^{4+} and Re^{3+} with XPS after pretreatment with He, but possible XPS-induced reduction under the ultrahigh vacuum pressure conditions employed clouds these findings for the initial state of the unactivated catalyst. In situ FT-IR measurements with CO as a probe molecule showed that the rhenia is both partially and fully reduced from the carbon monoxide vibrational band positions.⁵ Several researchers found that H_2 reduction of supported rhenia/ Al_2O_3 catalysts with low rhenia loadings resulted in in situ XANES and EXAFS features from both partially oxidized (Re^{4+}) and metallic (Re^0) rhenia.^{4,6} Stoyanova et al. reported detection of Re^{6+} after olefin metathesis with ex situ UV-vis studies.⁷ These UV-vis measurements, however, were taken under ambient conditions, where the oxidation state of the rhenia is known to be altered by exposure to molecular O_2 and moisture.⁸ The nature of the rhenia sites on alumina upon activation with olefins and during olefin metathesis is still not known because of the absence of in situ and operando spectroscopic characterization studies in the literature.

The objective of this study is to understand the activation process and nature of activated surface rhenia sites on alumina

during olefin metathesis. Direct monitoring of the activated surface rhenia sites on alumina under different environmental conditions was achieved with state of the art in situ spectroscopic characterization techniques (Raman, UV-vis, IR, and X-ray absorption spectroscopy (XAS)). The in situ characterization measurements revealed that rhenia shuttles between the Re^{7+} and Re^{5+} oxidation states upon activation and during olefin metathesis.

2. EXPERIMENTAL SECTION

2.1. Catalyst Synthesis. The supported $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalysts were prepared by impregnation of 65–70 wt % aqueous solution of perrhenic acid, HReO_4 (Sigma-Aldrich), onto two different Al_2O_3 supports (Harshaw batch no. DD351 and Engelhard batch no. H5433C) with BET surface areas of 180 and 170 m^2/g , respectively. Using ICP estimations from our previous studies,^{9,10} the actual ReO_x loadings are approximated to be 9.4% and 15.6% for the two catalysts used in this study. The 9.4% $\text{ReO}_x/\text{Al}_2\text{O}_3$ (Harshaw) catalyst was used for the in situ Raman studies because lower fluorescence from this alumina support gave rise to higher quality in situ Raman spectra at lower temperatures. The reaction studies were performed with the 15.6% $\text{ReO}_x/\text{Al}_2\text{O}_3$

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(Engelhard) catalyst, since only a limited amount of the discontinued Harshaw alumina was available. An incipient wetness point of 1.0 mL of H₂O/g was used. The alumina support was first calcined at 500 °C for 16 h before being impregnated with the aqueous perrenic acid solution, and the powders were stirred for 30 min. After impregnation, the samples were initially dried overnight under ambient conditions, further dried at 120 °C for 2 h in flowing air (AirGas, ultrahigh purity (UHP)), and calcined in the flowing air by heating at 1 °C/min and held at 500 °C for 4 h (Thermodyne furnace Model 48000).

2.2. In Situ UV–Vis Spectroscopy during Propylene Metathesis. The in situ UV–vis spectra of the catalysts were collected with a Varian Cary SE UV–vis–NIR spectrophotometer with the Harrick Praying Mantis accessory. A magnesium oxide sample was used as a standard for obtaining the background absorbance. Approximately 5–25 mg of each catalyst in finely ground powder form was loaded into the in situ environmental cell (Harrick, HVC-DR2). The catalysts were initially dehydrated at 500 °C under oxidizing conditions (10% O₂/Ar) and the UV–vis spectra (200–800 nm) of the dehydrated samples were subsequently collected after 30 min in flowing propylene (0.2–1% C₃[≡]/He) at 70 and 150 °C, using a scan rate of 15 nm/min and a signal averaging time of 0.6 s. The UV–vis spectra of reference compounds (iododioxobis (triphenylphosphine) rhenium(V) (Sigma-Aldrich, 99.98%), trichlorooxobis (triphenylphosphine) rhenium(V) (Sigma-Aldrich, 99.99%), ReO₃ (Alfa Aesar, 99%) and ReO₂ (Alfa Aesar, 99.995%)) were collected under ambient conditions.

2.3. In Situ Raman Spectroscopy during Propylene Adsorption/Desorption. The Raman spectra of the supported ReO_x/Al₂O₃ catalysts were obtained with a Horiba-Jobin Yvon LabRam HR instrument equipped with three laser excitations (532, 442, and 325 nm) and a liquid-N₂-cooled CCD detector (Horiba-Jobin Yvon CCD-3000 V). The 442 nm laser was chosen, since it minimized sample fluorescence. The spectral resolution was ~1 cm⁻¹, and the wavenumber calibration was checked using the silica standard line 520.7 cm⁻¹. The lasers were focused on the samples with a confocal microscope using a 50× objective (Olympus BX-30-LWD). The spectra were typically collected at 30 s/scan for five scans with a 200 μm hole. Approximately 5–25 mg of each catalyst in powder form was loaded into the in situ environmental cell (Harrick, HVC-DR2) possessing a SiO₂ window and O-ring seals, which were kept cool by flowing water. The catalysts were initially dehydrated at 500 °C by heating at 10 °C/min after 1 h inflowing 10% O₂/Ar (Airgas, certified, 9.989% O₂/Ar balance) at 30 mL/min. The cell was cooled in Ar to 30 °C before introducing the reactive 1% propylene (C₃[≡])/He flow. The in situ Raman spectra were collected after the following treatment: 60 min of flowing 1% propylene (C₃[≡])/He, followed by flushing with Ar for another 60 min and then increasing the catalyst temperature to 200 °C under the flowing Ar atmosphere.

2.4. In Situ X-ray Absorption Spectroscopy during Propylene Adsorption/Desorption. The in situ Re L₁-edge X-ray absorption spectroscopy (XAS) experiments were performed in transmission mode at beamlines X19A and X18B of the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory with ionization chamber detectors for measuring incident and transmitted beam intensities. A third ionization chamber was also used to detect the beam through a reference Re foil for energy calibration and

alignment purposes. A plug flow reactor cell with a quartz capillary tube (i.d./o.d. 0.9/1.0 mm) was used for in situ XAS measurements. The catalysts were pretreated at 500 °C in flowing 10% O₂/He and cooled to the reaction temperature of interest (70 or 150 °C) in He. A flowing 1% propylene (C₃[≡])/He mixture was used to activate the catalysts and perform olefin metathesis. Data processing and analysis were performed using Athena and Artemis software.¹¹

2.5. In Situ Diffuse Reflectance Infrared-Fourier Transform Spectroscopy (DRIFTS) during Propylene Adsorption/Desorption. The in situ DRIFT spectra were collected with a Thermo Nicolet 8700 FT-IR spectrometer equipped with a Harrick Praying Mantis attachment (Model DRA-2) for diffuse reflectance spectroscopy. Spectra were taken using a MCT detector with a resolution of 4 cm⁻¹ and an accumulation of 72 scans. Approximately 5–25 mg of each catalyst in powder form was loaded into the in situ environmental cell (Harrick, HVC-DR2). The collection of the initial background was performed by first optimizing the beam path and IR absorption signal using the height of the full Harrick sample cup and then removing the Harrick cell and placing a reflective mirror in the laser path. A spectrum was collected using the reflective mirror and was used as the background spectrum throughout the experiment.

The catalysts were initially dehydrated at 500 °C in flowing 10% O₂/Ar and cooled down in Ar to 30 °C. The catalysts were subsequently exposed to flowing 1% propylene (C₃[≡])/He for 45 min at 30 mL/min and finally flushed with Ar for 45 min to remove any residual physically adsorbed species before collecting the spectra. The in situ DRIFTS difference spectra were obtained by subtracting the spectrum of the dehydrated catalyst from that obtained after reaction with both collected at the same temperature. For the temperature-programmed experiments, the catalyst was initially dehydrated as indicated above, exposed to the reactive flow of 1% C₃[≡]/He (30 mL/min) at 30 °C to adsorb propylene, and flushed with Ar (30 mL/min) for another 45 min and the temperature was then increased at 10 °C/min with spectra collected every 30 °C. For the C₄[≡] adsorption/C₂⁼ titration studies, the catalyst was initially exposed to flowing 1% C₄[≡] (*trans*-2-butene)/Ar (30 mL/min) for 60 min at 30 °C followed by titration with flowing 1% C₂⁼/Ar (30 mL/min) at 30 °C for 30 min.

2.6. Temperature-Programmed Surface Reaction (TPSR) Spectroscopy. The temperature-programmed surface reaction experiments were performed using an Altamira Instruments (AMI-200) system. The outlet gases were connected to an online Dymaxicon Dycor mass spectrometer (DME200MS) and a TCD detector for analysis. Typically, ~100–300 mg of catalyst was loaded into the U-tube reactor. Blank tests with known concentrations of olefins were run for the mass spectrometer (MS) calibration before the experiments. The signals for the mass spectra were also normalized with catalyst weight for comparison. The following MS *m/z* values were used for detection of the reactants and products: propylene (*m/z* 42), ethylene (*m/z* 27), 2-butene (*m/z* 56), acetaldehyde (*m/z* 43), formaldehyde (*m/z* 30), carbon dioxide (*m/z* 44), acetone (*m/z* 58), O₂ (*m/z* 32), methane (*m/z* 16), and water (*m/z* 18). The MS cracking patterns were carefully determined with blank runs using the calibration gases and used to correct for the background MS signals. Cracking of propylene gives rise to *m/z* 43, and the propylene cracking contributions to CH₃CHO (*m/z* 43) were subtracted from the final MS signals. Cracking of 2-butene gives rise to *m/z* 27, 28,

30, and 41 values. Unless otherwise noted, the catalysts were dehydrated in 10% O₂/Ar at 500 °C (30 mL/min) for 30 min and cooled in flowing Ar (30 mL/min) to the reaction temperature.

2.6.1. TPSR in Flowing C₃=/Ar or C₄=/Ar. The same pretreatment and cooling steps as in the above experiments were utilized. After the pretreatment and cooling steps, the catalyst was allowed to interact with flowing C₃= for ~30 min at room temperature. A separate experiment was also performed wherein the catalyst was immediately heated at 10 °C/min to 500 °C in flowing 1% C₃=/Ar.

2.6.2. O₂ Temperature Programmed Oxidation (TPO) after Adsorption and Desorption of C₃=. Procedures similar to those in the Raman experiments were employed. Propylene was adsorbed on the catalyst at 30 °C from flowing 1% C₃=/Ar for 60 min, followed by flushing with Ar for another 60 min and increasing the temperature in flowing Ar to 200 °C to desorb any remaining physically adsorbed species. After the temperature was lowered to 30 °C in flowing Ar, the TPO experiment was performed by introducing a flow of 2% O₂/Ar, increasing the catalyst temperature to 500 °C at 10 °C/min, and monitoring the oxidation products with the online MS.

2.6.3. Adsorption of C₃D₆ and Titration with C₃H₆. After the aforementioned pretreatment steps, the supported 15.6% ReO_x/Al₂O₃ catalyst was treated with deuterated propylene (C₃D₆, 99% atom D, CDN Isotopes) at 30 °C. The surface intermediates formed were immediately titrated with flowing H–C₃= at the same temperature for 30 min, and the titration was continued during TPSR by heating at a rate of 10 °C/min to 500 °C.

3. RESULTS

3.1. In Situ Raman Spectroscopy during Propylene Adsorption/Desorption. The in situ Raman spectra of the supported 9.4% ReO_x/Al₂O₃ catalyst before and during C₃= adsorption/desorption are shown in Figure 1.

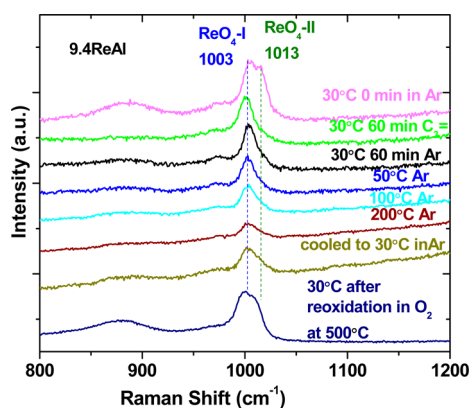


Figure 1. In situ Raman spectra of the supported 9.4% ReO_x/Al₂O₃ catalyst before, during, and after propylene adsorption/reaction/desorption. Spectra were normalized using the 1013 cm⁻¹ Raman band.

Prior to propylene exposure, the Raman spectrum of the dehydrated catalyst exhibits two bands at ~1003 and ~1013 cm⁻¹ that have been shown to originate from two distinct isolated dioxo surface ReO₄ sites on the Al₂O₃ support.¹⁰ The Raman bands labeled ReO₄-I and ReO₄-II correspond to surface ReO₄ species anchored at basic (μ₁-Al_{IV} and -Al_{VI}) and

acidic (μ₂- and μ₃-Al_{VI}) surface hydroxyl sites of the Al₂O₃ support, respectively (the Roman subscript refers to the number of oxygen atoms surrounding the Al cation).^{12,13} Adsorption of propylene on the catalyst preferentially decreases the intensity of the surface ReO₄-II sites, indicating selective adsorption of C₃= on these rhenia sites. Flushing the catalyst with Ar for 60 min does not restore the initial surface ReO₄-II sites, indicating the irreversibility of the propylene–rhenia interaction. Heating the catalyst to 200 °C in flowing Ar in an attempt to react or desorb the organic surface intermediate(s), however, also does not restore the ReO₄-II Raman band at ~1013 cm⁻¹, suggesting either retention of coordinated olefinic surface intermediates or removal of oxygen from the surface ReO₄-II species. The Re=O oxo bonds of the surface ReO₄-II species could only be regenerated by exposure to flowing 10% O₂/Ar at 500 °C for 30 min. The modest decrease in the intensity of the Raman band from the surface ReO₄-I sites is due to darkening of the catalyst from propylene adsorption (related to C₃= adsorption on the surface ReO₄= sites) and possibly partial reduction of the surface rhenia sites that possess a darker color. The presence of surface hydrocarbon intermediates after the propylene adsorption/desorption cycle is confirmed by formation of CO₂, CO, and H₂O during TPO as shown in Figure S1 in the Supporting Information. Olefin products were not detected during TPO. The Raman band for the surface ReO₄-II sites is only restored upon heating the catalyst in O₂/Ar, which combusts the surface hydrocarbon intermediates and fully oxidizes the surface rhenia.

3.2. Propylene Adsorption/Metathesis and TPSR Spectroscopy. Exposure of the supported 15.6% ReO_x/Al₂O₃ catalyst to flowing C₃=/Ar at room temperature exhibits an induction period of several minutes for formation of C₂= and C₄=, indicating that the metathesis reaction is taking place as shown in Figure 2. A minor amount of CO₂ (*m/z* 44) is produced, but its weak signal may just be residual noise. Neither acetone (*m/z* 58) nor alcohols (methanol, ethanol, and propanol) were detected as reaction products during the activation period. Water (H₂O) and O₂ initially appear and are related to displacement of a small amount of residual adsorbed moisture and O₂ by the stronger adsorption of propylene on the catalyst. Small amounts of acetaldehyde (CH₃CHO) (*m/z* 43) and formaldehyde (HCHO) (*m/z* 30) are also produced (their signals have been corrected for propylene's and 2-butene's MS cracking contributions to *m/z* 43 and 30, respectively). Formation of CH₃CHO is also observed during CH₃CH=CHCH₃ adsorption, where *m/z* 43 is not a 2-butene cracking product, confirming the formation of CH₃CHO as a reaction product (see Figure S2 in the Supporting Information). In contrast, HCHO (*m/z* 30) is not observed from 2-butene adsorption, since surface C₁ fragments are not present in the H₃CCH=CHCH₃ molecule (see Figure S2), further suggesting that HCHO is a real product from CH₃CH=CH₂ adsorption. Interestingly, the ratio of CH₃CHO/HCHO formed is ~4–5 during propylene adsorption, reflecting the greater propensity for formation of CH₃CHO than HCHO during activation.

Subsequent temperature programming of the catalyst in flowing 1% C₃=/Ar, shown in Figure 3, continues to form C₂= and C₄=.

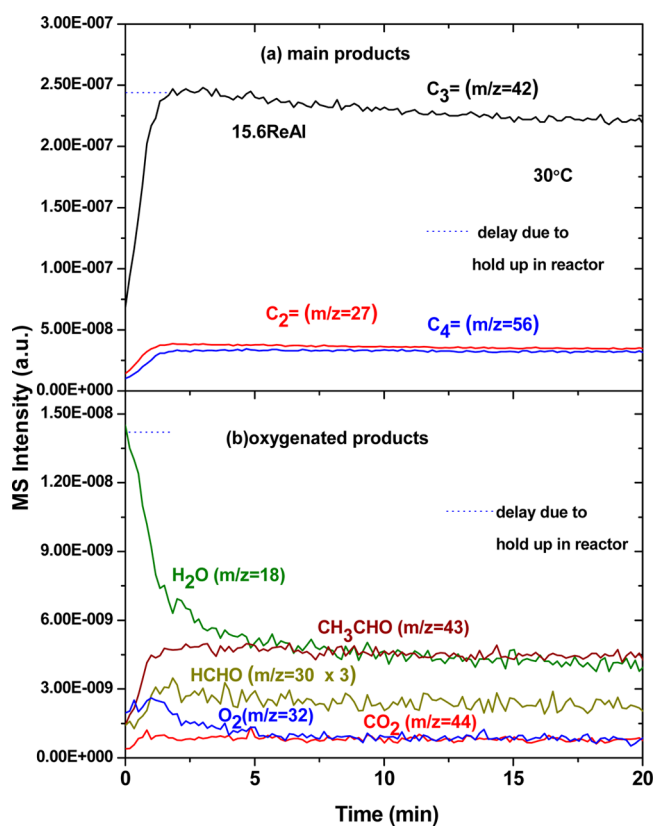


Figure 2. Time-resolved evolution of products during activation of supported 15.6% $\text{ReO}_x/\text{Al}_2\text{O}_3$ with $\text{C}_3=$ at 30 °C: (a) main olefin products; (b) oxygenated products. The acetaldehyde (m/z 43) and formaldehyde (m/z 30) signals were background-corrected for cracking of $\text{CH}_2=\text{CHCH}_3$ in the MS.

~3.5 during TPSR, reflecting the preferential formation of CH_3CHO over HCHO . These oxidation reactions take place with oxygen from the surface ReO_x sites and thus cause partial reduction of the surface rhenia sites on alumina. These aldehydes are reaction products at high temperatures, since the concentration of olefins, especially propylene, is significantly diminished above 300 °C and olefin cracking in the MS cannot contribute to these m/z signals.

3.3. In Situ XAS (XANES/EXAFS) during $\text{C}_3=$ Adsorption/Metathesis. The oxidation state of the surface rhenia sites on alumina during exposure to propylene was monitored with in situ XANES at 70 and 150 °C, and the spectra for the supported 15.6% $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalyst are presented in Figure 4. The strong XANES pre-edge feature (12533 eV) reflects the ReO_4 coordination of the initial dehydrated surface Re^{7+} species.¹⁰ The intensity of the XANES pre-edge is slightly less than that for the reference trioxo(triphenylsilyloxy) compound, indicating that less than three $\text{Re}=\text{O}$ bonds are present for the initial surface rhenia site.¹⁰ The XANES pre-edge is barely perturbed by self-metathesis of propylene at 70 °C. Unfortunately, it is difficult to distinguish with XANES between $\text{Re}=\text{O}$ and $\text{Re}=\text{C}$ bonds during metathesis, since rhenia would be present as Re^{7+} in both structures. The similar bond distances for $\text{Mo}=\text{O}$ (1.7 Å) and $\text{Mo}=\text{C}$ (1.8 Å) were predicted by DFT calculations for propylene metathesis by supported $\text{MoO}_x/\text{Al}_2\text{O}_3$ catalysts.¹⁴ At 150 °C, the XANES pre-edge may be slightly decreased by the self-metathesis of propylene that may reflect the presence of a minor amount of reduced surface rhenia sites.

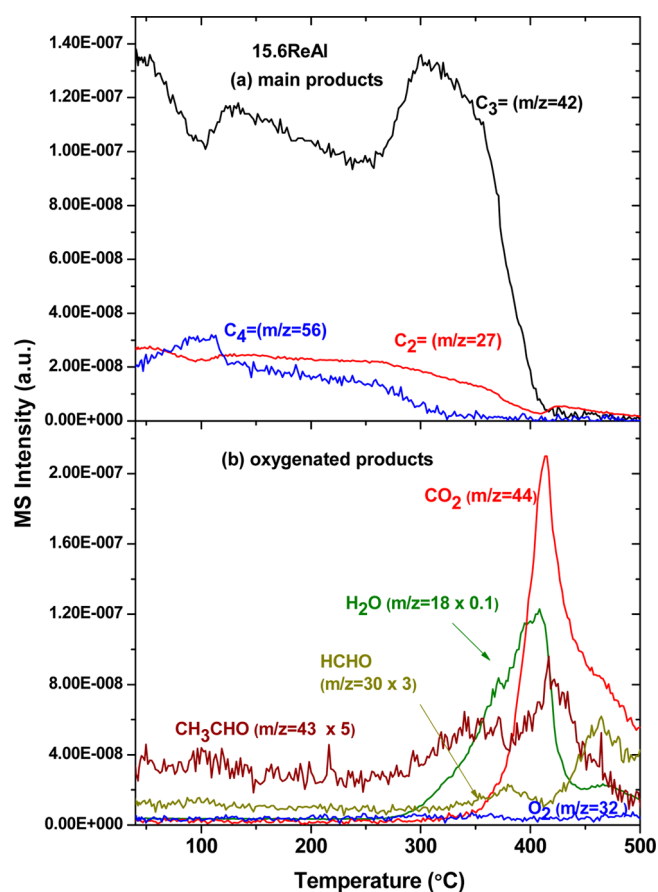


Figure 3. Products formed during $\text{C}_3=$ /Ar-TPSR from 15.6% $\text{ReO}_4/\text{Al}_2\text{O}_3$: (a) olefins; (b) oxygenates.

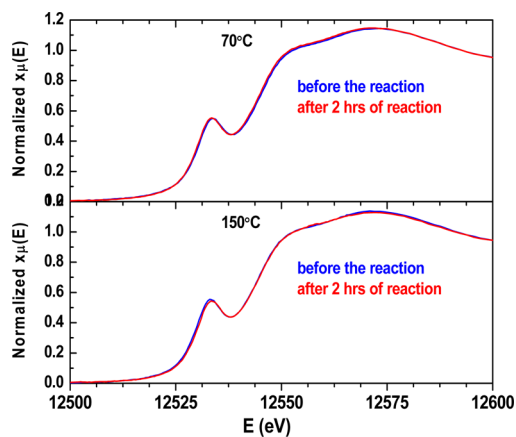


Figure 4. In situ Re L_1 -edge XANES spectra of the supported 15.6% $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalyst before (blue) and during $\text{C}_3=$ metathesis (red) at 70 °C (top) and 150 °C (bottom).

The corresponding in situ EXAFS spectra for the dehydrated catalyst before and during propylene metathesis at 70 and 150 °C are presented in Figure 5. Before exposure to propylene, the EXAFS peak at 1.1 Å (uncorrected for the photoelectron phase shift) corresponds to the terminal $\text{Re}=\text{O}$ bonds of the surface rhenia sites¹⁰ and the absence of $\text{Re}-\text{Re}$ features at 3–4 Å reflects the isolated nature of the initial surface ReO_4 sites. At 70 °C, the EXAFS spectrum is not perturbed by the propylene metathesis reaction presumably from conversion of $\text{Re}=\text{O}$ bonds to $\text{Re}=\text{C}$ bonds. At 150 °C, however, the intensity of

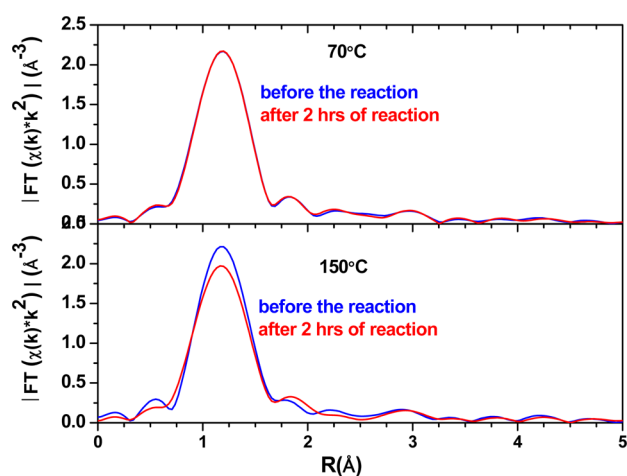


Figure 5. Magnitudes of Fourier-transformed k^2 -weighted in situ Re L_1 -edge EXAFS spectra in non-phase-corrected R space for the dehydrated supported 15.6% $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalyst before (blue) and during propylene metathesis (red) at 70 °C (top) and 150 °C (bottom).

the EXAFS $\text{Re}=\text{O}$ peak is decreased during the reaction. Such changes in EXAFS intensity may be caused by either (a) the reduction in the coordination number of $\text{Re}=\text{O}$ bonds, (b) increased disorder in their lengths, or (c) both such effects. When two models corresponding to the effects (a) and (b) were constructed to fit the experimental data, the qualities of the fit (reduced chi squared) were obtained to be comparable. Hence, EXAFS analysis cannot discriminate between these models, but it can estimate the maximum reduction in the CN under assumption that no changes in bond length disorder occurred. The result of such an estimate, reported in S3, is that on average the loss of a maximum of $\sim 10\%$ of $\text{Re}=\text{O}$ bonds may have occurred for each Re atom during propylene self-metathesis at 150 °C. The absence of $\text{Re}-\text{Re}$ features at 3–4 Å during propylene metathesis reflects that the surface rhenia sites remain isolated during the propylene metathesis reaction.

3.4. In Situ UV–Vis during Propylene Adsorption/Metathesis. Additional insights about the oxidation states of surface ReO_x during olefin metathesis is provided by in situ UV–vis spectroscopy. The UV–vis spectra of the reduced Re^{6+} , Re^{5+} , and Re^{4+} reference compounds exhibit bands from d–d transitions and are presented in Figure S4 in the Supporting Information. The ReO_3 reference consists of Re^{6+} sites that give rise to a sharp band at ~ 540 nm. The iododioxobis-(triphenylphosphine)rhenium(5+) dioxo reference exhibits bands at 260, 300–353, and 560 nm while the mono-oxo trichlorooxobis-(triphenylphosphine)rhenium(5+) reference contains bands at 260, 300–353, and 445 nm. The difference in the location of the 445 and 560 nm bands between these two Re^{5+} reference compounds is most likely related to their different $\text{Re}=\text{O}$ oxo bonds (dioxo vs mono-oxo). The ReO_2 reference compound possesses Re^{4+} sites and only yields a very broad band at ~ 400 nm and does not give rise to distinct UV–vis d–d transition bands.

The in situ UV–vis spectrum of the initial dehydrated supported 15.6% $\text{ReO}_4/\text{Al}_2\text{O}_3$ catalyst in flowing He is shown in Figure 6a and does not possess any d–d transition bands in the 300–800 nm region from reduced surface rhenia sites, reflecting the presence of only Re^{7+} sites for this catalyst with a strong ligand-to-metal charge transfer (LMCT) band at 240 nm. The in situ UV–vis spectra of the supported 15.6% $\text{ReO}_x/$

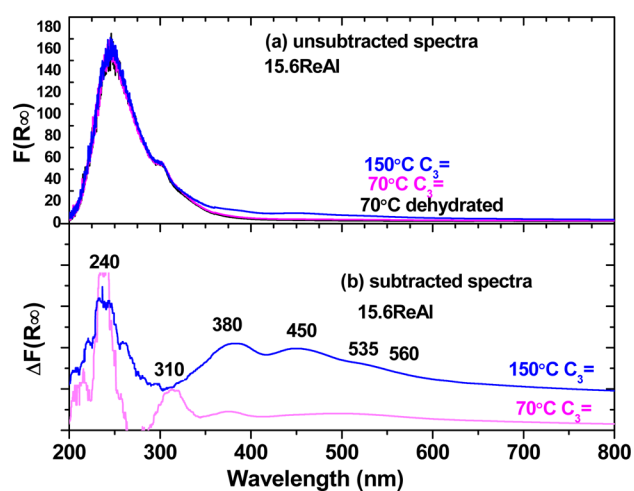


Figure 6. (a) In situ UV–vis spectra of the supported 15.6% $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalyst before reaction in flowing He (70 °C) and during $\text{C}_3=$ metathesis at 70 and 150 °C. (b) In situ UV–vis difference spectra obtained by subtraction of the spectrum in flowing He at 70 °C prior to propylene metathesis (bottom).

Al_2O_3 catalyst in flowing He and propylene at 70 and 150 °C are shown in Figure 6a. Weak d–d transitions from reduced surface rhenia species appear after exposure to propylene in the 300–800 nm region. In order to enhance the typically weak d–d transition bands from the reduced rhenia sites, the spectrum of the dehydrated catalyst was subtracted from the spectra during propylene metathesis, as shown as Figure 6b. The UV–vis d–d bands in the difference spectra increase with temperature, reflecting the greater number of reduced surface rhenia sites at high temperatures during propylene metathesis. The observation of reduced surface rhenia sites is a consequence of the lower concentration of surface reaction intermediates at higher temperatures, which results in a greater population of reduced surface Re^{5+} species (recall that rhenia coordination with olefins leads to oxidation of Re^{5+} to Re^{7+}). This is supported by the in situ UV–vis spectra, which demonstrate that desorption of surface intermediates at 200 °C in flowing He enhances the intensity of the d–d transitions (see Figure S5 in the Supporting Information). Increasing the partial pressure of propylene further increases the concentration of the reduced surface rhenia species on alumina (see Figure S6 in the Supporting Information).

The in situ UV–vis spectra at 70 and 150 °C in the flowing propylene environment closely match those of the reduced mono-oxo Re^{5+} (353 and 450 nm), dioxo Re^{5+} (560 nm), and possibly some Re^{6+} (540 nm) reference compounds. The in situ UV–vis bands (380, 450, and 560 nm) closely match the Re^{5+} reference compounds (see Figures S3 and S6 in the Supporting Information) and those reported for Re^{5+} organometallic complexes.^{15,16} Similar UV–vis bands in the 330–530 nm region are observed for a variety of dioxorhenium(5+) complexes¹⁵ and monodentate imidorhenium(5+) complexes.¹⁶ This suggests that the reduced surface rhenia species are present as Re^{5+} and some Re^{6+} sites on the Al_2O_3 support under the propylene metathesis reaction conditions with the concentration of the Re^{5+} being dominant. This is also in agreement with high-field high-frequency (HFHF) EPR measurements that confirm the presence of some paramagnetic Re^{6+} and the absence of EPR-active paramagnetic Re^{4+} sites.¹⁷

Unfortunately, surface Re^{5+} sites are EPR silent, since they are not paramagnetic.

3.5. In Situ IR Spectroscopy during Propylene Adsorption/Metathesis. The in situ IR spectra of propylene adsorption suggest that an adsorbed propylene π complex is the dominant surface species, which complicates detection of surface reaction intermediates. The IR spectra for the gas-phase olefins are presented in Figure S7 in the Supporting Information for comparison and are dominated by bands at $\sim 2800\text{--}3200\text{ cm}^{-1}$ from C–H vibrations.^{18–20} The in situ IR spectra after propylene adsorption at 25 °C on the Re-free Al_2O_3 support and 15.6% $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalyst are presented in Figure 7. For the alumina support exposed to flowing $\text{C}_3^=/\text{Ar}$,

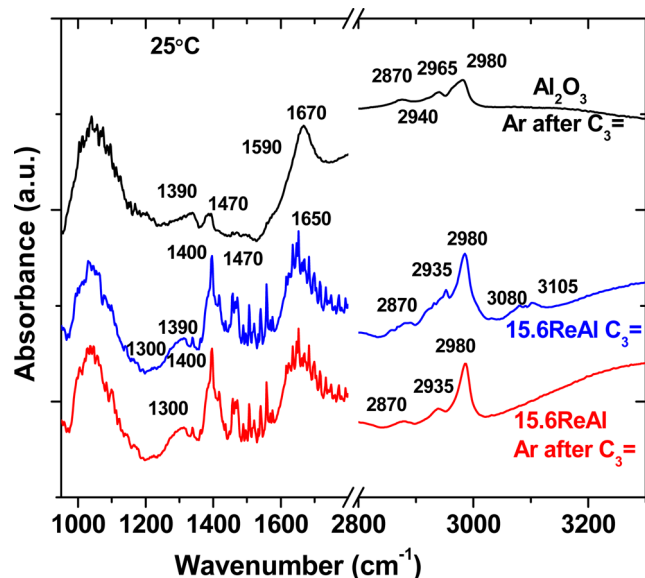


Figure 7. In situ difference IR spectra of the 15.6% $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalyst and pure Al_2O_3 support under various conditions at 25 °C. IR bands were not present in the 1800–2800 cm^{-1} range.

the IR bands are characteristic of surface propylene complexes ($\delta_s(\text{CH}_3)$ (1390 cm^{-1}), $\nu(\text{C}=\text{C})$ (1590 (shoulder) and 1670 cm^{-1}), $\nu_s(\text{CH}_2)$ (2870 cm^{-1}), $\nu_{\text{as}}(\text{CH}_2)$ (2940 cm^{-1}), and $\nu_{\text{as}}(\text{CH}_3)$ (2965 and 2980 cm^{-1})) but lack the characteristic $=\text{C}\text{--}\text{H}$ stretching bands above 3000 cm^{-1} . The 1670 cm^{-1} $\nu(\text{C}=\text{C})$ band is similar to that of gas-phase propylene (i.e., weakly bound), while the very weak 1590 cm^{-1} shoulder could indicate a trace of surface propylene allyl complex. For the supported 15.6% $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalyst in flowing $\text{C}_3^=/\text{Ar}$, IR bands are present from both gas-phase propylene (2920, 2935, 2950, 3080, and 3105 cm^{-1}) and an adsorbed species at $\delta(=\text{CH})$ (1300 cm^{-1}), $\delta_s(\text{CH}_3)$ (1390 cm^{-1}), $\delta_s(\text{CH}_2)$ of vinyl group ($-\text{CH}=\text{CH}_2$) (1400 and 1415 cm^{-1}), $\delta_{\text{as}}(\text{CH}_3)$ (1450 cm^{-1}), $\delta_s(\text{CH}_2)$ (1470 cm^{-1}), $\nu(\text{C}=\text{C})$ (1650 cm^{-1}), $\nu_s(\text{CH}_2)$ (2870 cm^{-1}), $\nu_{\text{as}}(\text{CH}_2)$ (2940 cm^{-1}), and $\nu_{\text{as}}(\text{CH}_3)$ (2980 cm^{-1}).^{19,20} When the catalyst is flushed with Ar, the bands at 3080 and 3105 cm^{-1} disappear, indicating that they are from gas-phase or weakly adsorbed propylene. The IR bands are generally in agreement with an adsorbed propylene π complex (vs weakly bound propylene and allyl for Al_2O_3) except for the appearance of a 1400 cm^{-1} vinyl group band and the absence of $=\text{C}\text{--}\text{H}$ stretches above 3000 cm^{-1} .²⁰ The adsorption of propylene on the Al_2O_3 support sites further complicates analysis of the IR spectra from the supported $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalysts.

The thermal stability of the surface intermediates on the supported 15.6% $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalyst resulting from propylene adsorption at room temperature was monitored in flowing Ar with TP-IR spectroscopy, and the spectra are presented in Figure 8. The spectrum at 30 °C under flowing propylene

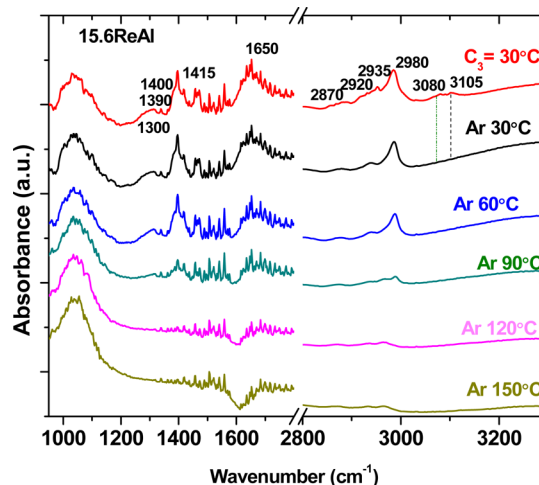


Figure 8. Temperature-programmed in situ difference IR spectra of the 15.6% $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalyst in flowing Ar after $\text{C}_3^=$ adsorption at 30 °C.

exhibits bands from gas-phase propylene and an adsorbed propylene π complex (see above for band assignments).^{18–20} All bands related to the surface propylene π complex decrease in intensity with temperature and disappear by 120 °C. Some minor bands at 2870, 2925, and 2960 cm^{-1} remain at 150 °C and may indicate the presence of a minor adsorbed surface complex.

3.6. Chemically Probing the Surface Intermediates Present during Propylene Metathesis. The nature of the surface intermediates present during propylene adsorption/metathesis was chemically probed by initially adsorbing C_3D_6 ($\text{D}\text{--}\text{C}_3^=$) at room temperature for 30 min and then immediately titrating the resulting D-containing surface intermediates with flowing C_3H_6 ($\text{H}\text{--}\text{C}_3^=$). The initial adsorption of C_3D_6 at 30 °C produces C_2D_4 and $2\text{--}\text{C}_4\text{D}_8$, indicating that olefin metathesis is taking place as shown in Figure 9. When the propylene gas flow is switched from $\text{D}\text{--}\text{C}_3^=$ to $\text{H}\text{--}\text{C}_3^=$, the MS signals for $\text{D}\text{--}\text{C}_3^=$, $\text{D}\text{--}\text{C}_2^=$ and $\text{D}\text{--}\text{C}_4^=$ simultaneously plummet, reflecting the strong dependence of formation of the deuterated reaction products on the propylene partial pressure of $\text{D}\text{--}\text{C}_3^=$. After the switch from $\text{D}\text{--}\text{C}_3^=$ to $\text{H}\text{--}\text{C}_3^=$ (see Figure 10), the isotopomers $\text{CD}_3\text{CD}=\text{CH}_2$, $\text{CH}_3\text{CH}=\text{CD}_2$, and $\text{CD}_2=\text{CH}_2$ are initially formed and their MS signals peak within ~ 2 min, reflecting the presence of residual surface $=\text{CD}_2$ and $=\text{CDCH}_3$ intermediates. The simultaneous evolution profiles of these three isotopomers indicate that these olefin products are being formed with the same kinetics. The MS intensity of H-containing C_2H_4 and $2\text{--}\text{C}_4\text{H}_8$ reaction products also increases as the $\text{CH}_2=\text{CHCH}_3$ partial pressure increases during the isotope switch, reflecting their dependence on the $\text{H}\text{--}\text{C}_3^=$ partial pressure. The absence of the $\text{D}_3\text{CCD}=\text{CHCH}_3$ isotopomer product indicates that the reaction pathways to make the propylene ($\text{CH}_2=\text{CDCH}_3$ and $\text{CH}_3\text{CH}=\text{CD}_2$) and ethylene ($\text{H}_2\text{C}=\text{CD}_2$) isotopomers are more facile (further supported by the absence of $\text{D}\text{--}\text{C}_4^=$ formation at elevated temperatures).

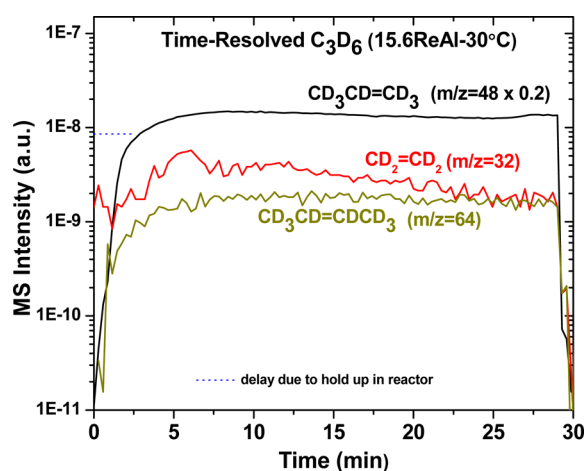


Figure 9. Products formed during C_3D_6 metathesis by supported 15.6% ReO_x/Al_2O_3 in flowing 1% C_3D_6/Ar at 30 °C.

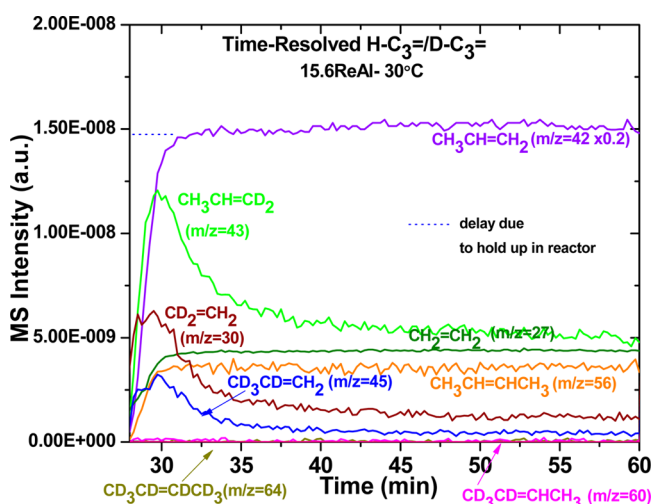


Figure 10. Time-resolved metathesis products during C_3H_6 titration of adsorbed C_3D_6 (30 min) at 30 °C on supported 15.6% ReO_x/Al_2O_3 catalyst.

The ratio of $=CD_2/=CDCD_3$ products is ~ 7 , revealing that surface $Re=CD_2$ intermediates are the most abundant reaction intermediates during propylene metathesis. Surprisingly, only $\sim 16\%$ of the D-containing surface intermediates were titrated at 30 °C by C_3H_6 and $\sim 84\%$ of the D-containing products were formed at elevated temperatures (>30 °C) during TPSR. This indicates that most of the surface olefin intermediates are strongly bound to the catalyst and are difficult to titrate at 30 °C.

4. DISCUSSION

4.1. Nature of Activated Surface ReO_x Sites on Al_2O_3 .

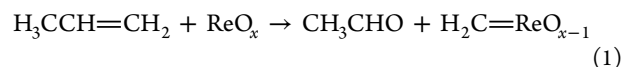
The initially oxidized surface ReO_4 sites on Al_2O_3 consist of isolated surface rhenia sites (absence of $Re-Re$ features at 3–4 Å in EXAFS (see Figure 5) and $Re-O-Re$ vibrations in Raman¹⁰). Two distinct surface dioxo ($O=$)₂ ReO_2 sites, however, are present and are anchored at basic and acidic surface hydroxyl sites of alumina (Figure 1).¹⁰ Only the surface ReO_4 sites anchored at acidic alumina surface hydroxyls are activated by olefins, as shown by in situ Raman spectroscopy revealing the selective interaction of propylene with the $Re=O$ bond of this site (Figure 1). At low temperatures (70 °C), the

XANES/EXAFS spectral features are not perturbed (see Figures 4 and 5), which may reflect the similar characteristics of $Re=O$ and $Re=C$ bonds.¹⁴ In situ UV–vis shows that some reduced rhenia sites are formed during propylene self-metathesis at mild temperatures.

At high temperatures (150 °C), the surface rhenia sites are perturbed by the propylene self-metathesis reaction conditions. The in situ EXAFS suggests a $\sim 10\%$ decrease in the $Re=O$ character (Figure 5). The presence of reduced surface Re^{5+} and some Re^{6+} sites during propylene metathesis are confirmed by the in situ UV–vis spectra (Figure 6). The greater concentration of reduced surface rhenia species at 150 °C is most probably related to the lower concentration of surface intermediates at high temperatures, since the surface intermediates oxidize the reduced rhenia sites back to Re^{7+} . The activated rhenia sites are coordinatively unsaturated and readily bond to carbene intermediates such as $=CH_2$ and $=CHCH_3$. The number of reduced surface rhenia sites is directly related to partial pressure of olefins (Figure S6 in the Supporting Information). The in situ EXAFS also reveals that the surface ReO_x sites remain isolated during propylene self-metathesis at elevated temperatures (Figure 5).

4.2. Surface Intermediates. It was not possible to identify the propylene self-metathesis surface reaction intermediates with IR spectroscopy, since the IR spectra were dominated by the vibrations of adsorbed propylene π complexes on both surface ReO_x and alumina support sites and gas-phase propylene (during metathesis). The propylene isotopic switch ($D-C_3= \rightarrow H-C_3=$) clearly showed that metathesis products with $=CD_2$ and $=CDCD_3$ fragments formed, implicating the presence of surface $Re=CD_2$ and $Re=CDCD_3$ reaction intermediates.

4.3. Activation Mechanism. Activation of the surface ReO_x sites on alumina at room temperature yields oxygenated (CH_3CHO and $HCHO$) products, reflecting the removal of some oxygen from the surface ReO_x sites during the catalyst activation period (pseudo-Wittig mechanism).^{21,22} The greater formation of CH_3CHO in comparison to that of $HCHO$ suggests that the $=CHCH_3$ fragment is more prone to oxidation than the $=CH_2$ fragment during activation (see Figure 2). The isotopic $D-C_3 \rightarrow D-C_3=$ switch study confirms that a much higher concentration of the surface $=CD_2$ in comparison to that of surface $=CDCD_3$ intermediates remains on the activated surface (Figure 10). This suggests that the $=CHCH_3$ fragment of propylene is initially mostly involved in removal of an oxygen atom from the surface ReO_x site and the $=CH_2$ fragment of propylene is the most abundant reactive intermediate (mari) that is left behind to coordinate with the unsaturated surface ReO_x site, as shown by the reaction step



This reaction step is irreversible since the initial fully oxidized surface ReO_x sites cannot be obtained by trying to desorb or react the adsorbed intermediates at elevated temperatures (Figure 1). The initial fully oxidized surface ReO_x sites can only be formed by combusting the surface intermediates and reoxidizing the partially reduced surface rhenia site (Figure 1 and Figure S1 in the Supporting Information).

At higher temperatures ($T > 300$ °C), the removal of oxygen from the surface rhenia sites becomes more aggressive, reflected by the formation of combustion products (CO_2 and H_2O), as

well as CH₃CHO and HCHO, that causes deeper reduction of the surface rhenia sites. The absence of olefin metathesis at such elevated temperatures indicates that there is a preferred oxidation state and structure for activated surface rhenia sites on alumina on exposure to olefins at mild temperatures. Consequently, over-reduction of the surface rhenia sites creates surface rhenia sites that are not active for olefin metathesis.

5. CONCLUSIONS

For the first time, in situ spectroscopic techniques were applied to directly monitor the dynamic changes taking place during activation of supported ReO_x/Al₂O₃ catalysts during propylene self-metathesis. Two distinct fully oxidized dioxo surface (O=)₂ReO₂ sites are present on the alumina support, and only the surface ReO₄ anchored at acidic alumina sites become activated by olefins. Propylene activation of the surface ReO₄ site on the alumina support proceeds via extraction of an oxygen atom from the surface rhenia site and formation of aldehydes, primarily CH₃CHO (pseudo-Wittig mechanism). Activation primarily creates surface Re⁵⁺ and a minor amount of surface Re⁶⁺ sites (the latter may be due to an unselective reaction pathway). Both surface Re=CH₂ and Re=CHCH₃ species are formed on the activated rhenia sites, as demonstrated by titration with gas-phase propylene, with the surface Re=CH₂ being the most abundant reactive intermediate. The surface Re=carbenes oxidize the reduced surface rhenia sites back to Re⁷⁺. The initial catalyst can only be regenerated by an oxidation treatment at elevated temperatures that combusts the surface hydrocarbon intermediates and fully oxidizes the surface rhenia sites back to the initial Re⁷⁺ oxidation state.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01944.

EXAFS analysis and additional TPSR, XAS, UV–vis, and IR results (Figures S1–S9) (PDF)

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Notes

The authors declare no competing financial interest.

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