Molecular Design of Supported MoO$_x$ Catalysts with Surface TaO$_x$ Promotion for Olefin Metathesis

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ABSTRACT: A series of supported 3% MoO$_x$ catalysts were synthesized by incipient-wetness impregnation of a 5−15% TaO$_x$ surface-modified γ-Al$_2$O$_3$ support. The catalysts were characterized by in situ spectroscopies (diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), Raman, UV−vis, X-ray absorption spectroscopy (XAS)) and multiple chemical probes (C$_2$H$_4$/C$_3$H$_6$TPSR, steady-state propylene metathesis, NH$_3$-IR adsorption). The supported tantalum oxide phase was present as surface TaO$_x$ species to occur at different surface hydroxyls. This shifted the anchoring of MoO$_x$ species from basic (Al-OH) to neutral (Al$_2$-OH) to more acidic (Al$_3$-OH) surface hydroxyls as well as perturbation of the remaining alumina surface hydroxyls by the surface TaO$_x$ sites. The TaO$_x$ surface-modified γ-Al$_2$O$_3$ support increased the number of activated surface MoO$_x$ sites (Ns) by ~6× and the turnover frequency (TOF) by ~10×, resulting in an increased activity of ~60×. It was found that the specific anchoring surface hydroxyls rather than the extent of oligomerization of the surface MoO$_x$ sites control the number of activated MoO$_x$ sites and TOF for propylene metathesis. No relationships between the nature of the surface Lewis/Wis Bronsted acid sites and Ns and TOF were found to be present.

KEYWORDS: metathesis, propylene, molybdate, Raman, DRIFTS, UV−vis, XAS

1. INTRODUCTION

Propylene is a critical chemical intermediate that is produced from the refinery, steam cracking, and on-purpose methods. The olefin metathesis reaction, as an on-purpose method for propylene production, is a reversible reaction that helps meet the global shortage of propylene. The cleavage and reformation of C=C double bonds in ethylene and 2-butene permit the production of two propylene molecules.~1−6 Industrial heterogeneous supported MoO$_x$/Al$_2$O$_3$ catalysts have been applied in the shell higher olefin process (SHOP) to produce linear higher olefins since 1977.~7 Although heterogeneous supported MoO$_x$ catalysts are easily prepared, there are multiple surface MoO$_x$ structures due to the nonuniform nature of the surfaces of oxide supports, which requires the use of advanced molecular-level characterization techniques to determine the catalytic active sites. For example, three distinct surface MoO$_x$ structures are present on the Al$_2$O$_3$ support (isolated di-oxo MoO$_x$ on basic Al-OH, oligomeric MoO$_x$/Al$_2$OH and acidic Al$_3$-OH, and crystalline MoO$_x$ nanoparticles).~6,7 The catalytic activity of supported MoO$_x$ catalysts is significantly influenced by the selection of the oxide support.~8−12 The SiO$_2$/Al$_2$O$_3$ mixed oxide support is a highly effective support for promoting olefin metathesis in comparison to the one component Al$_2$O$_3$ or SiO$_2$ support. Anchoring active sites at acidic surface hydroxyls of the mixed oxide support results in a greater number of activated sites.~13 This observation motivates the current investigation to examine the influence of other mixed oxide supports, such as supported MoO$_x$/TaO$_x$/Al$_2$O$_3$ catalysts, for olefin metathesis. The acidity of surface Bronsted sites is often proposed to be related to improved olefin metathesis activity on mixed oxide support.~9,14 For example, Hahn et al. examined surface MoO$_x$ sites on various oxide supports (SiO$_2$, Al$_2$O$_3$, SiO$_2$−Al$_2$O$_3$) with pyridine-IR adsorption and found that the ethylene/2-butene cross-metathesis activity increased with (i) increasing amounts
of Bronsted acid sites (ii) increasing oligomerization degree of the surface MoO₃ sites and (iii) decreasing amounts of Lewis acid sites. It was claimed that protonation of propene to surface Mo(+)isopropoxide was driven by Bronsted acidic Mo-OH during activation. Li et al. investigated MoO₃ sites on the HPO / γ-Al₂O₃ mixed oxide support with H NMR and proposed that the moderate Bronsted acidity for moderate MoO₃ loadings may contribute to the ethylene/2-butene cross-metathesis activity by involving into the initial MoO₃ site activation.

Supporting data are generally lacking and the nature of the MoO₃ sites and oxide support sites have not been well investigated. The absence of in situ investigation on well-defined model supported MoO₃ catalysts has inhibited the fundamental understanding of this important catalytic reaction. To design a highly active model promoted MoO₃/Al₂O₃ catalyst, the basic alumina hydroxyls need to be selectively capped with an acidic promoter that will allow MoO₃ to selectively anchor at the more acidic surface hydroxyls of the alumina support.

In the present study, a TaOₓ–MoO₃ promoter was used to surface modify the Al₂O₃ support for propylene self-metathesis to ethylene and 2-butene by supported MoO₃/Al₂O₃ catalysts. The surface TaOₓ promoter was selected since TaOₓ is not active for olefin metathesis and gives rise to weak Raman bands that will not overshadow the Raman bands of the surface MoO₃ sites. The following aspects will be examined: (i) the anchoring sites of MoO₃ on unpromoted and Ta-promoted Al₂O₃ support, (ii) the nature of surface MoO₃ sites under dehydrated and propylene metathesis reaction conditions, and (iii) the influence of surface Lewis and Bronsted acid sites upon the activity of the propylene metathesis reaction. The objective of the present study is to establish the structure–activity relationship for olefin metathesis by supported Ta-promoted MoO₃/Al₂O₃ catalysts. The origin of the improved propylene metathesis activity on Ta-promoted MoO₃/Al₂O₃ catalysts is the consequence of modifying the MoO₃ anchoring locations on the surface hydroxyls of Al₂O₃.

2. EXPERIMENTAL DETAILS

2.1. Catalyst Synthesis. The Al₂O₃ support (Sasol, Puralox, 200 m²/g) was initially calcined at 500 °C for 16 h in flowing air to remove any combustible impurities. The Al₂O₃ support was surface-modified by incipient-wetness impregnation (IWI) of an ethanol solution of tantualum ethoxide (Ta-(OC₂H₅)₅, Sigma-Aldrich, 99.98%) inside a molybdenum alkoxide (Ta-(OC₂H₅)₅, Sigma-Aldrich, 99.98%). The supported 3%MoO₃/Al₂O₃ catalysts were collected at 120 °C for 10 min and then flushed with Ar (Air Gas, UHP, 30 mL/min) for 30 min. The DRIFTS spectra of dehydrated catalysts were collected at 120 °C with 10% O₂/Ar (Air Gas, UHP, 30 mL/min) for 30 min. The dehydration procedure for NH₃/IRI spectra was the same as indicated above. The NH₃/He (Airgas, 2000 ppm, 30 mL/min) was flowing at 120 °C for 30 min and then flushed with He (Air Gas, UHP, 30 mL/min) for 30 min. The adsorbed N₂ was finally desorbed by ramping the temperature at 10 °C/min to 500 °C. The in situ DRIFTS spectra were collected during the NH₃ adsorption and temperature ramping. All of the DRIFTS spectra were normalized by the dehydration spectra of the oxide supports.

2.3. In Situ Raman Spectroscopy. The in situ Raman spectra were obtained by a Horiba Labram HR Evolution spectrometer equipped with 4 laser sources (633, 532, 442, and 325 nm). The 442 nm laser was used for collecting in situ Raman spectra to minimize the sample fluorescence. The laser was focused through a confocal microscope with an X10 objective (Olympus MPLN10x). The Raman spectra were calibrated by a silicon standard possessing a reference peak at 520.7 cm⁻¹. Catalysts were loaded into an in situ reaction cell (Harrick Scientific HVC-MRA-5) cup packed with quartz wool, which was temperature-controlled by a Harrick ATC Temperature Controller unit. The spectra were collected with a 100 μm hole and 3 scans (20 s/scan) by a CCD camera detector (Horiba Synapse BIDD scientific), resulting in a spectral resolution of 1 cm⁻¹. Pure TiO₂ (P-25, 1%) was physically mixed with catalysts to be used as the internal standard for normalization due to the absence of Raman peaks from the pure Al₂O₃ support. The gas flow rates were monitored with the same mass flow controllers as indicated above. The procedure for collecting in situ Raman spectra was as follows: the catalyst was dehydrated at 500 °C in flowing 10% O₂/Ar (Air Gas, UHP, 30 mL/min) for 1 h. The temperature was then cooled to 50 °C and flushed with Ar (Air Gas, UHP, 30 mL/min) for 30 min. Subsequently, the catalysts were exposed to 5% C₃H₆/Ar (Praxair, Purity 99%, 30 mL/min) at 50 °C for 1 h and finally flushed with Ar (Air Gas, UHP, 30 mL/min) for 30 min. Subsequently, the catalysts were exposed to 5% C₃H₆/Ar (Praxair, Purity 99%, 30 mL/min) at 30 °C for 1 h and finally flushed with Ar (Air Gas, UHP, 30 mL/min) for 30 min. The catalysts were then heated to 200 °C. The 5% C₃H₆/Ar was flowing again for 1 h and flushed with Ar at 200 °C. The in situ Raman spectra were collected after dehydrogenation and during propylene metathesis at 30 and 200 °C.

2.4. In Situ UV–Vis Diffuse Reflectance Spectroscopy (DRS). The in situ UV–Vis spectra of the supported MoOₓ catalysts were obtained with a UV–vis-NIR spectrophotometer (Agilent Cary 5000). Approximately, 20 mg of the catalyst powder was loaded into an in situ reaction cell described above. The collection of each UV–vis spectrum takes ~0.6 s in the 3227 https://doi.org/10.1021/acscatal.1c06000 ACS Catal. 2022, 12, 3226–3237.
200–800 nm range. A MgO white standard was used for the reference of background absorbance. The gas flow rates were monitored with the same mass flow controllers as indicated above. The edge energy (Eg) values calculated from the UV–vis spectra were determined by the intercept of the straight line for the low-energy rise of a plot of [F(R)/hν] versus the incident photon energy (hν). The procedure for collecting in situ UV–vis spectra was the same as indicated in the in situ Raman experiments.

2.5. In Situ X-ray Absorption Spectroscopy (XAS). The in situ Mo K-edge X-ray absorption spectroscopy data were obtained at beamline 7-BM in the National Synchrotron Light Source-II (NSLS-II) of the Brookhaven National Laboratory (BNL). The XAS spectra were collected by ionization chamber detectors that measured transmission beam intensities through the sample and the reference (Mo) foil was used for energy calibration and alignment. Fluorescence data from the samples were measured using a PIPS detector. The catalyst pellets (~0.2 g) were loaded into an in situ reaction cell (Nashner–Adler). A MoO₃ compound was used as the reference for comparison. The procedure for collecting the in situ XAS spectra was similar to that for the Raman experiments described above, but 2.5% C₂H₄/H₂ was only flowing at 200 °C. The Athena and Artemis software programs were utilized for data processing and analysis. The details of the edge X-ray absorption fine structure (EXAFS) fitting method are presented in the previous work. The edge energy (Eg) values calculated from the UV–vis spectra were determined by the intercept of the straight line for the low-energy rise of a plot of [F(R)/hν] versus the incident photon energy (hν). The procedure for collecting the in situ XAS spectra was similar to that for the Raman experiments described above, but 2.5% C₂H₄/H₂ was only flowing at 200 °C. The Athena and Artemis software programs were utilized for data processing and analysis. The details of the edge X-ray absorption fine structure (EXAFS) fitting method are presented in the previous work. It is well established that the (110) facet of γ-Al₂O₃ is preferentially covered by Brønsted acid sites at the gas–solid interface.

2.6. Propylene Temperature-Programmed Surface Reaction (TPSR). The C₃H₆/TPSR spectra were obtained by an Altamira Instruments system (AMI-200). The catalysts (~0.2 g) were loaded into a U-tube quartz reactor. The dehydration procedure was similar as indicated above in Raman experiments. After flushing with Ar (Air Gas, UHP, 30 mL/min) for 1 h, the gas flow was switched to 2% C₂H₄/Ar (Praxair, Purity 99%, 30 mL/min) and held at 30 °C for several minutes to stabilize the MS signal. The temperature was then ramped at 10 °C/min up to 600 °C. An online Dycor ProLine Process Mass Spectrometer (MS) was employed to analyze the outgoing gases. The monitoring mass/charge channels were m/z = 18 (H₂O), m/z = 27 (C₂H₆), m/z = 42 (C₃H₆), m/z = 44 (CO₂), and m/z = 56 (C₄H₆). The MS signals were calibrated and corrected for cracking contributions from different components.

2.7. Ethylene/2-Butene Titration. The C₂H₄/C₄H₈ titration spectra were obtained by the same Altamira Instruments system (AMI-200). The initial dehydration procedure was the same as the above Raman experiments. After cooling down to 200 °C and flushing with Ar for 30 min, 2-butene was chemisorbed on the catalyst by flowing 1% C₃H₆/Ar (Praxair, Purity 99%, 30 mL/min) at 200 °C for 30 min. Afterward, the gas flow was immediately switched to 1% C₂H₄/Ar (Praxair, Purity 99%, 30 mL/min) for 30 min to titrate the adsorbed surface intermediates from 2-butene chemisorption. The same mass/charge channels were recorded as for the above C₂H₆/TPSR experiments. The number of activated surface MoO₃ sites was calculated by the amount of C₂H₄ produced during C₃H₆ → C₂H₄ titration with the assumption that only one surface Mo==CHCH₃ intermediate was present on the surface. The MS signals were calibrated and corrected for cracking contributions from different components.

2.8. Steady-State Propylene Metathesis. The steady-state propylene self-metathesis catalytic activity was obtained in a fixed-bed reactor under differential conditions (propylene conversion <15%). Both the inlet and outlet of the gas tubes were heated to 200 °C to avoid the condensation of the propylene reactant and products. The conversion was obtained. An online gas chromatograph (Agilent GC 6890) equipped with a GS-Alumina (Agilent 1153552) column connected to a flame ionization detector (Agilent Model G1531) was employed to analyze the outgoing gases from the reactor. The catalytic activities (mmol/g/h) were calculated by normalizing the conversion of propylene by the flow rate and catalyst weight. The turnover frequency (TOF) values were calculated by normalizing the steady-state activity by the number of activated MoO₃ sites derived from C₂H₄/C₃H₆ titration. The GC was calibrated for all of the reaction products.

3. RESULTS

3.1. In Situ DRIFTS of Surface Hydroxyl Anchoring Sites. The in situ DRIFTS spectra were collected to identify the surface hydroxyls of the Al₂O₃ support that anchor the surface TaOₓ and MoO₃ sites and are presented in Figure S1 and the corresponding difference spectra are presented in Figures S2 and 1. The bare Al₂O₃ support has multiple surface hydroxyls: isolated Al-OH (HO-1-AlV) at 3787 cm⁻¹, HO-µ₁-AlV at 3756 cm⁻¹, HO-µ₁-AlV at 3741 and 3730 cm⁻¹, bridged Al₂-OH (HO-µ₂-AlV) at 3694 cm⁻¹), and tri-coordinated Al₃-OH (HO-µ₂-AlV at 3674 cm⁻¹). It is well established that the (110) facet of γ-Al₂O₃ is preferentially anchored on the support's surface.

Figure 1. In situ DRIFTS difference spectra of the surface hydroxyl region of dehydrated supported MoO₃/TaOₓ/Al₂O₃ catalysts (120 °C). The spectrum of the dehydrated Al₂O₃ support was subtracted from the spectrum of the 3MoAl catalyst. The spectra of dehydrated surface-modified TaO₆/Al₂O₃ supports were subtracted from the spectra of the corresponding 3MoTaAl catalysts.
exposed (70–83%), while the (100) only represents a minor facet (17%).19,21,22 The population of the γ-Al2O3 (111) facet is much less significant and can be neglected.23 The HO-µ1-AlIV at 3787 cm⁻¹, HO-µ1-AlIV at 3741/3730 cm⁻¹, and HO-µ2-AlIV at 3694 cm⁻¹ are located on the Al (110) facet, while HO-µ1-AlIV at 3765 cm⁻¹ and HO-µ2-AlIV at 3674 cm⁻¹ are located on the Al (100) facet.19,20 The more basic surface hydroxyls correspond to the higher wavenumber peaks, while the lower wavenumber peaks are associated with neutral and more acidic surface hydroxyls.24 Thus, the acidity of Al2O3 surface hydroxyl follows the trend: most basic Al-OH (HO-µ1-AlIV), less basic Al-OH (HO-µ1-AlIV and HO-µ2-AlIV), neutral Al3-OH (HO-µ2-AlV), and more acidic Al3-OH (HO-µ3-AlV). The surface hydroxyl density of Al2O3 is ~6–9 OH/nm² with a ratio of Al3-OH:Al2-OH:Al-OH surface hydroxyls of ~1:3:2:1 as determined by 1H NMR.25,26

The surface Ta2O5 promoter anchors at all five types of the alumina surface hydroxyls, as indicated in Figure S2. It has been shown in prior studies that the dispersion of one metal oxide onto another metal oxide can generate new surface M1-Oxide onto another metal oxide can generate new surface M1-°Al3°(OH)x-M2°Brønsted acid sites,27,28 and thus, the newly formed peak ~3520 cm⁻¹ is assigned to the Al-(OH)x-Ta Brønsted acid sites.29 The positive peak ~3785–3775 cm⁻¹ is assigned to shifting of the basic Al-OH hydroxyl induced by the nearby surface Ta2O5 sites since the Ta-OH vibration is reported at lower wavenumbers (~3680–3743 cm⁻¹).30 Even though the preferential anchoring sites of Ta2O5 on Al2O3 are not clear from the spectra, the DRIFTS results reveal that the surface Ta2O5 promoter modifies the surface chemistry of the Al2O3 support, thereby modifying the available anchoring sites for anchoring of the MoOx species.

For the unmodified surface MoOx/Al2O3 catalyst, the surface MoOx sites preferentially anchor at HO-µ1-AlIV (3787 cm⁻¹) and HO-µ1-AlIV (3765 cm⁻¹) surface hydroxyls. A minor amount of HO-µ2-AlIV (3674 cm⁻¹) also appears to be involved in anchoring MoOx species. The addition of MoOx to the surface-modified Ta2O5/Al2O3 support shows that the MoOx species mainly anchor at the HO-µ1-AlIV (3765 cm⁻¹), HO-µ1-AlIV (3741/3730 cm⁻¹), HO-µ1-AlIV (3694 cm⁻¹), HO-µ2-AlIV (3674 cm⁻¹), and the newly formed Al-(OH)x°-Ta (3520 cm⁻¹) Brønsted acid sites. A minor amount of HO-µ1-AlIV (3787 cm⁻¹) is also consumed by the anchoring of MoOx. With the increase of Ta2O5 loading (5–15%), MoOx sites anchor at HO-µ1-AlIV (3765 cm⁻¹), HO-µ2-AlIV (3741/3730 cm⁻¹), and HO-µ2-AlIV (3694 cm⁻¹). The anchoring of MoOx at the Ta-perturbed Al-OH (3785–3775 cm⁻¹) is not significant since the peak difference is minimal after anchoring of MoOx. In summary, compared to the unmodified supported MoOx/Al2O3 catalyst, the surface MoOx sites on the supported MoOx/Ta2O5/Al2O3 catalysts preferentially anchor at the HO-µ1-AlIV (3765 cm⁻¹), HO-µ1-AlIV (3741/3730 cm⁻¹), HO-µ2-AlIV (3694 cm⁻¹), and HO-µ2-AlIV (3674 cm⁻¹) surface hydroxyls.

### 3.2. In Situ Raman Spectroscopy

#### 3.2.1. Dehydrated Catalysts

The in situ Raman spectra of the surface-modified Ta2O5/Al2O3 support and supported MoOx catalysts under dehydrated conditions are presented in Figures S3, S4, and 2. The γ-Al2O3 support does not give rise to any Raman bands.16 For the surface-modified Ta2O5/Al2O3 support, two main Raman bands are present at 860 and 945 cm⁻¹ corresponding to the ν3(Ta-O-Al) and ν3(Ta=O) stretches of the surface Ta2O5 sites, respectively. The presence of oligomeric surface Ta2O5 sites is indicated by Raman bands at 617 and 715 cm⁻¹ corresponding to ν3(Ta-O-Ta) and ν3(Ta-O-Ta), respectively. The Raman bands at 270 and 340 cm⁻¹ are characteristic of δ(Ta-O-Ta) and δ(Ta-O-Ta) bending modes.31,32 For the supported MoOx/Ta2O5/Al2O3 catalysts, the Raman bands from surface Ta2O5 sites are too weak to be detected and the Raman spectra are dominated by the molybdenum oxide component. The absence of strong and sharp Raman bands at 820 and 960 cm⁻¹ demonstrates that crystalline MoOx nanoparticles are not present in these catalysts. The strong Raman band at 996–1001 cm⁻¹ corresponds to the ν8(Mo=O) stretch of the surface MoOx sites. The unpromoted 3MoAl catalysts exhibit the ν8(Mo=O) at ~996 cm⁻¹ associated with isolated MoOx sites anchored at the basic Al-OH surface hydroxyls.6,16 The blue shift of ν8(Mo=O) from 996 to 1001 cm⁻¹ with Ta2O5 surface modification reflects increasing oligomerization of surface MoOx sites with increasing surface Ta2O5 coverage. The blue shift is also observed in the in situ DRIFTS Mo=O overtone region (Figure S5). All of the supported MoOx catalysts also exhibit a band at 850 cm⁻¹ from the bridging ν3(Mo=O-Al) vibration.

#### 3.2.2. Propylene Metathesis Reaction Conditions

The in situ Raman spectra of the supported MoOx catalysts (120 °C, 800–1200 cm⁻¹).

The spectra indicate that for the supported 3MoAl catalyst, the intensity of the ν3(Mo=O) band is minimally perturbed at both 30 and 200 °C. In contrast, the ν3(M=O) band of the supported 3Mo15TaAl catalyst is only minimally perturbed at 30 °C, but there is a moderate decrease in intensity at 200 °C. This observation reflects the ability of propylene to activate the surface MoOx sites present on the Ta2O5 surface-modified alumina support.

#### 3.3. UV–Vis DRS Spectroscopy

#### 3.3.1. Dehydrated Conditions

The in situ UV–vis spectra and edge energy (Eg) values of dehydrated supported MoOx/Al2O3 catalysts at 120 °C are presented in Figure 4 and Table 1. The surface Ta2O5 sites on Al2O3 exhibit UV–vis edge energy values of ~5.0–4.6 eV that redshift with increasing surface Ta2O5 loading (5–15%). The shift in the absorption edge of the supported MoOx catalysts was found to be minimal at 30 °C, but there is a moderate decrease in intensity at 200 °C. This observation reflects the ability of propylene to activate the surface MoOx sites present on the Ta2O5 surface-modified alumina support.
UV−vis edge energy reflects the degree of oligomerization of the surface MoO\textsubscript{x} sites, which are minimally affected by the presence of the surface TaO\textsubscript{x} sites. The MgMoO\textsubscript{4} reference compound consists of isolated MoO\textsubscript{4} sites and exhibits a high UV−vis edge energy of ∼4.5 eV with a single ligand-to-metal charge transfer (LMCT) peak at 250 nm.\textsuperscript{6,16,33} The (NH\textsubscript{4})\textsubscript{2}Mo\textsubscript{2}O\textsubscript{7} reference compound contains MoO\textsubscript{x} chains with a UV−vis edge energy (E\textsubscript{g}) value of ∼3.5 eV and two LMCT peaks at 250 and 320 nm reflecting the oligomeric structure.\textsuperscript{6,16,33} The supported 3MoAl catalyst has an intermediate edge energy value of ∼3.9 eV with two comparable intensity LMCT peaks at 240 and 285 nm, suggesting that isolated surface MoO\textsubscript{x} sites co-exist with oligomeric surface MoO\textsubscript{x} sites (Figure S7). The supported 3MoTaAl catalysts have a slightly lower edge energy ∼3.8 eV with an increase in the ratio of the 285/240 nm LMCT peaks with increasing surface TaO\textsubscript{x} coverage reflects the presence of greater amounts of oligomeric surface MoO\textsubscript{x} sites (Figure S7). The UV−vis LMCT peaks at ∼240 and 270–290 nm of the dehydrated supported MoO\textsubscript{x} catalysts indicate that the surface MoO\textsubscript{x} sites are fully oxidized as Mo\textsuperscript{(+6)} under dehydrated conditions.\textsuperscript{16} This is further confirmed by the absence of UV−vis d−d peaks at ∼350–800 nm from reduced surface MoO\textsubscript{x} sites. Thus, the surface MoO\textsubscript{x} sites are present in the Mo\textsuperscript{6+} oxidation state and consist of both isolated and oligomeric sites, with the extent of oligomerization increasing with surface TaO\textsubscript{x} coverage.

3.3.2. Propylene Metathesis Reaction Conditions. The in situ UV−vis difference spectra of the supported MoO\textsubscript{x} catalysts under propylene metathesis reaction conditions at 30 and 200 °C are presented in Figure 5. The LMCT peaks at 245–280 nm from the fully oxidized Mo\textsuperscript{(+6)} are minimally perturbed at 30 °C and the absence of peaks in the d−d region from reduced Mo sites. This suggests that the surface MoO\textsubscript{x} sites on both the supported 3MoAl and 3Mo15TaAl catalysts possess surface Mo\textsuperscript{(+6)} sites at 30 °C. Only when the reaction temperature is raised to 200 °C, the supported 3Mo15TaAl catalyst exhibits a very weak and broad peak (only visible in difference spectra) at ∼435 nm in the d−d region with the LMCT peaks of fully oxidized Mo\textsuperscript{(+6)} minimally perturbed. The possible presence of some reduced surface Mo sites, however, could not be determined since adsorbed olefins also give rise to UV−vis peaks in the same region.\textsuperscript{34−36} In summary, the isolated and oligomeric surface MoO\textsubscript{x} sites appear to be minimally perturbed by the propylene metathesis reaction conditions.

3.4. In Situ X-ray Absorption Spectroscopy (XAS). The in situ X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra at the Mo K-edge of the supported MoO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalysts under dehydrated conditions and propylene metathesis reaction conditions are presented in Figures 6 and S8. The EXAFS fitting results are presented in
Tables S1–S2 and Figures S9–S10. The MoO₄ coordination without inversion symmetry has a strong pre-edge peak due to the 1s(Mo) → 4d(Mo) + 2p(O) transition, but this transition is suppressed for the regular MoO₆ coordination with inversion symmetry. A weak pre-edge peak due to this transition for MoO₆ coordination is present, however, for the distorted MoO₆ coordination (MoO₃ reference compound). Thus, the relatively strong pre-edge peak of all of the supported MoOₓ catalysts at 20 003 eV is consistent with the presence of MoO₄ surface sites. The XANES edge jump (maximum of the first derivative) of all of the supported MoOₓ catalysts at ~20 015 eV is in the same position as that of the Mo⁶⁺O₃ reference compound, indicating the oxidation state of surface MoOₓ sites to be Mo(+6). The k²-weighted Mo K-edge EXAFS spectra demonstrate a strong peak at 1.2 Å (not corrected for photoelectron phase shift) corresponding to the terminal Mo=O bond that is shorter than the Mo=O bond at 1.6 Å in the MoO₂ reference compound with regular MoO₆ coordination in the first shell (1–2 Å) of the Mo center. There is no Mo–Mo interaction in the second shell (3–4 Å) of the surface Mo center. The same Mo=O peak position suggests that the Mo=O bond lengths are the same for all the supported MoOₓ catalysts. The surface MoOₓ sites are minimally perturbed during the propylene metathesis reaction at 200 °C for all of the supported MoOₓ catalysts. Given that oxygen and carbon atoms have close atomic masses, the difference between Mo–O and Mo–C interactions cannot be captured by EXAFS. Quantitative model fitting of EXAFS yields a Mo=O bond at ~1.74 Å (Tables S1 and S2). The model fitted coordination number (CN) of the Ta-promoted MoOₓ/Al₂O₃ catalyst increases slightly from 3.9(4) to 4.3(4) as the concentration of TaOₓ increases from 0 to 15%, reflecting the increasing amount of oligomerized surface MoO₅/₆ sites on the Ta-promoted catalysts.

3.5. Chemically Probing Surface Acid Sites with NH₃-IR. The in situ DRIFTS spectra of Al₂O₃, TaOₓ/Al₂O₃, supported 3%MoOₓ/Al₂O₃, and supported 3%MoOₓ/TaOₓ/Al₂O₃ catalysts after NH₃ chemisorption are presented in Figure 7. All of the spectra exhibit the presence of surface Lewis acid sites (δₐs(NH₃*) and δₛ(NH₃*) at ~1619 and 1252 cm⁻¹, respectively) and Brønsted acid sites (δₐs(NH₄⁺*) and δₛ(NH₄⁺*) at ~1447–1480 and 1684–1697 cm⁻¹, respectively). The initial bare Al₂O₃ support exhibits the presence of both surface Lewis and Brønsted acid sites. The Brønsted acidity of the Al₂O₃ support is relatively weak since Brønsted acidity is not detected when chemically probed by the pyridine weaker base. The IR δₛ(NH₃*) and δₛ(NH₄⁺*) vibrations will be used for comparison of acidity strength since they are much stronger bands. The essentially same peak position of δₛ(NH₄⁺*) indicates that the acid strength of the surface Lewis acid sites is similar for all of the catalysts. The vibrations from the surface Lewis acid sites are predominantly associated with the Al₂O₃ and TaOₓ/Al₂O₃ supports since the surface MoOₓ coverage is relatively low (0.8 Mo/nm²) compared to the surface TaOₓ coverage (0.7, 1.4,
The addition of both surface MoOx sites and the TaOx surface modifier introduces weaker Bronsted acid sites, as indicated by the red shift of $\delta_\text{Brønsted}$ peak. With increasing surface TaOx coverage, the Bronsted acidity of the supported 3MoTaAl catalysts is dominated by the weaker surface TaOx Bronsted acid sites. The Bronsted acidity strength introduced by MoOx is in-between that of Al2O3 and surface TaOx sites as indicated by the moderate red shift of $\delta_\text{Brønsted}$ peak. The strength of surface Bronsted acidity follows the trend Al2O3 > 3MoAl > 15TaAl > 3Mo5TaAl > 3Mo15TaAl. Since DRIFTS is not quantitative, only the relative ratios of the Bronsted/Lewis acid sites can be compared: Al2O3 (1.54) > 3MoAl (1.46) > 3Mo5TaAl (1.32) > 15TaAl (1.29) > 3Mo15TaAl (1.21). The peak areas of the Bronsted acid sites follow the trend: 15TaAl (16.7) > 3Mo5TaAl (16.3) > 3Mo15TaAl (15.7) > 3MoAl (15.6) > Al2O3 (12.7). In summary, all of the catalysts have surface Lewis acid sites with similar strength, while the addition of the surface MoOx and TaOx sites introduces weaker surface Bronsted acid sites.

### 3.6. Propylene-TPSR

The C3H6-TPSR spectra of the supported MoOx catalysts are presented in Figure 8. The supported 3MoAl catalyst produces C3H6 from 30 to 600 °C with a peak temperature (Tp) of $\sim$480–500 °C. The supported 3MoTaAl catalysts, however, form C3H6 in several temperature ranges: $\sim$50–150 °C (Tp = 65 °C), $\sim$225–375 °C (Tp = 280–310 °C), and $\sim$375–600 °C (Tp = 480–510 °C). The C3H6-TPSR spectra suggest that there are probably 3 distinct active surface MoOx sites in these catalysts with their specific activity increasing with the decreasing Tp value. Both the amount of C3H6 produced and specific activity tend to increase with increasing surface TaOx coverage reflecting the promotional effect of the surface TaOx sites upon propylene metathesis by the supported MoOx/TaOx/Al2O3 catalysts.

#### 3.7. Ethylene/2-Butene Titration (Number of Active Sites)

The number of catalytic active sites involved in olefin metathesis can be determined from the number of propylene molecules formed during ethylene/2-butene titration. The time-resolved titration spectra are presented in Figure 9.

Figure 8. Propylene-TPSR spectra for the supported 3%MoOx/Al2O3 catalysts from 30 to 600 °C ($n = 0, 1, 5, 10, 15$).

Figure 9. Time-resolved MS spectra of C3H6 produced during the titration of surface Mo==CHCH3 with C2H4 for the supported MoOx catalysts (200 °C).
Table 2. Fraction of Activated Surface MoOx Sites Calculated from C2H4/C4H8 Titration, Steady-State Activity, and Propylene Metathesis Turnover Frequency (TOF)

<table>
<thead>
<tr>
<th></th>
<th>3MoAl</th>
<th>3MoTaAl</th>
<th>3Mo10TaAl</th>
<th>3Mo15TaAl</th>
</tr>
</thead>
<tbody>
<tr>
<td>fraction of active surface MoOx sites</td>
<td>3.2%</td>
<td>16.3%</td>
<td>18.8%</td>
<td>18.1%</td>
</tr>
<tr>
<td>steady-state activity (mmol/g/h)</td>
<td>0.0056</td>
<td>0.2274</td>
<td>0.2986</td>
<td>0.3466</td>
</tr>
<tr>
<td>TOF (s⁻¹)</td>
<td>2.4 × 10⁻⁴</td>
<td>1.9 × 10⁻³</td>
<td>2.1 × 10⁻³</td>
<td>2.6 × 10⁻³</td>
</tr>
</tbody>
</table>

addition of surface TaOx sites to the Al2O3 support. Thus, the TOF value for surface MoOx sites is significantly promoted by surface modification of the Al2O3 support with surface TaOx sites.

4. DISCUSSION

4.1. Surface Anchoring Hydroxyls for MoOx Sites. The surface hydroxyls of the Al2O3 and TaOx/Al2O3 supports serve as the anchoring sites for the deposition of the TaOx and MoOx species (Figure 1). The MoOx species for the supported 3MoAl catalyst preferentially anchor at the most basic Al-OH (HO-μ1-Al1) and less basic Al-OH (HO-μ1-Al3) surface hydroxyls with a minor amount also anchoring at the less basic Al-OH (HO-μ1-Al3) and acidic Al1-OH surface hydroxyls. The anchoring of the surface TaOx sites on Al2O3, however, indiscriminately involves all five types of the surface hydroxyls and form new Brunsted acid Al-(OH)-Ta sites. Consequently, the anchoring of the surface TaOx species affects the remaining surface hydroxyls available for the subsequent anchoring of the MoOx species. The surface TaOx sites partly cap the most basic Al-OH (HO-μ1-Al1) surface hydroxyls, thus, shifting the anchoring of MoOx to the less basic Al-OH (HO-μ1-Al1) and HO-μ1-Al1, neutral Al2-OH, and acidic Al1-OH surface hydroxyls usually observed with the anchoring of MoOx at intermediate surface coverage.

For the supported ReOx/TaOx/Al2O3 catalyst system, TaOx surface modification of Al2O3 was previously found to shift the anchoring of ReOx species from the most basic Al-OH (HO-μ1-Al1) to the neutral Al2-OH and acidic Al1-OH surface hydroxyls. Although the trend with surface TaOx modification is similar for both the supported ReOx/TaOx/Al2O3 and MoOx/TaOx/Al2O3 catalyst systems (less anchoring at the most basic surface hydroxyls and anchoring at less basic, neutral, and acidic surface hydroxyls), the specific anchoring sites of ReOx and MoOx are not exactly the same probably because of the different acidity of the MoOx and ReOx species.

4.2. Molecular Structure of Dehydrated Surface MoOx Sites. The dehydrated supported 3MoAl catalyst contains both isolated surface MoOx sites (LMCT peak at ~240 nm (Figure S7), higher UV–vis Eg value (Table 1), and lower EXAFS coordination number (Table S1)) and oligomeric MoOx6/6 sites (LMCT peak at ~285 nm (Figure S7), intermediate UV–vis Eg value (Table 1), and higher EXAFS coordination number (Table S1)). The dehydrated supported 3MoTaAl catalysts also contain isolated MoOx and oligomeric MoOx6/6 sites with the fraction of oligomeric MoOx6/6 sites increasing with surface TaOx coverage (increase in the UV–vis peak at ~285 nm relative to ~240 nm (Figure S7), blue shift of the ν(Mo=O) band position (Figure 2), and higher EXAFS coordination number (Table S1)). For all of the supported MoOx catalysts, the oxidation state of MoOx sites is predominantly Mo(+6) (absence of d–d peaks and XANES edge jump). The change of the molecular structure of the surface MoOx sites on the supported 3MoTaAl catalysts is a consequence of the modification of the available anchoring surface hydroxyls on the Al2O3 support brought about by TaOx surface modification.

The molecular structure of the surface MoOx sites supported on Al2O3 has been extensively studied with in situ Raman,6,16,42 XAS,7,42,43 in situ UV–vis,6,46 and density functional theory (DFT).6,24,46 Three distinct surface MoOx sites are present on Al2O3 that depend on the surface MoOx coverage. At low surface coverage (<1 Mo/nm²), the surface is dominated by isolated di-oxo MoOx sites. At high surface coverage (1–4.6 Mo/nm²), both isolated di-oxo MoOx sites and oligomeric mono-oxo MoOx6/6 sites co-exist. Above monolayer coverage (>4.6 Mo/nm²), crystalline MoOx nanoparticles form on top of the surface MoOx monolayer.5,7,16,42,43 The molecular structure of the surface MoOx sites for the supported 3MoAl catalyst reported herein agrees with structures of the surface MoOx sites on MoOx/Al2O3 at low MoOx surface coverage previously reported in the literature. The molecular structures of the surface MoOx sites for the supported 3MoTaAl catalysts, however, correspond to the structures present at intermediate surface MoOx coverage of the supported 9–13% MoOx/Al2O3 catalysts (Figure 2 and Table 1). The number of terminal oxo Mo=O bonds depends on the specific support: di-oxo and mono-oxo MoOx sites co-exist on Al2O3,6,16 ZrO2,16,47 and TiO2,48 and di-oxo MoOx sites on SiO2.16,49,49 Since the MoOx species mainly anchor at the Al1-OH surface hydroxyls of TaOx surface-modified Al2O3, both di-oxo and mono-oxo surface MoOx sites most likely co-exist for the supported 3MoTaAl catalysts. Only when one of the anchoring sites for the MoOx Species is selectively capped by the surface TaOx site, the number of terminal Mo=O bonds in the remaining surface MoOx site can be clearly determined with isotopic 18O–16O exchange.46 Two distinct surface ReOx sites were identified on supported ReOx/Al2O3 catalysts. The surface TaOx sites completely block the formation of the surface ReOx-I sites at basic hydroxyls and shift anchoring of the surface ReOx species to more neutral and acidic surface hydroxyls.15 The observed molecular structural change of the surface MoOx sites for the supported 3MoTaAl catalyst suggests that surface TaOx on Al2O3 similarly blocks anchoring of MoOx species at basic surface hydroxyls (Figures 1, S1, and S2). The blocking effect of the surface TaOx sites for the supported MoOx/Al2O3 catalysts, however, is weaker than that for the corresponding supported ReOx/Al2O3 catalysts, where all of the isolated surface ReOx sites at low coverage become blocked since not all of the isolated surface MoOx sites are blocked by the surface TaOx sites. Consequently, isolated surface MoOx sites are still present for the supported MoOx/TaOx/Al2O3 catalyst.

4.3. Molecular Structure of Surface MoOx Sites during Propylene Metathesis. To perform propylene metathesis, the surface MoOx sites require activation by propylene, resulting in the removal and replacement of terminal Mo=O bonds by surface molybdenum carbenes (Mo=CH3 and Mo=CHCH3).50 The molecular structures of the surface MoOx sites of the supported 3MoAl catalyst are not perturbed during propylene metathesis at 30 and 200 °C (minimal changes in Raman (Figure 3), UV–vis (Figure 5),
and XAS (Figure S8 and Tables S1, S2)). In contrast, the surface MoO₄ sites for the supported 3MoTaAl catalysts are modestly activated under propylene metathesis reaction at 200 °C (Figure 3, decrease in Raman intensity from propylene coordination). The oxidation state of the surface MoO₃ sites for both 3MoAl and 3MoTaAl catalysts under propylene metathesis reaction remains dominated by Mo(+6) (minimal perturbation of the UV–vis LMCT peak (Figures 4 and S5) and XANES edge jump (Figures 6 and S8)) since the dehydrated surface MoO₃ sites and activated molybdenum carbene both exhibit Mo(+6) (Figure 5).

The nature of the surface MoO₃ sites on Al₂O₃ during propylene metathesis has recently been examined by in situ Raman spectroscopies as a function of MoO₃ loading. For supported MoO₃/Al₂O₃ catalysts at low surface MoO₃ coverage, the isolated MoO₃ sites dominate under propylene metathesis reaction conditions and do not become activated at low temperatures (<200 °C). The findings in the present study for the supported 3MoAl catalyst during propylene metathesis (Figure 3) are in agreement with the previously reported findings.

The in situ Raman spectra of supported ReO₄/Al₂O₃ catalysts revealed that the surface ReO₄-II sites anchored at basic Al-OH surface hydroxyls are minimally activated during propylene metathesis, while the surface ReO₄-II sites anchored at neutral Al-OH and more acidic Al-OH are extensively activated at low temperatures (<200 °C). The Ta-surface-modified supported ReO₄/Al₂O₃ catalysts only contain the surface ReO₄-II sites; formation of surface ReO₄-I is not present since the basic Al-OH sites have been capped by the surface TaOₓ sites and are extensively activated at low temperatures (30 °C). Similar to the Ta-surface-modified supported ReO₄/Al₂O₃ catalysts, activation of the surface MoO₄ sites for the Ta-surface-modified supported MoO₃/Al₂O₃ catalyst by propylene is enhanced because some of the basic Al-OH surface hydroxyls are capped by the surface TaOₓ sites that increase anchoring of the MoO₄ species at less basic, neutral, and more acidic surface hydroxyl sites (Figures 1, S1, and S2).

4.4. Structure–Activity Relationship for Propylene Metathesis. Typically, the fraction of activated surface metal alkylidene species is only a fraction of the total supported metal oxides. The steady-state reaction and C₃H₆/C₄H₈ titration reveals that both the number of activated surface MoO₃ sites and the TOF values increase with surface TaOₓ coverage (Table 2: 3MoI5TaAl > 3MoI0TaAl > 3MoS5TaAl > 3MoAl). A similar trend is also found for activation (C₃H₆-TPSR) of the supported MoO₃ catalysts at low, intermediate, and high temperatures (Figure 8: 3MoI5TaAl > 3MoI0TaAl > 3MoS5TaAl > 3MoAl). These trends correspond to two changes (i) anchoring surface hydroxyls for the surface MoO₃ sites and (ii) extent of oligomerization of the surface MoO₃ sites. Given that both variables are varying at the same time, it appears at first difficult to determine the contributions of these variables to activation and TOF. However, the analogous supported ReO₄/TaOₓ/Al₂O₃ catalysts only contain isolated surface ReO₃ sites and the surface TaOₓ changes the anchoring surface hydroxyls of the surface ReO₃ sites. Given that both olefin metathesis catalyst systems behave similarly with surface metal oxide coverage and surface TaOₓ modification, it appears that the dominant factor is the anchoring sites and not the oligomerization extent of the surface MoO₃ sites.

DFT calculations of activated surface Mo-alkylidene sites found that the location of the surface MoO₃ sites on the Al₂O₃ support influences the activity of the surface Mo-alkylidene toward ethylene addition. The calculations predicted that on the (100) and (110) facets of Al₂O₃, when Mo-alkylidene was anchored at neutral Alₓ-OH or more acidic Alₓ-OH surface hydroxyls, the surface MoO₃ sites were less stable with a decreased electron density of the molybdenum center, making the geometry of the surface Mo-alkylidene more suitable for olefin addition. Both monomeric and dimeric MoO₃ sites can become activated sites, but the latter requires a lower activation energy. Dimeric surface MoO₃ sites are more stable on the Al (100) facet, while isolated MoO₃ sites are more stable on the Al (110) facet. These studies indicate that the isolated surface Mo-alkylidene is less active than since such sites prefer to form the less active square-pyramidal molybdacyclobutane surface intermediate. Thus, the DFT calculations also indicate the importance of surface anchoring sites for activation of surface MoO₃ sites for olefin metathesis.

For Ta-free supported MoO₃/Al₂O₃ catalysts, the amount of C₃H₆ formation during C₃H₆-TPSR at high temperatures remains constant with surface MoO₃ coverage. On the Ta-surface-modified MoO₃/Al₂O₃ catalysts, however, the amount of C₃H₆ production at high temperatures increases with surface TaOₓ coverage (Figure 8). This difference is ascribed to the modification of the basic Al-OH surface hydroxyls by the surface TaOₓ sites involved in anchoring isolated surface MoO₃ sites (Figures 1, S1, and S2). Analogously, the increase in production of C₃H₆ at intermediate and low temperatures is related to the perturbation of the surface hydroxyls by the surface TaOₓ sites involved in anchoring the MoO₃ species at less basic Al-OH (HO-μ₂-Alₓ) and neutral Alₓ-OH of Al(110) and less basic Al-OH (HO-μ₂-Alₓ) and acidic Alₓ-OH of Al(100), respectively. Thus, the activation and specific catalytic activity of surface MoO₃ sites on the Al₂O₃ support can be tuned by modification of the available surface hydroxyl anchoring sites.

4.5. Influence of Surface Lewis/Bronsted Acidity on Propylene Metathesis. In the present study, the dehydrated supported MoO₃ catalysts were found to possess very similar strength of Lewis acids (dominated by Lewis acid sites of the Al₂O₃ and TaOₓ/Al₂O₃ supports) and slightly weaker Bronsted acid sites (Figure 7). A relationship between Lewis acidity and propylene metathesis activity could not be established since the Lewis acidity is dominated by the oxide supports at the low surface MoO₃ coverage (0.8 Mo nm⁻² that corresponds to ~18% of the monolayer) employed in the present study. There is no relationship between Bronsted acid strength and propylene metathesis activity since the addition of surface TaOₓ sites decreases the strength of the Bronsted acid sites, while the propylene metathesis activity increases. The amount of Bronsted acid sites also does not relate with propylene metathesis activity since both the supported 3MoAl and 3MoI5TaAl catalysts have comparable amounts of Bronsted acid sites and the supported 3MoI5TaAl catalyst is much more active for propylene metathesis.

The surface acidity properties of surface TaOₓ and MoO₃ sites on Al₂O₃ have been documented in several studies. Adsorption of pyridine on the Mo-free supported TaOₓ/Al₂O₃ indicated that (i) at low surface TaOₓ coverage, only weak Lewis acid sites are present and the amount of Lewis acids sites increase with TaOₓ loading, and (ii) at high surface TaOₓ coverage, the amount of Bronsted acid sites increase and
the strength of the Lewis acid sites decrease with increasing TaO\textsubscript{x} loading.\textsuperscript{62} For supported MoO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalysts, NH\textsubscript{3}-TPD reveals that the total amount of acid sites initially increases and then decreases with increasing surface MoO\textsubscript{x} coverage.\textsuperscript{65} Pyridine-IR adsorption on supported MoO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalysts indicates that the amount of Bronsted acid sites linearly increases with the addition of surface MoO\textsubscript{x} sites. The trend of the amount of Lewis acid sites with surface MoO\textsubscript{x} coverage, however, is still under debate. Boorman et al. and Turek et al. found the amount of Lewis acid sites increase with MoO\textsubscript{x} addition, while Segawa et al. found the opposite trend.\textsuperscript{23,65,66} The different surface acidity trends proposed from literatures may be related to the use of different Al\textsubscript{2}O\textsubscript{3} support materials. Recent DFT calculations proposed that the surface silanol of SiO\textsubscript{2} interact with surface MoO\textsubscript{x} sites constituting Bronsted acid sites that could play a key role in activating the surface active sites.\textsuperscript{66} To minimize the influence of the oxide support contribution, pyridine-IR adsorption studies need to be performed since ammonia is too strong a basic probing molecule. Attempts have also been made to determine possible correlations between propylene metathesis activity and surface Lewis/Bronsted acidity of supported MoO\textsubscript{x} catalysts. Hahn et al. and Li et al. proposed a correlation between Bronsted acidity and ethylene/2-butene cross-metathesis activity as addressed in the Introduction section.\textsuperscript{5,14} Uchagawkar et al. examined supported MoO\textsubscript{x}/Silicate(TUD-1) catalysts with pyridine-IR adsorption and found that the amount of surface Lewis acid sites linearly correlated to the ethylene/2-butene cross-metathesis activity.\textsuperscript{10} Otroschenko et al. investigated supported MoO\textsubscript{x} catalysts on individual (ZrO\textsubscript{2}, TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}) and mixed oxide supports (ZrO\textsubscript{2}−SiO\textsubscript{2}, ZrO\textsubscript{2}−PO\textsubscript{4}, TiO\textsubscript{2}−SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}−SiO\textsubscript{2}) with pyridine-IR adsorption and NH\textsubscript{3}-TPD. No general relationships between olefin metathesis activity and strength/amount of Lewis/Bronsted sites could be established.\textsuperscript{12} A general conclusion about the influence of surface acid sites on olefin metathesis cannot be made from the above literature findings since these studies are clearly not consistent with each other. Possible reasons for these different observations are the use of oxide supports from different sources and the presence of surface impurities. The present detailed study, however, finds that there are no relationships between surface Lewis or Bronsted acid sites and olefin metathesis.

5. CONCLUSIONS

A series of novel TaO\textsubscript{x}−surface-modified supported MoO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalysts for propylene metathesis were successfully synthesized and well-characterized. The TaO\textsubscript{x} surface modifier perturbs the surface hydroxyl chemistry of the Al\textsubscript{2}O\textsubscript{3} support, which alters the available surface hydroxyls for subsequent anchoring of the MoO\textsubscript{x} species. Consequently, the surface MoO\textsubscript{x} species anchor at basic Al−OH surface hydroxyls perturbed by TaO\textsubscript{x} more neutral Al\textsubscript{3}−OH, and acidic Al\textsubscript{2}−OH surface hydroxyls that facilitate activation and propylene metathesis activity of the resulting surface MoO\textsubscript{x} sites. The resulting catalytic properties are dependent on the anchoring surface hydroxyls and not on the extent of oligomerization of the surface MoO\textsubscript{x} sites and surface Lewis/Bronsted acidity. This study demonstrates for the first time that olefin metathesis activity, number of active sites (Ns), and TOF for supported MoO\textsubscript{x} catalysts can be tuned by modifying the nature of the anchoring surface hydroxyls on the Al\textsubscript{2}O\textsubscript{3} support.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c06000.

- DRIFTS spectra (3500−3900 cm\textsuperscript{-1}); DRIFTS difference spectra (3500−3900 cm\textsuperscript{-1}); Raman spectra (TaO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}); Raman spectra (200−1200 cm\textsuperscript{-1}); DRIFTS spectra (1800−2150 cm\textsuperscript{-1}); UV−vis spectra (TaO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}); UV−vis spectra deconvolution; XANES/EXAFS spectra after reaction; EXAFS fitting (k space) under dehydration and after reaction; EXAFS fitting (R space) under dehydration and after reaction (PDF)

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**Notes**

The authors declare no competing financial interest.

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