Tuning the Number of Active Sites and Turnover Frequencies by Surface Modification of Supported ReO$_4$/(SiO$_2$–Al$_2$O$_3$) Catalysts for Olefin Metathesis

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**ABSTRACT:** A series of supported ReO$_4$ catalysts were synthesized by incipient-wetness impregnation of perrenic acid onto one component (Al$_2$O$_3$ and SiO$_2$) and surface-modified mixed-oxide supports (SiO$_2$/Al$_2$O$_3$, Al$_2$O$_3$/SiO$_2$, and ZSM-5 (Si/Al = 15)), characterized with *in situ* molecular spectroscopy (Raman, DRIFTS, UV–vis, and XAS), and chemically probed (ammonia chemisorption, C$_2$H$_4$/C$_4$H$_8$-titration, C$_3$H$_6$-TPSR, and steady-state propylene self-metathesis). The initial dehydrated surface rhenia species were coordinated to the oxide supports as isolated Re$^7$O$_4$ sites. For the Al-containing supports, dioxo surface (O═O)Re(−O)$_2$ sites appear to be the preferred coordination. The number of activated surface ReO$_4$ sites during metathesis is determined by the oxide support ligands (3% ReO$_4$/ZSM-5 > 3% ReO$_4$/5% AlO$_x$/SiO$_2$ > 3% ReO$_4$/5% SiO$_2$/Al$_2$O$_3$ > 3% ReO$_4$/Al$_2$O$_3$ ≈ 3% ReO$_4$/SiO$_2$). The specific activity (TOF) is also controlled by the oxide support ligands (3% ReO$_4$/Al$_2$O$_3$ > 3% ReO$_4$/5% SiO$_2$/Al$_2$O$_3$ ≫ 3% ReO$_4$/ZSM-5 ≈ 3% ReO$_4$/5% AlO$_x$/SiO$_2$ ≫ 3% ReO$_4$/SiO$_2$). The overall propylene metathesis activity (N × TOF), however, is dominated by the number of activated sites (N). Consequently, the enhanced overall activity of surface ReO$_4$ supported on SiO$_2$–Al$_2$O$_3$ mixed-oxide supports is related to the greater number of activated surface ReO$_4$ sites. The overall propylene metathesis activity was not related to the local surface ReO$_4$ molecular structure or the strength of the Bronsted acid sites, since the same rhenia structures appeared to be present on all of the active catalysts and the strengths of the Bronsted acid sites were comparable for all of the active catalysts, respectively.

**KEYWORDS:** metathesis, propylene, Raman, DRIFTS, UV–vis, XAS, TPSR, active sites

1. INTRODUCTION

The olefin metathesis reaction has become an indispensable reaction to help meet the global shortage of propylene for the past few decades. This reversible reaction allows cleavage and rearrangement of C=–C double bonds in ethylene and 2-butene (cross-metathesis) to produce two propylene molecules.\textsuperscript{11}–\textsuperscript{13} Industrial heterogeneous olefin metathesis catalysts consist of transition-metal oxides (Re, Mo, W) dispersed on an Al$_2$O$_3$, Al$_2$O$_3$–SiO$_2$, or SiO$_2$ support.\textsuperscript{14}–\textsuperscript{16} Supported ReO$_4$ catalysts have received much interest in the catalysis research community because they are the most active and selective metathesis catalysts that are able to operate at room temperature.\textsuperscript{1}–\textsuperscript{7} The choice of the oxide support significantly influences the olefin metathesis activity of supported ReO$_4$ catalysts. Among oxide supports, only the surface ReO$_4$ sites on Al-containing supports (Al$_2$O$_3$ and Al$_2$O$_3$–SiO$_2$) possess a high number of activated surface rhenia sites for olefin metathesis at room temperature.\textsuperscript{8}–\textsuperscript{11} Even for the most effective Al$_2$O$_3$ support, not all of rhenia anchoring sites lead to activation of rhenia for olefin metathesis. The effectiveness of the anchoring surface hydroxyls on Al$_2$O$_3$ for activating the surface rhenia sites varies in the order Al$_2$–OH > Al–OH–Al > Al–OH,\textsuperscript{11} which tracks with the acidity of the anchoring surface hydroxyls. Many studies have proposed that surface acidity plays an important role in the olefin metathesis reaction.\textsuperscript{12}–\textsuperscript{14} For example, the Al$_2$O$_3$–SiO$_2$ mixed-oxide supports are known to introduce surface Lewis and Bronsted acid sites and are also highly effective oxide supports for activating surface ReO$_4$ sites for olefin metathesis.\textsuperscript{15}–\textsuperscript{18} These studies, however, have not provided supporting data for the conclusions that the surface acidity plays an important role in olefin metathesis and have not even investigated the nature of the surface AlO$_x$, SiO$_x$, and ReO$_x$ sites present in these mixed-oxide supports.
The focus of this study is to determine the origin of enhanced performance of the surface ReO_x sites on Al_2O_3−SiO_2 mixed-oxide supports. This will be achieved by examining the following aspects of supported ReO_x/(Al_2O_3−SiO_2) catalysts: (i) the nature of the surface ReO_x sites on Al_2O_3, SiO_2, and Al_2O_3−SiO_2 mixed-oxide supports (model AlO_x/SiO_2, model SiO_2/Al_2O_3, and ZSM-5 (Si/Al = 15)) under dehydrated conditions, (ii) the number of activated surface ReO_x sites, and (iii) the surface chemistry of the oxide supports (coordination of surface SiO_2 and AlO_x sites, surface hydroxyl chemistry, and surface acid chemistry (Lewis and Bronsted acid sites)). The origin of the enhanced propylene metathesis activity on Al_2O_3−SiO_2 mixed-oxide-supported ReO_x catalysts is the consequence of surface ReO_x sites anchoring on the more acidic surface hydroxyls, which facilitates activation of the surface rhena sites by propene.

2. EXPERIMENTAL DETAILS

2.1. Catalyst Synthesis. The supported ReO_x catalysts were prepared by incipient-wetness impregnation (IWI) of aqueous perhenic acid (75−80%, HReO_4, Alfa Aesar) on various supports (Al_2O_3, SiO_2, 5% AlO_x/SiO_2, 5% SiO_2/Al_2O_3, ZSM-5). The Al_2O_3 support has a surface area of ∼200 m^2/g (Sasol, Puralox), the SiO_2 support has a surface area of ∼350 m^2/g (Cabot, Cab-O-Sil, EH-5), and the ZSM-5 support has a surface area of ∼400 m^2/g (Zeolyst, CBV3024E, Si/Al = 15). The surface-modified 5% AlO_x/SiO_2 (SiAl) support was prepared by IWI of the SiO_2 support with an isobutanol solution of aluminum sec-butoxide (C_4H_9AlO_3, 95%, Alfa Aesar) inside a glovebox (Vacuum Atmospheres, Omni-Lab Vac 101965). The surface-modified 5% SiO_2/Al_2O_3 (SiAl) support was prepared by IWI of the Al_2O_3 support with a toluene solution of tetraethyl orthosilicate (99%, Sigma-Aldrich) inside a glovebox. Both mixed-oxide supports were initially dried overnight in a glovebox and then calcined in air at 500 °C for 4 h. The Al_2O_3 support was calcined at 500 °C for 16 h and SiO_2/ZSM-5 at 500 °C for 4 h, respectively, before impregnation of perhenic acid. After impregnation of aqueous perhenic acid at room temperature, the catalysts were initially dried overnight under ambient conditions, further dried at 120 °C for 2 h in flowing air, and finally calcined by ramping the temperature at a rate of 1 °C/min to 500 °C and held at 500 °C for 4 h. The final synthesized catalysts are 3% ReO_x/Al_2O_3 (3ReAl), 3% ReO_x/5% AlO_x/SiO_2 (3ReSiAl), 3% ReO_x/5% SiO_2/Al_2O_3 (3ReSiAl), 3% ReO_x/SiO_2 (3ReSi), and 3% ReO_x/ZSM-5 (3ReZSM).

2.2. In Situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). The in situ DRIFTS spectra were collected with a FT-IR spectrometer (Thermo Scientific Nicolet 8700) attached with an in situ reaction cell (Harrick Praying Mantis HVC-DRA2 with a CaF_2 window). The resolution was set as 4 cm^-1 with 98 scans for each spectrum on a mercury−cadmium−telluride (MCT) detector. Brooks mass flow controllers (Model 5850E) controlled the gas flow rates. The in situ reaction cell was sealed with a Viton O-ring and was loaded with ∼20 mg of loose catalyst powder. The following procedure was used for collecting the in situ DRIFTS: catalysts were initially dehydrated at 400 °C for 1 h with 10% O_2/90% Ar (Air Gas, UHP, 30 mL/min) to desorb moisture. The catalysts were subsequently cooled to 120 °C with 10% O_2/90% Ar and flushed with UHP Ar (Air Gas, UHP, 30 mL/min) for 30 min. The in situ FT-IR spectra of the dehydrated catalysts were collected at 120 °C with 10% O_2/90% Ar. The in situ DRIFTS spectra were also collected after NH_3 adsorption and desorption as a function of temperature. The initial dehydration procedure was the same as above. The catalysts were then exposed to flowing NH_3/He (Airgas, 2000 ppm, 30 mL/min) at 120 °C for 30 min and subsequently flushed with He (Air Gas, UHP, 30 mL/min) for 30 min. The NH_3 desorption was performed by temperature-programming the catalyst in He at a rate of 10 °C/min to 400 °C. The in situ DRIFTS spectra were collected after ammonia adsorption and during the temperature programming.

2.3. In Situ Raman Spectroscopy. The in situ Raman spectra of the supported ReO_x catalysts were collected with a Horiba-Jobin Yvon LabRam HR (high-resolution) spectrometer. Although the Raman spectrometer is equipped with three lasers (532, 442, and 325 nm), only the 442 nm excitation was employed in the present study because this excitation minimized the sample fluorescence. The laser was focused through a confocal microscope with a 50× objective (Olympus BX-30-LWD). Before spectra were collected, the Raman spectrometer was calibrated with a silicon standard possessing a reference peak at 520.7 cm^-1. The spectral resolution of the spectrometer is ∼1 cm^-1, and the spectra were collected with 3 scans (20 s/scan) and a 200 μm hole. The procedure for collecting the in situ Raman spectra is similar to the above procedure given for collecting the in situ DRIFTS spectra.

2.4. In Situ UV−vis Diffuse Reflectance Spectroscopy (DRS). The in situ UV−vis spectra were collected with a UV−vis−NIR spectrophotometer (Agilent Cary Series 5000). Around 20 mg of catalyst powder was loaded into the Harrick Praying Mantis in situ reaction cell described above. The UV−vis spectra were collected in the 200−800 nm range with an acquisition time of ∼0.6 s per spectrum. The MgO white standard was used for the background absorbance correction. The UV−vis edge energy (E_g) of each catalyst was calculated by the intercept of the straight line for the low-energy rise of a plot of [F(R)hν]^2 versus the incident photon energy (hν). The detailed procedure for calculating the UV−vis E_g value can be found in ref 19. The procedure for collecting the in situ UV−vis spectra is similar to the above procedure given for collecting the in situ DRIFTS spectra.

2.5. In Situ X-ray Absorption Spectroscopy (XAS). The in situ Re L_1-edge X-ray absorption spectroscopy measurements were performed at beamlines X19A and X18B in the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory (BNL). Ionization chamber detectors for measuring incident and transmitted beam intensities were used to collect the XAS spectra. A third ionization chamber was used to detect the beam through a reference Re foil for energy calibration and alignment. The catalysts were loaded into a plug flow reactor with a quartz capillary tube (ID/OD = 0.8/1.0 mm). The catalysts were dehydrated at 500 °C with 10% O_2/90% He (Air Gas, UHP, 30 mL/min) for 1 h and then cooled to 70 °C and flushed with flowing ultrahigh-purity He. Afterward, the catalysts were exposed to flowing 1% C_3H_6/He (Praxair, purity 99%, 30 mL/min). The XAS spectra of the catalysts were collected in situ, under the dehydrated and propylene self-metathesis conditions. The reference compounds, consisting of trioxy(tri phenylsiloxyl)rhodium(VII) (Sigma-Aldrich, 99.9%), ReO_3 (Alfa Aesar, 99%), and Re_2O_3 (Alfa Aesar, 99%), were measured under ambient conditions after diluting with boron nitride (Sigma-Aldrich, 99%) to yield a 5−10% Re concentration. Athena and Artemis software was employed for data processing and analysis.20
2.6. C$_3$H$_6$-Temperature-Programmed Surface Reactions (TPSR).

The TPSR experiments were performed on an Altamira instruments system (AMI-200). Approximately 0.2 g of the catalyst was loaded into a quartz U-tube and held in place by quartz wool from below and above. The catalysts were initially dehydrated at 400 °C with 10% O$_2$/90% Ar (Air Gas, UHP, 30 mL/min) for 1 h and then cooled to room temperature (30 °C). After flushing with UHP Ar (Air Gas, UHP, 30 mL/min) for 30 min, a flow of 1% C$_3$H$_6$/99% Ar (Praxair, purity 99%, 30 mL/min) was introduced into the reactor and held at 30 °C for several minutes to stabilize the mass spectrometer (MS) signal. The reactor was then temperature programmed at 10 °C/min up to 400 °C. The exiting gases from the reactor were analyzed with an online Dycor ProLine Process MS instrument. The mass channels monitored were m/z 18 (H$_2$O), m/z 27 (C$_2$H$_6$), m/z 42 (C$_3$H$_6$), m/z 44 (CO$_2$), and m/z 56 (C$_4$H$_8$). The MS signals were corrected for cracking contributions from different components, and the olefin signals were calibrated.

2.7. C$_2$H$_4$/C$_4$H$_8$ Titration.

The catalysts were initially dehydrated as described above for the in situ DRIFTS procedures. The catalyst was subsequently cooled to 30 °C with 10% O$_2$/90% Ar and flushed with UHP Ar (Air Gas, 30 mL/min) for 30 min. The catalyst was then exposed to flowing 1% C$_4$H$_8$/99% Ar (Praxair, purity 99%, 30 mL/min) for 30 min to chemisorb 2-butene. Afterward, the gas flow was immediately switched to 1% C$_2$H$_4$/99% Ar (Praxair, Purity 99%, 30 mL/min) for 30 min to titrate the adsorbed surface intermediates from 2-butene chemisorption. The same mass spectrometer m/z values were monitored as for the C$_3$H$_6$-TPSR measurements given above. The amount of C$_3$H$_6$ produced during the C$_2$H$_4$/C$_4$H$_8$ titration was used to quantify the number of surface Re–CHCH$_3$ intermediates with the assumption that the activated surface rhenia site only coordinates one surface —CHCH$_3$ intermediate. For 3ReZSM5, the number of activated ReO$_x$ sites was roughly estimated by the number of 2-butene molecules produced in the first 2-butene production peak during C$_3$H$_6$-TPSR. The estimated fraction of activated ReO$_x$ sites was corrected by the 2-butene peak area ratio for 3ReZSM5:3Re5AlSi:3Re5SiAl. The MS was calibrated for the propylene signal.

2.8. Steady-State C$_3$H$_6$ Metathesis.

The steady-state propylene self-metathesis catalytic reactions were performed in a fixed-bed reactor. Both the inlet and outlet of the gas tubes were heated to 200 °C to avoid the condensation of the propylene reactant and products (C$_2$H$_4$, C$_4$H$_8$, CO$_2$, CO, and H$_2$O) on the exit lines. Approximately 0.2 g of the catalyst was loaded in the downflow glass tube and held in place with quartz wool below and above. A clamshell furnace around the glass tube was used to control the reactor temperature. The catalysts were initially dehydrated at 500 °C for 30 min with 10% O$_2$/90% Ar (Air Gas, UHP, 100 mL/min), and then the reactor was cooled to 70 °C with 10% O$_2$/90% Ar and flushed with UHP Ar (Air Gas, UHP, 30 mL/min). A flow rate of 1% C$_3$H$_6$/99% Ar (Praxair, Purity 99%, 100 mL/min) was used for the reactant mixture. The propylene metathesis conversion was collected after 60 min of reaction, and a steady-state conversion was achieved. The exiting gases from the reactor were analyzed with an online gas chromatograph (Agilent GC 6890) equipped with a GS-Alumina (Agilent 1153552) column connected to a flame ionization detector (Agilent Model G1531). The GC was calibrated for all of the reaction products. The conversion of propylene was normalized by the flow rate and catalyst weight to yield the catalytic activity (mmol/(g · h)). The turnover frequency (TOF) values were calculated by normalizing the steady-state activity by the number of activated ReO$_x$ sites determined from the C$_3$H$_6$/C$_4$H$_8$ titration and from C$_3$H$_6$-TPSR for 3ReZSM5.
3. RESULTS

3.1. In Situ DRIFTS of Surface Hydroxyl Anchoring Sites. The in situ DRIFTS spectra of the surface hydroxyls of the Re-free oxide supports and supported ReO\textsubscript{x} catalysts are presented in Figure 1, and the corresponding difference spectra are shown in Figure S1. In general, the surface hydroxyls that vibrate at higher wavenumbers are more basic and the surface hydroxyls vibrating at lower wavenumbers are more acidic.\textsuperscript{21,22} The 3Al\textsubscript{2}O\textsubscript{3} support exhibits multiple surface hydroxyls: terminal Al–OH (\text{O}_4\text{Al}–\text{OH}, \text{O}_3\text{Al}–\text{OH}, and \text{O}_2\text{Al}–\text{OH}), bridged \text{O}_4\text{Al}–\text{OH}–\text{Al}_2\text{O}_3, and tricoordinated (\text{O}_3\text{Al})_3–\text{OH} with their wavenumbers increasing, respectively.\textsuperscript{23,24} The IR spectrum of the supported 3ReAl catalyst reveals that ReO\textsubscript{2} anchors on all of the surface hydroxyls, while predominantly anchoring at the basic Al–OH surface hydroxyls (3787, 3768, 3728 cm\textsuperscript{-1}) of the Al\textsubscript{2}O\textsubscript{3} support. The model supported SiAl mixed-oxide support reveals that Si\textsubscript{O} selectively anchors at basic Al–OH (3787, 3768, 3728 cm\textsuperscript{-1}) and neutral Al–OH–Al (3694 cm\textsuperscript{-1}) surface hydroxyls. Both terminal Si–OH and Al–(OH)\textsuperscript{−}–Si Bronsted acid sites are present for SiAl, as was previously shown.\textsuperscript{15} The addition of rhena to the SiAl mixed-oxide support (3ReSiAl) shows that the ReO\textsubscript{2} predominantly anchors at residual basic Al–OH (3743 cm\textsuperscript{-1}), acidic Al–OH (3670 cm\textsuperscript{-1}) and the more acidic Al–(OH)\textsuperscript{−}–Si surface hydroxyls (broad negative band at \textasciitilde3580 cm\textsuperscript{-1}; Figure S1). The SiO\textsubscript{2} support possesses terminal Si–OH (3742 cm\textsuperscript{-1}) and geminal Si–OH–Si–OH (a broad band from 3727 to 3755 cm\textsuperscript{-1}) surface hydroxyls with surface metal oxides generally anchoring to the terminal Si–OH surface hydroxyls, but the decrease in the intensity of the Si–OH vibration was too small to be noticeable in Figure 1.\textsuperscript{15} On the model SiAlSi support, the surface hydroxyls that were consumed and created could not be detected with DRIFTS because of the very strong Si–OH vibration that dominates the spectrum. The corresponding Raman spectra, however, reveal that Al\textsubscript{x}O\textsubscript{y} anchors at the Si–OH surface hydroxyls (see section 3.2.). The ZSM-5 (Si/Al = 15) mixed oxide possesses multiple surface hydroxyls, and the order of decreasing acidity is Brønsted acid sites O4Al–OH, O3Al–OH, O2Al–OH, and terminal Al–OH (3787 cm\textsuperscript{-1}). The ZSM-5 (Si/Al = 15) mixed oxide possesses multiple surface hydroxyls, and the order of decreasing acidity is Brønsted acid sites O4Al–OH, O3Al–OH, O2Al–OH, and terminal Al–OH (3787 cm\textsuperscript{-1}). The ZSM-5 (Si/Al = 15) mixed oxide possesses multiple surface hydroxyls, and the order of decreasing acidity is Brønsted acid sites O4Al–OH, O3Al–OH, O2Al–OH, and terminal Al–OH (3787 cm\textsuperscript{-1}). The ZSM-5 (Si/Al = 15) mixed oxide possesses multiple surface hydroxyls, and the order of decreasing acidity is Brønsted acid sites O4Al–OH, O3Al–OH, O2Al–OH, and terminal Al–OH (3787 cm\textsuperscript{-1}). The ZSM-5 (Si/Al = 15) mixed oxide possesses multiple surface hydroxyls, and the order of decreasing acidity is Brønsted acid sites O4Al–OH, O3Al–OH, O2Al–OH, and terminal Al–OH (3787 cm\textsuperscript{-1}). The ZSM-5 (Si/Al = 15) mixed oxide possesses multiple surface hydroxyls, and the order of decreasing acidity is Brønsted acid sites O4Al–OH, O3Al–OH, O2Al–OH, and terminal Al–OH (3787 cm\textsuperscript{-1}). The ZSM-5 (Si/Al = 15) mixed oxide possesses multiple surface hydroxyls, and the order of decreasing acidity is Brønsted acid sites O4Al–OH, O3Al–OH, O2Al–OH, and terminal Al–OH (3787 cm\textsuperscript{-1}).

Table 1. In Situ UV–vis Edge Energies (eV) of Supported ReO\textsubscript{x} Catalysts under Dehydrated Conditions at 120 °C

<table>
<thead>
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<th>catalyst</th>
<th>3ReAl</th>
<th>3ReSiAl</th>
<th>3ReAlSi</th>
<th>3ReSi</th>
<th>3ReZSM5</th>
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<tr>
<td>UV–vis edge energy (dehydrated)</td>
<td>4.4</td>
<td>4.6</td>
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The in situ UV–vis edge (E\textsubscript{g}) values of the supported ReO\textsubscript{x} catalysts under dehydrated conditions are presented in Table 1. Reference oligomeric rhenia structures exhibit a low edge energy of \textasciitilde2.8 eV, and isolated rhenia structures have a high edge energy of \textasciitilde4.0 eV.\textsuperscript{11,19} All of the supported ReO\textsubscript{x} catalysts possess a high UV–vis E\textsubscript{g} value of \textasciitilde4.4–4.6 eV characteristic of isolated surface ReO\textsubscript{3} sites. Additionally, the oxidation state of rhenium is Re(+7), as indicated by the single ligand to metal charge transfer (LMCT) band at \textasciitilde240–245 nm and the absence of bands in the d–d region (350–800 nm) from reduced rhenia sites, as shown in Figure 2.

The in situ X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra at the Re L\textsubscript{1}-edge of the supported ReO\textsubscript{x} catalysts under dehydrated conditions are presented in Figure 3. For rhenia sites with ReO\textsubscript{3} coordination and inversion symmetry, the signal intensity in the 2s \rightarrow 5d transition region in XANES is suppressed (see XANES ReO\textsubscript{3} reference compounds in Figure S2) but is enhanced for ReO\textsubscript{4} coordination without an inversion symmetry.\textsuperscript{11,28,29} The oxidation state of rhenium is known to correlate with the adsorption edge energy.\textsuperscript{11,30} Consequently, the strong XANES pre-edge feature at 12536 eV demonstrates that the surface rhenia sites on all of the supported catalysts possess ReO\textsubscript{3} coordination and the high XANES edge position (maximum of the first derivative) of \textasciitilde12548 eV reveals the oxidation state to be Re(+7) (Figure S3). The pre-edge intensity for 3ReAl is slightly lower than those of the other catalysts, indicating a higher symmetry of the local Re environment. The k\textsuperscript{2}-weighted Re L\textsubscript{1}-edge EXAFS spectra show that there are no strong peaks at a high R distance of \textasciitilde2.5–4 Å (uncorrected for photoelectron phase shift), consistent with the isolated nature of the surface ReO\textsubscript{3} sites, which is, in turn, consistent with the conclusions made on the basis of the UV–vis edge energy measurements. The peaks at \textasciitilde1.2 Å correspond to a terminal Re=O bond that is shorter than the Re=O bond corresponding to a peak at \textasciitilde1.5 Å in ReO\textsubscript{3} reference compounds that do not possess terminal Re=O bonds (Figure S2).\textsuperscript{14} The similar Re=O peak position at \textasciitilde1.2 Å for all of the supported ReO\textsubscript{x} catalysts suggests that the Re=O bond lengths for all of the surface rhenia sites are similar. The lower intensity of the peak at 1.2 Å for the supported 3ReAl and 3ReSi catalysts indicates that these surface rhenia sites either have a lower Re=O bond character or are more disordered in comparison to the other supported rhenia catalysts. The slightly stronger intensity for 3ReSi at 2–
4 Å is a consequence of the relatively low signal to noise ratio in this catalyst data. The Re environments in all of the supported rhenia catalysts are minimally perturbed during self-metathesis of propylene at 70 °C, as indicated in Figure S4. Quantitative analysis yields the Re L1-edge EXAFS data of dehydrated catalysts. The k-range for FT was from 2 to 8 Å−1. Catalysts were dehydrated at 500 °C in flowing O2/Ar and cooled to 70 °C in flowing O2/Ar and the spectra collected at 70 °C in flowing Ar.

The in situ Raman spectra of supported ReOx catalysts and Re-free oxide supports under dehydrated conditions are presented in Figure 4 and Figure S7, respectively, and the absence of strong vibrations at 1002 cm−1 for the supported 3ReSi catalyst indicates that crystalline Re2O7 nanoparticles are not present as indicated in Figure S4. The Raman bands correspond to the vibration of dehydrated conditions at 120 °C (800–1200 cm−1). The Raman band for the ν(Re=O) stretch is sharpest for the supported 3ReSi catalyst, reflecting preferential anchoring of the rhenia only on the isolated Si−OH sites. The Raman band for the ν(Re=O) stretch at ~1011 cm−1 for the surface Al2O3 modified SiO2 support is much broader because of the presence of multiple anchoring sites (Si−OH, Al−OH, Al−OH−Al, and Al−(OH)−Si) on this mixed-oxide support. Additionally, the absence of the Si−OH Raman band indicates that alumina anchors at the Si−OH surface hydroxyls (see Figure S7), and the absence of Si−OH bonds for the supported 3ReSAlSi catalyst suggests that rhenia is also anchoring at the surface Al−OH surface hydroxyls. The Raman band for the ν(Re=O) stretch at ~1011 cm−1 of the supported 3ReZSM5 catalyst is broadest as a consequence of the presence of multiple anchoring sites (Al−OH−II from Al2O3 NPs, external silanols Si−OH, extraframework Al−OH, and Al−(OH)−Si) with preferential anchoring of rhenia at the Al−OH−II and Al−(OH)−Si surface hydroxyls. The main ν(Re=O) stretching modes at ~1011 cm−1 and a weak shoulder at ~1020 cm−1 for the supported 3ReZSM5 catalyst indicate that there are two possible surface rhenia sites on the ZSM-5 support. The Al2O3 support possesses multiple surface hydroxyls (Al−OH, Al−OH−Al, and Al1−OH), and rhenia predominantly anchors at the basic Al−OH surface hydroxyls, resulting in a ν(Re=O) stretch band at a low wavenumber of ~1002 cm−1 for the supported 3ReAl catalyst (~20% monolayer coverage). The surface SiO2 modified Al2O3 support possesses multiple anchoring sites (Al−OH, Al−OH−Al, Al1−OH, Si−OH, and Al−(OH)−Si) with preferentially anchoring at the basic Al−OH, acidic Al1−OH surface, and more acidic Al−(OH)−Si surface hydroxyls, resulting in a broader ν(Re=O) stretching band at ~1011 cm−1 for the supported 3ReSSiAl catalyst. Additionally, the position of the ν(Re=O) stretching is also dependent on the nature of the anchoring surface hydroxyl site indicating a slight distortion of the surface ReOx sites: 3ReZSM5 > 3ReSi ≈ 3ReSAlSi ≈ 3ReSSiAl > 3ReAl.

3.3. Surface Acid Sites Chemically Probed with NH3-IR. The in situ DRIFTS spectra of the oxide supports after NH3 adsorption are presented in Figure S8. With the exception of the SiO2 support, which does not contain any detectable surface acid sites, all of the other oxide supports exhibit the presence of surface Brunsted acid sites (δs(NH4+*) and δi(NH4+*) at ~1450–1490 and 1697–1740 cm−1, respectively) and surface Lewis acid sites (δs(NH4+*) and δi(NH4+*) at ~1245–1326 and 1623 cm−1, respectively).

Figure 3. (A) Re L1-edge XANES data of dehydrated catalysts. (B) Fourier transform (FT) magnitude of the k2-weighted Re L1-edge EXAFS data of dehydrated catalysts. The k-range for FT was from 2 to 8 Å−1. Catalysts were dehydrated at 500 °C in flowing O2/Ar and cooled to 70 °C in flowing O2/Ar and the spectra collected at 70 °C in flowing Ar.

Figure 4. In situ Raman spectra of supported ReOx catalysts under dehydrated conditions at 120 °C (800–1200 cm−1).
AlO₃ modification of the SiO₂ support introduces some Lewis and Bronsted acid sites, as indicated by the type of surface ammonia species. The Al₂O₃ support exhibits the presence of both surface NH₄⁺ species from Lewis acid sites and surface NH₄⁺⁺ species from Bronsted acid sites. The surface NH₄⁺ species must be associated with weak Bronsted acid sites, since the weaker base pyridine does not show the presence of any species must be associated with weak Brønsted acid sites, since the presence of any Bronsted acid sites.

Surface SiO₂ modification of the Al₂O₃ support decreases the number of surface NH₄⁺ species chemisorbed at Bronsted acid sites and minimally affects the number of surface NH₄⁺⁺ species chemisorbed at Lewis acid sites. The ZSM-5 support possesses both Lewis and Bronsted acid sites. The vibrational position reflects the strength of the acid sites. Although the δₓ(NH₄⁺⁺) and δₓ(NH₄⁺⁺⁺) vibrations are similar for Al, SSiAl, and SiAl, the strengths of the Lewis acid sites (δₓ(NH₄⁺⁺⁺)) follow the trend ZSM-5 > SiAl > SSiAl > Al ≫ Si, while the strengths of Bronsted acid sites (δₓ(NH₄⁺⁺⁺)) follow the trend ZSM-5 > SiAl ≈ SSiAl ≈ Al ≈ Si. The in situ DRIFTS spectra of supported ReOₓ catalysts after ammonia adsorption are presented in Figure 5.

The in situ DRIFTS spectra of supported ReOₓ catalysts after ammonia adsorption and evacuation at 120 °C (1100–1800 cm⁻¹).

![In situ DRIFTS spectra of supported ReOₓ catalysts after NH₃ adsorption and evacuation at 120 °C](image)

The in situ DRIFTS spectra of supported ReOₓ catalysts after NH₃ adsorption and evacuation at 120 °C (1100–1800 cm⁻¹).

![C₃–/C₄⁺TPSR spectra of the supported ReOₓ catalysts](image)

3.4. C₃H₆-TPSR Spectra. The TPSR spectra from flowing 1% C₃H₆/99% Ar during temperature programming of the catalyst bed from 30 to 400 °C are presented in Figure 6 and Figure S9. For the Re-free oxide supports, only the ZSM-5 support possesses activity during C₃H₆-TPSR, as presented in Figure S10. The ZSM-5 support exhibits a unique ability to readily adsorb propylene and convert propylene to ethylene, 2-butenes, and even benzene above 100 °C, which is related to its strong Bronsted acid sites present in the zeolite cages. The significant activity of the ZSM-5 support complicates determining the activity contribution of the surface rhenium sites on the ZSM-5 support. The supported 3ReSi and 3ReAl catalysts are essentially inactive for propylene self-metathesis in the temperature range of 30–400 °C. Surface SiO₂ modification of the Al₂O₃ support modestly increases the propylene self-metathesis activity for the supported 3ReSSiAl catalyst. Surface AlO₃ modification of the SiO₂ support, however, significantly increases the propylene self-metathesis activity for the supported 3ReSiAl catalyst. The supported 3ReZSM5 catalyst is the most active for propylene self-metathesis with 2-butenes production at ~153 and ~252 °C. The significant decrease in the C₃⁺ signal for the supported 3ReZSM5 catalyst during C₃⁻-TPSR is a consequence of the ability of the porous zeolite support to absorb significant amounts of propylene (see Figure S10). The C₄⁺-TPSR spectral findings indicate that surface modification of an oxide support by a second metal oxide has the potential to facilitate activation of the surface ReOₓ sites.

3.5. C₃⁻/C₄⁺ Titration of Surface Intermediates. The C₃⁻/C₄⁺ titration measurement was performed to quantify the number of surface Re=CHR intermediates formed by adsorption of 2-butene. For the Re-free SiO₂ and Al₂O₃ supports (SiAl, SiAl, and ZSM-5 were not examined), the C₃⁻/C₄⁺ titration did not yield C₃⁺, indicating the absence of catalytic sites for olefin metathesis on these oxide supports at 30 °C, as presented in Figure S11. The strong Bronsted acid sites inside the zeolite cage, however, are able to convert C₃⁻ to the C₅⁻ and C₄⁺ products. The time-resolved MS signals...
during the titration at 30 °C are presented in Figure 7. The reversibility of the olefin metathesis reaction allows for quantification of the surface reaction intermediates from both the forward and reverse reaction pathways, which is consistent with the concept of microscopic reversibility.\textsuperscript{1,13,34,35} The production of propylene from the $C_2^+/C_4^-$ titration indicates that the surface Re$=$CHCH$3$ intermediates titrated by $C_2^-$ occur in the first 5 min after switching from $C_2^+$ to $C_2^-$. The slight delay for the SiO$_2$-based catalysts (3Re5AlSi and 3ReSi) may be related to the much higher surface area of these supports relative to the Al$_2$O$_3$-based supports (3ReAl and 3ReSiAl). The quantity of propylene formed from the titration of $C_2^+/C_4^-$ at 30 °C for the 3ReZSM$5$ catalyst could not be directly determined, since propylene was not desorbed because of its complete sorption by the zeolite nanopores. The number of $C_2^-$ molecules formed, however, was roughly estimated from the number of 2-butenes molecules desorbed during $C_2$-TPSR below 200 °C (see Figure 6), and the fraction of activated sites was found to be $\sim 8.5\%$. The relative quantity of surface Re$=$CHCH$_3$ intermediates on the supported ReO$_x$ catalysts vary as 3ReZSM$5$ $\gg$ 3ReSi > 3ReSAlSi > 3ReAl $\approx$ 3ReSi. The fraction of surface ReO$_x$ sites that become activated during the $C_2^+/C_4^-$ titration is given in Table 2. The supported 3ReAl and 3ReSi catalysts possessed very few active sites. Surface modification of the oxide supports, however, increased the number of activated sites by $\sim 5\%$ for 3ReSAlSi, $\sim 22\%$ for 3ReSAlSi, and $\sim 28\%$ for 3ReZSM$5$.

### 3.6. Steady-State C$_2^+$ Metathesis Reaction

The steady-state catalytic activity of the supported ReO$_x$ catalysts for propylene self-metathesis is presented in Figure 8. The olefin metathesis activity of the supported ReO$_x$ catalysts at 70 °C follows the trend 3ReZSM$5$ $\gg$ 3ReSAlSi $\approx$ 3ReSi > 3ReAl $\gg$ 3ReSi (essentially inactive). Note that the ZSM-5 supported ReO$_x$ catalyst is not active for the olefin conversion reaction at 70 °C (see Figure 6). The propylene self-metathesis activity data reveal several trends: (i) anchoring rhenia on AlO$_x$ sites results in greater catalytic activity in comparison to anchoring rhenia on SiO$_2$ sites (3ReAl $\gg$ 3ReSAlSi and 3ReSi), (ii) anchoring of rhenia to surface SiO$_2$ modified Al$_2$O$_3$ results in higher catalytic activity (3ReSAlSi $> 3$ReAl), and (iii) the supported 3ReZSM$5$ exhibits a higher activity related to the presence of Al in framework and extraframework sites. The activity values were converted to TOF values from a knowledge of the number of activated sites (see Table 2), and the TOF values follow the trend 3ReAl $> 3$ReSAlSi $> 3$ReZSM$5$ $\approx$ 3ReSAlSi $> 3$ReSi, as indicated in Table 2. It appears that both the number of activated surface ReO$_x$ sites and the TOF values are changing with surface modification of the oxide supports.

### 4. DISCUSSION

#### 4.1. Anchoring Sites for Surface ReO$_x$

The surface hydroxyls on oxide supports serve as the anchoring sites for the dispersed surface ReO$_x$ sites,\textsuperscript{36,37} and the nature of the surface hydroxyls also varies with surface modification. The Al$_2$O$_3$ support contains basic Al$=$OH$ $ neutral Al$=$OH$ $Al$, and acidic Al$=$OH$ $ surface hydroxyls, with rhenia preferentially anchoring at basic Al$=$OH hydroxyls with minor amounts of neutral Al$=$OH$ $Al and acidic Al$=$OH$ $ surface hydroxyls for the low-loading rhenia catalyst.\textsuperscript{11} Surface modification of the Al$_2$O$_3$ support with anchoring of silica preferentially consumes the basic Al$=$OH and some neutral Al$=$OH$ $Al and acidic Al$=$OH$ $ surface hydroxyls and forms nonacidic Si$=$OH and Bronsted acid Al$=$ (OH)$^+$ Si sites (see Figure S1). This observation is in agreement with the characterization of the

![Figure 7](https://dx.doi.org/10.1021/acscatal.0c05279)

**Figure 7.** Time-resolved MS spectra of $C_7$H$4$ produced during the titration of surface Re$=$CHCH$3$ with $C_7$H$4$ at 30 °C for the supported ReO$_x$ catalysts.

![Figure 8](https://dx.doi.org/10.1021/acscatal.0c05279)

**Figure 8.** Steady-state catalytic activity of supported ReO$_x$ catalysts for propylene self-metathesis at 70 °C (1% $C_7$/$99\%$ Ar).

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**Table 2. Fractions of Activated Surface ReO$_x$ sites Calculated from $C_2^+/C_4^-$ Titration, Steady-State Activities, and TOF Values**

<table>
<thead>
<tr>
<th></th>
<th>3ReAl</th>
<th>3ReSAlSi</th>
<th>3ReSiAlSi</th>
<th>3ReSi</th>
<th>3ReZSM$5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>fraction of activated surface ReO$_x$ sites (%)</td>
<td>0.3</td>
<td>1.4</td>
<td>6.5</td>
<td>0.3</td>
<td>$\sim 8.5$</td>
</tr>
<tr>
<td>steady-state activity (mmol/g·h)</td>
<td>0.48</td>
<td>0.84</td>
<td>0.72</td>
<td>0.0</td>
<td>1.2</td>
</tr>
<tr>
<td>TOF (s$^{-1}$)</td>
<td>0.33</td>
<td>0.14</td>
<td>0.025</td>
<td>0.0</td>
<td>0.032</td>
</tr>
</tbody>
</table>
surface hydroxyls present on the amorphous SiO2−Al2O3 mixed oxide chemically probed with CO2, pyridine, and alkylamine.16,38 Similar conclusions were reached from in situ IR studies with CO and NH3 on surface SiO2 modified Al2O3.7,18 Anchoring of rhenia on the SSiAl support sequentially consumes the residual basic Al−OH, additional neutral Al−OH−Al, acidic Al−OH, and the newly formed Bronsted acid Al−(OH)−−Si surface hydroxyls. Consequently, the rhenia becomes anchored to more acidic Al-containing surface hydroxyls (Al−OH and Al−(OH)−−Si) after surface modification of Al2O3 with surface SiO2 because the less acidic Al-containing surface hydroxyl anchoring sites have been titrated by the surface SiO2 sites. The SiO2 support has terminal Si−OH and geminal Si−OH*−Si−OH, with the former being the preferred rhenia anchoring sites.19 Although the anchoring of alumina on the SiO2 support (SAiSi) surface hydroxyls could not be directly observed with in situ IR, previous in situ 1H and 27Al NMR and DFT calculations of the model SAiSi mixed oxide found that Al−OH−Al sites were formed with the surface hydroxyls consisting of nonacidic Si−OH, neutral Al−OH−Al, and Bronsted acid Al−(OH)−−Si.15,39 The Al2O3 was anchored on the SiO2 support by consumption of the Si−OH surface hydroxyls (Figure S7). The in situ IR spectra for 3ReSAiSi was dominated by the strong Si−OH vibration that prevented determining the anchoring of rhenia on the surface hydroxyls of SAiSi. It is most likely that rhenia anchors at the Bronsted acid Al−(OH)−−Si surface hydroxyls, since the Si−OH surface hydroxyls were consumed by the surface AlO overlayer. The ZSM-5 support used in the present investigation possessed surface hydroxyls from nonacidic external silanol Si−OH, basic extraframework Al−OH−II from Al2O3 nanoparticles, extraframework Al−OH−I with AlO4 coordination, and Bronsted acid Al−(OH)−−Si with AlO4/SiO4 coordination.26,27 Anchoring of rhenia on the ZSM-5 support was found to preferentially consume the basic extraframework Al−OH−II and Bronsted acid Al−(OH)−−Si. Wu et al. similarly concluded that rhenia preferentially anchored at Al−(OH)−−Si surface hydroxyls on ZSM-5 with minor consumption of Si−OH surface hydroxyls.40 The similarity in anchoring surface hydroxyls of 3ReSAiSi and 3ReZSM-5 indicates that the model 3ReSAiSi catalyst behaves similarly to the 3ReZSM5 catalyst without the presence of zeolitic cages. Note that Hensen et al. concluded from in situ IR with a CO chemical probe that the Al−(OH)−−Si Bronsted acid sites on amorphous SiO2−Al2O3 are weaker than the Al−(OH)−−Si Bronsted acid sites present in zeolites.16 The rhenia anchoring sites, therefore, depend on the nature of the surface hydroxyls that can be tuned by surface modification.

4.2. Initial Molecular Structures of Dehydrated Surface ReOx Sites. The surface ReOx sites on all of the oxide supports are isolated, as indicated by the high UV−vis F2 values and the absence of Re−Re bonds in the EXAFS at greater R distances (2−5 Å). The oxidation state of the surface ReOx sites is Re(+)7, as indicated by the LMCT band at ∼240−245 nm and the XANES edge position of ∼12548 eV.11,25,30,41 The surface rhenia sites are coordinated as ReO4/SiO4 coordination.26,27 Anchoring of rhenia on the ZSM-5 support used in the present study with CO, pyridine, and NH3 in situ IR studies with CO and NH3 on surface SiO2 modified Al2O3 indicates that the model 3Re5AlSi catalyst behaves similarly in anchoring surface hydroxyls of 3Re5AlSi and 3ReZSM5 catalysts. The anchoring of rhenia at the surface hydroxyls can also create Bronsted acid sites (for example, ReSi and ReAl), with the proton most likely present on the bridging Re−(OH)−− support bond. Such a protonated site is even more likely on oxide supports containing bridging Al−(OH)−−Si bonds. The surface ReOx sites for the supported 3ReSAiSi, 3ReSiAl, and 3ReZSM5 catalysts appear to be more ordered, as reflected by the more intense EXAFS Re=O peaks. While only one type of anchoring surface hydroxyl site on SiO2 (Si−OH) is involved in anchoring rhenia on SiO2, multiple types of anchoring surface hydroxyl sites are available for rhenia on Al2O3, and the mixed-oxide supports that result in broader Raman bands. The greatest number of activated surface rhenia sites are found for the SiO2−Al2O3 mixed-oxide supports (3ReZSM5, 3ReSiAl, and 3ReSAiSi). This trend is also found for activation of the supported rhenia catalysts during propylene self-metathesis (see Figure 6): 3ReSAiSi > 3ReSiAl > 3ReAl ≈ 3Re ≈ 0. A unique feature of SiO2−Al2O3 mixed-oxide supports is the presence of Al−(OH)−−Si surface hydroxyls for anchoring rhenia. The Al−(OH)−−Si Bronsted acid sites on ZSM5 are more acidic than the Al−(OH)−−Si Bronsted acid sites on SSiAl and SAiSi. This suggests that anchoring rhenia at acidic surface hydroxyls results in a greater number of activated surface rhenia sites. This follows the trend in activation of surface rhenia sites on Al2O3 where the number of activated sites increases with the acidity of the surface hydroxyls (basic Al−OH < neutral Al−OH−Al < more acidic Al−OH).11 The TOF value trend, however, varies in the order 3ReAl > 3ReSiAl > 3ReZSM5 > 3ReSAiSi > 3ReSi, indicating that anchoring of rhenia at Al−(OH)−−Si surface hydroxyls does not lead to highly active surface ReOx sites. The trends suggest that the most active surface ReOx sites form by coordination of rhenia to Al ligands and that the bonding of rhenia to Si ligands retards the specific activity (TOF). The enhanced activity of propylene self-metathesis by surface rhenia sites on SiO2−Al2O3 mixed-oxide supports is thus primarily related to the increase in number of activated ReOx sites and not enhancement of the TOF value. Anchoring of rhenia on the oxide supports tends to decrease the number of Lewis acid sites, mainly associated with oxygen vacancies, and generate Bronsted acid sites (e.g., 3ReSi). The Bronsted acid sites are associated with both the oxide support surface hydroxyls and the surface ReOx sites. The Lewis acid sites, which are mainly associated with the oxide supports at low rhenia loadings, cannot be used for correlations with olefin metathesis activity. A relationship between the number of activated rhenia sites and Bronsted acidity is not also found, since the strengths of the Bronsted acid sites are relatively constant for all of the supported ReOx catalysts (see Figure 5).
5. CONCLUSIONS

Surface modification of Al₂O₃ and SiO₂ supports with SiO₂ and AlO₃ respectively tunes the number of activated surface rhenia sites and their specific activity (TOF). Although the mixed-oxide supports increase the number of activated surface rhenia sites available for propylene metathesis, the specific activity (TOF) of the activated surface rhenia sites on the mixed-oxide supports is significantly lower for propylene metathesis. Consequently, the enhanced overall propylene metathesis activity (N×TOF) for supported Re/(SiO₂-Al₂O₃) catalysts is related to the greater number of activated surface ReO₃ sites and not increased TOF values. There does not appear to be a relationship between the propylene metathesis TOF and the local surface ReO₃ structure, because the same dioxo surface ReO₃ sites appear to be present on all Al-containing oxide supports. Anchoring of rhenia at Al-containing surface hydroxyls is critical for an enhanced propylene metathesis TOF (ReAl > ReSiAl ≈ ReZSM5 ≈ ReAlSi ≫ ReSi), which suggests that the oxide supports serve as ligands that control the propylene metathesis TOF for the surface ReO₃ active sites. There also does not appear to be a relationship between the propylene metathesis TOF and the Bronsted acid strength of the rhenia sites, since the Bronsted acid strengths are comparable for all catalysts active for propylene metathesis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acscatal.0c05279.

DRIFTS difference spectra, XANES/EXAFS spectra of Re references, Re L₁-edge position vs oxidation state, XANES/EXAFS spectra of catalysts after reaction, EXAFS fitting variables under dehydrated and reaction conditions, EXAFS fitting (k space and R space) under dehydrated conditions, EXAFS fitting (k space and R space) after reaction, Raman spectra of oxide supports, NH₃-IR spectra of oxide supports, C₃H₆ signal during space and C₃H₆-TPSR, C₅H₆-TPSR of ZSM-5, C₂H₄/C₄H₈ titration for oxide supports, and Lewis/Bronsted acidity strength (PDF).

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