

Active Site Descriptors from ^{95}Mo NMR Signatures of Silica-Supported Mo-Based Olefin Metathesis Catalysts

Zachariah J. Berkson, Ran Zhu, Christian Ehinger, Lukas Lätsch, Stefan P. Schmid, Darryl Nater, Stephan Pollitt, Olga V. Safonova, Snædís Björgvinsdóttir, Alexander B. Barnes, Yuriy Román-Leshkov, Gregory A. Price, Glenn J. Sunley, and Christophe Copéret*



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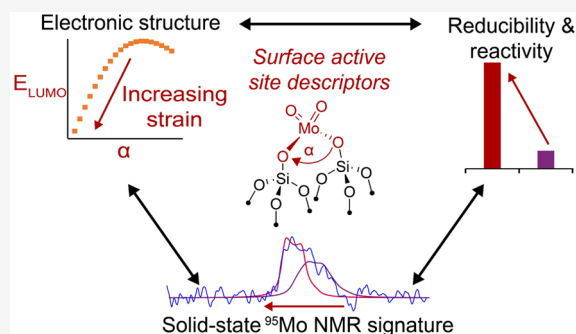


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ABSTRACT: The olefin metathesis activity of silica-supported molybdenum oxides depends strongly on metal loading and preparation conditions, indicating that the nature and/or amounts of the active sites vary across compositionally similar catalysts. This is illustrated by comparing Mo-based (pre)catalysts prepared by impregnation (2.5–15.6 wt % Mo) and a model material (2.3 wt % Mo) synthesized via surface organometallic chemistry (SOMC). Analyses of FTIR, UV–vis, and Mo K-edge X-ray absorption spectra show that these (pre)catalysts are composed predominantly of similar isolated Mo dioxo sites. However, they exhibit different reaction properties in both liquid and gas-phase olefin metathesis with the SOMC-derived catalyst outperforming a classical catalyst of a similar Mo loading by $\times 1.5$ – 2.0 . Notably, solid-state ^{95}Mo NMR analyses leveraging state-of-the-art high-field (28.2 T) measurement conditions resolve four distinct surface Mo dioxo sites with distributions that depend on the (pre)catalyst preparation methods. The intensity of a specific deshielded ^{95}Mo NMR signal, which is most prominent in the SOMC-derived catalyst, is linked to reducibility and catalytic activity. First-principles calculations show that ^{95}Mo NMR parameters directly manifest the local strain and coordination environment: acute ($\text{SiO}-\text{Mo}(\text{O})_2-\text{OSi}$) angles and low coordination numbers at Mo lead to highly deshielded ^{95}Mo chemical shifts and small quadrupolar coupling constants, respectively. Natural chemical shift analyses relate the ^{95}Mo NMR signature of strained species to low LUMO energies, which is consistent with their high reducibility and corresponding reactivity. The ^{95}Mo chemical shifts of supported Mo dioxo sites are thus linked to their specific electronic structures, providing a powerful descriptor for their propensity toward reduction and formation of active sites.



INTRODUCTION

Supported transition-metal oxides comprise an important class of heterogeneous catalysts with numerous industrial applications.^{1–5} Prominent examples include olefin metathesis catalysts used for the valorization of light olefins via the Shell higher olefin process (SHOP) and the Lummus Olefin Conversion Technology (OCT) process,^{6,7} which are based on supported Mo and W oxides, respectively (Figure 1a). These catalysts require relatively high operating temperatures and display rather low overall activity due mostly to the low quantities of active sites (typically estimated at <5%).⁸

While the precise structure(s) of the catalytic active sites in industrial olefin metathesis catalysts remain unknown, they are thought to correspond to high-valent M(VI) oxo alkylidenes formed in situ from a fraction of the initial dispersed oxo sites. Mo-based systems require significantly lower operating temperatures than their W-based analogues and are less prone to generate inactive bulk metal oxide particles through sintering during the preparation, activation, and regeneration processes. Previous studies of silica-supported Mo oxides have

shown that the catalytic activity for propene metathesis depends on Mo loadings with an optimum at ca. 1 Mo/nm².⁹ However, the small fractions of active sites suggest that specific (coordination) environments are required for their generation. The presence of proximate Brønsted acid sites, for instance, has been proposed to assist catalyst initiation.^{10,11} Furthermore, it has been suggested that the active sites originate from strained and correspondingly high-energy configurations of the tetrahedral Mo dioxo unit, which are more reactive and readily transformed for conversion into active sites.⁹ However, little is known of the structures and associated spectroscopic signatures of these sites and the structural differences between active, dormant, or inactive sites.

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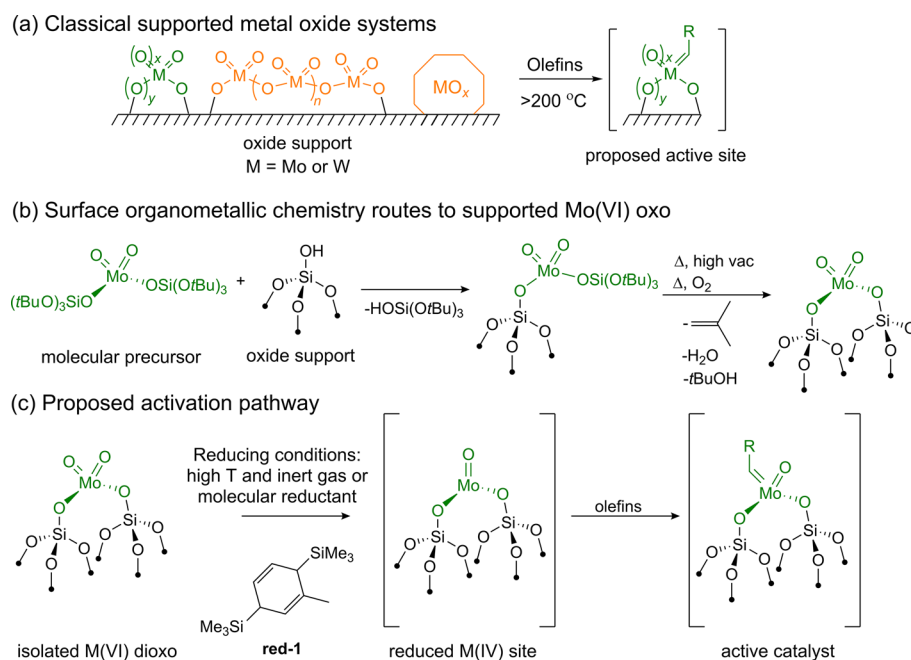


Figure 1. Olefin metathesis catalysts from supported metal oxo surface sites.

Accessing a molecular-level understanding of the (pre)catalytic active sites has been challenging because of the broad distributions of surface sites and small fractions of active species as most spectroscopic methods such as X-ray absorption spectroscopy (XAS) provide averaged information (*vide infra*).

The difficulty of characterization is also associated with the complexity of the surface species. Indeed, conventional catalyst synthesis methodologies such as incipient wetness impregnation (IWI) techniques yield broad distributions of surface species due in part to precipitation/dissolution phenomena that occur during synthetic steps carried out in the presence of water.¹² In that context, surface organometallic chemistry (SOMC) has emerged as a powerful method to generate well-defined surface sites from tailored molecular precursors.¹³ For example, isolated Mo oxo sites dispersed on highly dehydroxylated silica have been generated by grafting a molecular Mo siloxide precursor followed by a thermolysis step (Figure 1b).^{14,15} Mo K-edge XAS analysis supports the presence of highly dispersed Mo(VI) dioxo surface sites that can be readily activated for catalysis at relatively low temperatures (30–70 °C) under reducing conditions (Figure 1c) in particular using a molecular reducing agent.^{16,17} In fact, this activation process and associated low-temperature activity can also be extended to supported Mo oxide catalysts generated via conventional approaches albeit with lower activity,^{18,19} raising questions about the similarities and differences between catalysts synthesized via different routes and the precise nature of the (pre)catalytic active sites.

Following the recent development of a methodology to link the local geometry, electronic structure, and reactivity of Mo sites based on solid-state ⁹⁵Mo NMR combined with first-principles orbital analyses, demonstrated on molecular alkyne metathesis catalysts,²⁰ we examine here silica-supported Mo-based olefin metathesis catalysts prepared by classical and SOMC approaches. While FTIR, UV–vis, and XAS analyses are consistent with the presence of isolated Mo dioxo surface sites as the predominant species in all cases, high-field solid-

state ⁹⁵Mo NMR spectra resolve distinct spectroscopic signatures of different surface Mo sites whose relative amounts depend on preparation methods and Mo loadings. In particular, this study identifies a correlation between catalyst activity, the reducibility of metal sites, and ⁹⁵Mo NMR signatures. Detailed first-principles calculations show how the coordination geometry affects ⁹⁵Mo NMR parameters (isotropic chemical shifts and quadrupolar coupling constants) and establish that the most reactive sites associated with deshielded chemical shifts and small quadrupolar coupling constants are strained sites with an acute angle between anionic surface ligands, which are more readily reduced and activated for olefin metathesis.

RESULTS AND DISCUSSION

Catalyst Synthesis and Characterization. Silica-supported molybdenum oxide (pre)catalysts were synthesized by both IWI and SOMC approaches (Section S1.1) on a mesoporous fumed silica support (380 m²/g) for high metal loadings while maintaining appropriate sub-monolayer Mo coverage, thus enabling the acquisition of high-quality spectroscopic data. The IWI catalysts were prepared with Mo weight loadings of 2.5, 4.8, 7.8, and 15.6 wt % Mo determined by elemental analysis, corresponding to approximate surface densities of 0.42, 0.80, 1.3, and 2.6 Mo/nm². These catalysts are denoted **MoIWI**_{2.5}, **MoIWI**_{4.8}, **MoIWI**_{7.8}, and **MoIWI**_{15.6}, respectively. In parallel, a well-defined silica-supported Mo oxo catalyst was prepared by SOMC through the grafting of [Mo(O)₂(OSi(O^tBu)₂)₂](thf) on the same silica support dehydroxylated at 700 °C followed by consecutive thermal treatments under high vacuum and synthetic air,¹⁷ which is denoted **MoSOMC**_{2.3}. This approach yields a (pre)catalyst with a Mo loading of 2.3 wt % according to elemental analysis. The resulting Mo(VI) oxo sites are isolated and free of organic ligands as previously shown¹⁷ with a surface coverage of ca. 0.39 Mo/nm². The transmission FTIR spectrum of this material (Figure S2.1) shows features from both isolated and interacting OH groups with relative

intensities similar to $\text{MoIWI}_{2.5}$. Transmission FTIR spectra of the IWI-derived materials (Figure S2.2) show a decrease in the intensity of the signal from isolated Si–OH species as a function of the Mo loading and indicate the presence of H-bonded and/or interacting –OH species in all cases.

Notably, the Mo K-edge X-ray absorption spectra of Mo oxo (pre)catalysts derived from SOMC and IWI are nearly identical (Section S2.2), indicating that the overall structural motifs of the supported Mo oxo sites are the same. The XANES spectra of all of the (pre)catalysts show prominent pre-edge features at ca. 20006 eV, which is typical of tetrahedral Mo oxides,²¹ as well as edge energies at half maximum of ca. 20015 eV, which confirms that the oxidation state is Mo(VI) by comparison to Mo(VI)O_3 (Figures S2.3 and S2.4). The EXAFS spectra of the (pre)catalysts are also all very similar (Figure S2.5), indicating the presence of isolated Mo dioxo sites consistent with previous EXAFS analyses.¹⁶ $\text{MoIWI}_{15.6}$ shows additional features in both EXAFS and XANES regions, which can be attributed to the presence of Mo oxide particles or oligomers at such a high Mo loading.²¹ The UV–vis spectra of all (pre)catalysts (Figure S2.6) show features at approximately 230 and 280 nm assigned to ligand–metal charge transfer consistent with isolated Mo dioxo sites.^{21,22} $\text{MoIWI}_{15.6}$ shows additional broadening out to 400 nm, which has also been attributed to nanocrystalline Mo oxide particles.²² The XAS and UV–vis spectroscopic features of the (pre)catalysts are thus all mutually consistent and indicate that the predominant Mo surface species in all cases are isolated tetrahedral Mo dioxo sites having two Mo–O–Si linkages to the surface of the silica support, which is consistent with past computational and spectroscopic studies of molybdenum oxides supported on silica at low loadings.^{17,23} $\text{MoIWI}_{15.6}$ additionally possesses a detectable fraction of molybdate polymers and/or clusters formed at high Mo loadings.

Evaluation of Catalyst Performances. All catalysts were tested for 1-nonene metathesis in liquid-phase batch reactions and propene metathesis in gas-phase flow reactions. For the 1-nonene metathesis tests, the catalysts were activated at 70 °C with 2 equiv organosilicon reductant 1-methyl-3,6-bis-(trimethylsilyl)-1,4-cyclohexadiene (**red-1**) per Mo in the presence of 1-nonene (1 M concentration, 1000 olefin:1 Mo). Reactivity tests were run either in open reaction vials to allow for the release of ethylene and higher initial conversions, albeit leading to evaporation and lower conversion, or in closed reaction vials to allow for tracking of the reaction kinetics. In open reaction vials, the initial reaction rates per Mo of the IWI-derived catalysts are 7.3×10^{-2} , 8.5×10^{-2} , 7.8×10^{-2} , and $4.3 \times 10^{-2} \text{ s}^{-1}$ for $\text{MoIWI}_{2.5}$, $\text{MoIWI}_{4.8}$, $\text{MoIWI}_{7.8}$, and $\text{MoIWI}_{15.6}$, respectively (Figure 2a and Section S3.1). Notably, the SOMC-derived catalyst exhibits significantly higher initial activity ($11 \times 10^{-2} \text{ s}^{-1}$) on a per Mo basis than any of the IWI catalysts. The initial *E/Z* selectivities of the SOMC and IWI catalysts at low conversion are similar for all catalysts (2.1–3.1), suggesting that all of the catalysts have similar active site structures²⁴ but with different amounts.

Similar reaction trends are observed when the reactions are conducted in sealed vials though with lower initial rates for all catalysts and much lower product selectivities likely due to post-(metathesis) reactions with ethylene^{25,26} and/or olefin isomerization reactions (Table S3.2). Under these conditions, the differences between $\text{MoSOMC}_{2.3}$ and $\text{MoIWI}_{2.5}$ are even more pronounced, showing maximum metathesis product

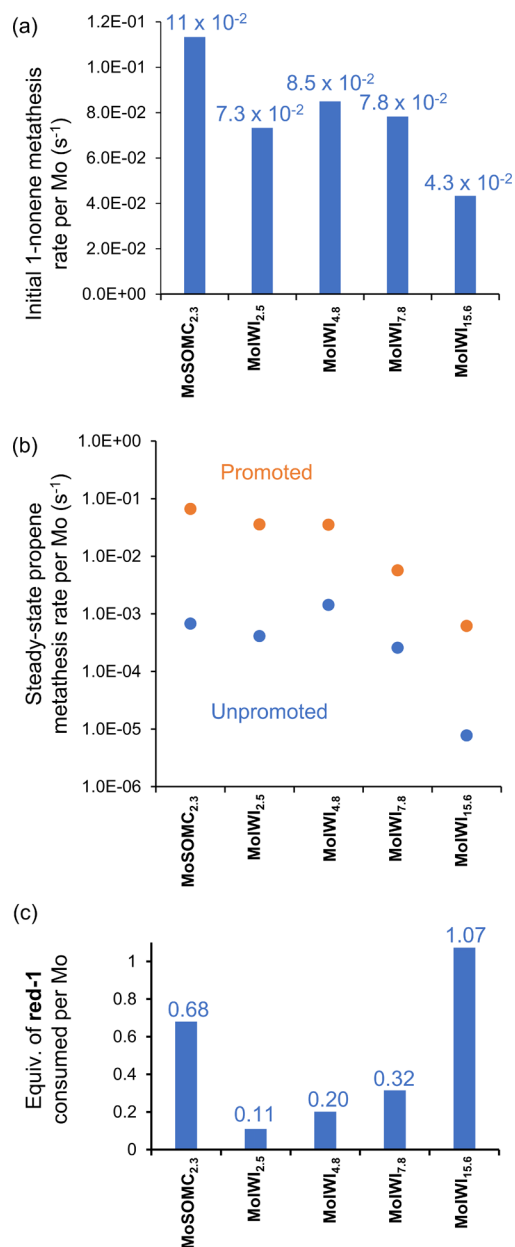


Figure 2. Summary of catalyst reactivity tests. (a) Initial 1-nonene homometathesis rates per Mo measured after 10 min of the reaction time at 70 °C. Reactions were run in open reaction vials under a N₂ atmosphere with 2 equiv **red-1** per Mo and 1000 equiv 1-nonene per Mo in 1,2-dichlorobenzene solvent. (b) Steady-state gas phase propene metathesis reaction rates per Mo either with (orange) or without (blue) 1 mol % 4MEs promoter. Note the log scale (see Figure S3.3 for comparison of data on a linear scale). Catalysts were activated at 400 °C in flowing dry air (3 h) followed by reduction at 500 °C in flowing He (3 h). Reactions were run at 180 °C in 30% propene balanced by He. (c) Equivalents of **red-1** consumed per Mo in each catalyst.

formation rates of 1.5×10^{-2} and 0.1×10^{-2} (mol product [mol Mo]⁻¹ [s]⁻¹), respectively. The selectivities for 1-nonene homometathesis products under these conditions are much lower for $\text{MoIWI}_{2.5}$ (14%) compared to $\text{MoSOMC}_{2.3}$ (73%), indicating that the IWI catalysts have additional types of reactive sites with competing reactivities.

Similar but more pronounced trends in reactivity are observed under steady-state gas-phase propene metathesis

conditions at 180 °C (Section S3.2). After activation at 500 °C in flowing He, the steady-state propene metathesis rates per Mo are 6.5×10^{-4} , 4.0×10^{-4} , 15×10^{-4} , 3.3×10^{-4} , and $0.074 \times 10^{-4} \text{ s}^{-1}$ for **MoSOMC**_{2,3}, **MoIWI**_{2,5}, **MoIWI**_{4,8}, **MoIWI**_{7,8}, and **MoIWI**_{15,6}, respectively (Figure 2b, blue). This trend approximately mirrors what is observed for the initial 1-nonene metathesis rates in the liquid phase at 70 °C, albeit the gas phase reaction rates are much lower despite the higher temperatures, possibly pointing to significantly lower amounts of active sites under these activation conditions. In the presence of 1 mol % of a mixture of organic promoter species (85% 2,3-dimethyl-2-butene and 15% 2,3-dimethyl-1-butene; denoted **4MEs**),¹¹ the steady-state propene metathesis rates increase by 1–2 orders of magnitude for all catalysts (Figure 2b, orange) to 7.8×10^{-2} , 3.6×10^{-2} , 3.7×10^{-2} , 0.74×10^{-2} , and $0.062 \times 10^{-2} \text{ s}^{-1}$ for **MoSOMC**_{2,3}, **MoIWI**_{2,5}, **MoIWI**_{4,8}, **MoIWI**_{7,8}, and **MoIWI**_{15,6}, respectively, corresponding to enhancement factors of ca. 120, 90, 25, 22, and 80. These enhancements in catalyst activity are similar in magnitude to values recently obtained for silica-supported W ($\times 26$ at 250 °C) and Mo ($\times 30$ at 200 °C) oxo catalysts and arise from the ability of the branched promoter olefins to facilitate proton transfers involved in the activation and renewal of catalytic sites.¹¹ The substantial increase in reaction rates and the very different enhancement factors suggest differences in the numbers of active sites formed as a function of the Mo loading and synthesis method. Repeated catalytic tests of **MoSOMC**_{2,3} and **MoIWI**_{2,5} under both unpromoted and promoted conditions show that the rates and promotional effects are consistent and reproducible (Table S3.5). Note that obtaining reproducible catalyst activity requires careful air-free handling and storage protocols (see Section S1.2 for details). The catalytic test results indicate that the SOMC-derived catalyst has a greater fraction of active sites under most reaction conditions compared to the otherwise similar IWI catalyst, showing higher reaction rates by a factor of $\times 1.5$ – 2.0 , depending on exact reaction conditions. Note that the direct titration of the number of active sites by chemical methods (e.g., cross-metathesis with isotopically labelled compounds) remains a challenge because of the constant formation and loss of active sites under different conditions,²⁷ leading to different amounts depending on the titrants used.²⁸ Overall these data indicate that the SOMC synthetic approach is more prone to generate active sites and the number of active sites for the IWI catalysts peaks around 0.8 Mo/nm², which is consistent with literature results.⁹ The marked differences in reactivity across these systems indicate that the numbers of active sites depend strongly on the synthesis procedure (SOMC vs IWI) as well as Mo loading, which contrasts with the similar average structure of the Mo sites observed by Mo K-edge XAS. This led us to further investigate the reactivity and surface structure of the materials.

Reducibility of Silica-Supported Mo Oxo Sites. The fraction of reducible Mo(VI) surface sites was estimated by titration with 1.5 equiv organosilicon reductant **red-1** (Section S3.3). Considering that such reductants typically operate via two-electron reduction processes,²⁹ consumption of 1 equiv **red-1** per Mo is expected for the conversion of Mo(VI) to Mo(IV). Instead, 0.12 and 0.68 equiv **red-1** are consumed for **MoIWI**_{2,5} and **MoSOMC**_{2,3}, respectively (Figure 2c). This suggests a stoichiometric reduction of only 12 and 68% of the total Mo present in these catalysts, indicating that a substantial fraction of Mo is irreducible. For **MoIWI**_{4,8}, **MoIWI**_{7,8}, and

MoIWI_{15,6}, 0.17, 0.29, and 1.07 equiv **red-1** are consumed, respectively, showing that, for the IWI series, the percentage of reducible Mo sites increases nearly linearly as a function of the loading. The high quantity of **red-1** consumed by **MoIWI**_{15,6} may be related to the easier reduction of Mo oxide particles/oligomers compared to isolated Mo oxo sites. As **MoSOMC**_{2,3} consumes a greater equivalence of **red-1** than any of the IWI catalysts except for **MoIWI**_{15,6}, the monodispersed Mo oxo sites generated by the SOMC-based approach are much more readily reducible compared to their counterparts derived from conventional IWI syntheses despite similar XAS and UV–vis characteristics. This accounts, at least in part, for the higher catalytic activity of **MoSOMC**_{2,3} compared to **MoIWI**_{2,5} as reduction is the first step in the initiation of catalytic active sites (Figure 1c). For IWI catalysts, the increasing fraction of reducible sites with increasing the Mo loading is in part attributable to the formation of more reducible Mo oxide particles and oligomers, which are not pre-catalysts for olefin metathesis. This raises questions regarding the precise differences in the structures of the Mo oxo sites resulting from different synthetic protocols and the relation to reducibility and reactivity.

Surface Brønsted and Lewis Acid Sites. Both Brønsted and Lewis acid sites are proposed to be important for olefin metathesis catalytic activity^{11,30} with Brønsted acid sites required for the formation of active sites and Lewis acid sites associated with coordinatively unsaturated Mo centers. Therefore, we examined the presence and nature of such acid sites by low-temperature solid-state ¹⁵N{¹H} cross-polarization (CP) magic angle spinning (MAS) NMR analysis of the fully oxidized (pre)catalysts contacted with ¹⁵N-pyridine and desorbed under high vacuum at room temperature. The chemical shift of adsorbed ¹⁵N-pyridine readily distinguishes Brønsted (209 ppm) and Lewis acid sites (230–280 ppm) and also enables the strength of the Lewis acid sites to be assessed with more shielded ¹⁵N chemical shifts associated with Lewis acid sites of increasing strength.³¹ The ¹⁵N{¹H} CP-MAS NMR spectra of the pyridine adsorbed (pre)catalysts (Figure 3 and Section S4.1) each show isotropic ¹⁵N NMR signals at 299, 287, 270, and 209 ppm though with different relative intensities. The ¹⁵N NMR signals at 299–287 ppm (green-shaded region) and 209 ppm (blue-shaded region) are assigned to pyridine weakly interacting at surface OH sites and pyridinium formed by deprotonation of stronger Brønsted acid sites, respectively, while the ¹⁵N NMR signals at 269 ppm (red shaded region) are assigned to pyridine adsorbed at Lewis acid sites, for example, coordinated to Mo centers. Though not strictly quantitative, the relative integrated ¹⁵N signal intensities (Table S4.1) allow relative quantities of Brønsted and Lewis acid sites to be compared across catalysts. Generally, the relative ¹⁵N signal intensities from pyridinium and pyridine on strong Lewis acid sites increase as a function of the Mo loading, while the signals from weakly interacting pyridine decrease. This indicates a nearly linear increase in both Brønsted and strong Lewis acid site densities as a function of the Mo loading (Figure S4.2), which is consistent with recent results on similar materials from NH₃ adsorption and FTIR spectroscopy.³² However, the distributions of Brønsted and Lewis sites do not account for the trends in catalytic reactivity as **MoIWI**_{7,8-py} and **MoIWI**_{15,6-py}, having the highest relative quantities of both types of acid sites, show diminished catalytic activity, which is likely linked to the presence of Mo oxide oligomers or particles. The two precatalysts with similar Mo

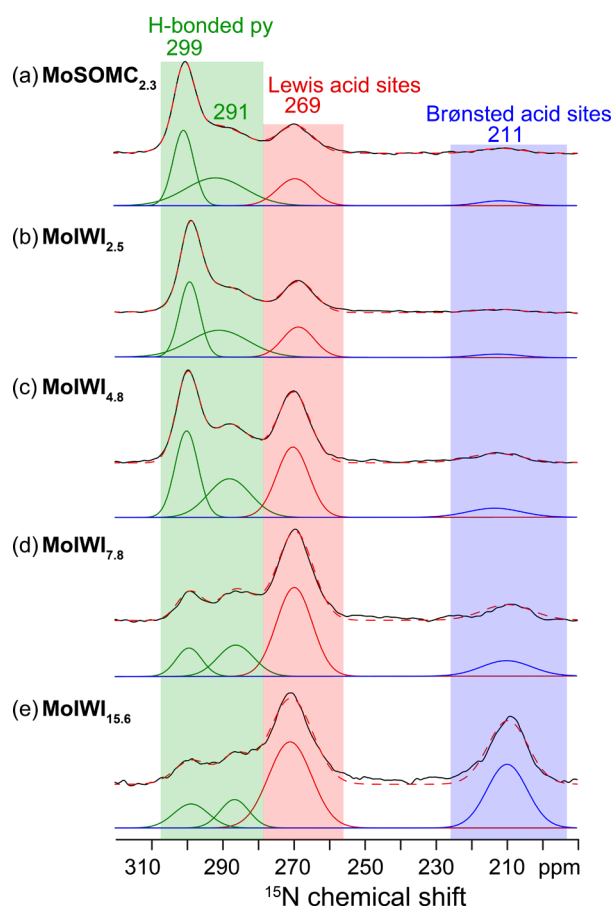


Figure 3. Isotropic region of the solid-state 1D $^{15}\text{N}\{^1\text{H}\}$ CPMAS NMR spectra of (a) $\text{MoSOMC}_{2.3}$, (b) $\text{MoIWI}_{2.5}$, (c) $\text{MoIWI}_{4.8}$, (d) $\text{MoIWI}_{7.8}$, and (e) $\text{MoIWI}_{15.6}$ after adsorption of ^{15}N -pyridine and desorption at room temperature under high vacuum. Spectra were acquired at 14.1 T, 8 kHz MAS, 100 K, and a ^{15}N - ^1H cross-polarization contact time of 2 ms. Black lines are experimental spectra and red dashed lines are lineshape simulations with fit components offset below. See Section S4.1 for full spectra and additional details of the analysis.

loadings prepared via SOMC or impregnation, namely, $\text{MoSOMC}_{2.3}\text{-py}$ and $\text{MoIWI}_{2.5}\text{-py}$, exhibit very similar ^{15}N NMR signal intensities with the SOMC-derived material showing a slightly higher ratio of Brønsted to Lewis acid sites.

Local Environments of Mo Sites from Solid-State ^{95}Mo NMR Analysis. Despite their apparent similarities with other characterization techniques, the different supported Mo oxo (pre)catalysts yield distinct ^{95}Mo NMR spectroscopic signatures that are linked to the structure and reactivity of the surface Mo sites. Solid-state ^{95}Mo MAS NMR spectra of catalyst materials are enabled by high magnetic fields and sensitivity-enhanced detection methods.^{20,33,34} Here, solid-state ^{95}Mo MAS NMR spectra of the different Mo-oxide based (pre)catalysts acquired at different magnetic field strengths and MAS rates resolve signals from different Mo dioxo species. Specifically, analyses of ^{95}Mo NMR spectra acquired at 14.1 T (600 MHz for ^1H) or 28.2 T (1.2 GHz for ^1H), which is the highest stable magnetic field available for solid-state NMR, provide evidence for four spectroscopically distinct Mo oxo species (Figure 4 and Section S4.2) with different associated isotropic ^{95}Mo chemical shifts (δ_{iso}) and quadrupolar coupling constants (C_Q). By using 3.2 mm-diameter MAS NMR rotors

and a combination of techniques for sensitivity enhancement, specifically low-temperature (100 K) measurement conditions, adiabatic double-frequency-sweep (DFS) pulses in the preparatory period,³⁵ and quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG) detection,³⁶ high ^{95}Mo NMR signal sensitivity is obtained at 14.1 T for all samples (Figure 4a,b and Figure S4.3). Each spectrum shows a broad distribution of the ^{95}Mo NMR signal intensity in the -80 to -300 ppm region, which is consistent with past solid-state ^{95}Mo NMR studies of silica-supported Mo oxides using lower magnetic field strengths;^{37,38} however, the ^{95}Mo NMR spectrum of $\text{MoSOMC}_{2.3}$ shows a substantially higher signal intensity in the deshielded -80 to -100 ppm region compared to $\text{MoIWI}_{2.5}$ (Figure S4.4a). The signal intensity in this region also increases as a function of the Mo loading for the IWI catalysts (Figure S4.4b). The differences between the SOMC and IWI-derived catalysts are even more apparent in the solid-state ^{95}Mo MAS NMR spectra of $\text{MoSOMC}_{2.3}$ and $\text{MoIWI}_{2.5}$ measured at 28.2 T (Figure 4c,d and Figure S4.5) where the very high magnetic field strength and fast-MAS conditions yield much better spectral resolution³⁹ albeit with lower signal-to-noise ratios due to the smaller rotor volumes (1.3 mm rotor diameter) and higher temperature (265 K). Fitting the experimental ^{95}Mo spectra of all the (pre)catalysts to a minimum number of simulated lineshapes with the same set of spectroscopic parameters (Tables S4.2 and S4.3) provides evidence for four spectroscopically distinct ^{95}Mo species. Specifically, three ^{95}Mo NMR signals are identified for $\text{MoSOMC}_{2.3}$ at 28.2 T: site I: $\delta_{\text{iso}} \approx -95$ ppm and $C_Q \approx 3.3$ MHz; site II: $\delta_{\text{iso}} \approx -126$ ppm and $C_Q \approx 4.0$ MHz; and site III, $\delta_{\text{iso}} \approx -135$ ppm and $C_Q \approx 6.1$ MHz. The same three signals are observed for $\text{MoIWI}_{7.8}$ along with an additional signal attributed to site IV with $\delta_{\text{iso}} \approx -47$ ppm and $C_Q \approx 7.3$ MHz. Based on signal-to-noise ratios of these spectra, uncertainties for these δ_{iso} values are estimated as ± 10 ppm and for the C_Q values as ± 0.5 MHz (see Section S4.2). The ^{95}Mo NMR spectra of all five (pre)catalysts measured at 14.1 T can each be fit to overlapping signals from site I and site II (Figure S4.3) though the spectrum of $\text{MoIWI}_{15.6}$ shows some additional complexity that may be related to the presence of Mo oxide particles as also evidenced by XAS and UV-vis spectroscopy (vide supra). Sites III and IV though likely present in all the IWI-derived (pre)catalysts are not resolved at 14.1 T and indeed would be broadened beyond detection due to second-order quadrupolar interactions at the lower field and the larger associated C_Q values of these sites (Figure S4.6). The resolution of signals from additional high- C_Q ^{95}Mo sites using very high magnetic field strengths (28.2 T) and fast MAS conditions (50 kHz) highlights the power of such state-of-the-art techniques for analysis of catalytic surfaces, especially if the signal sensitivity can be improved further, for instance, by hyperpolarization^{40–42} and/or indirect detection⁴³ methods.

Overall, the ^{95}Mo MAS NMR spectra resolve important differences between the SOMC-derived (pre)catalyst $\text{MoSOMC}_{2.3}$ and the other materials, specifically the prominence of the relatively narrow and deshielded signal from site I. Notably, the ^{95}Mo NMR signal intensity from site I, when normalized by the total number of scans in each NMR experiment so as to be proportional to the total quantity of site I in each material, is approximately the same for $\text{MoIWI}_{4.8}$, $\text{MoIWI}_{7.8}$, and $\text{MoIWI}_{15.6}$ (Figure S4.7), indicating that site I is formed at intermediate loadings for IWI catalysts (between 0.4 and 0.8 Mo nm^{-2}) and that the different reactivities of

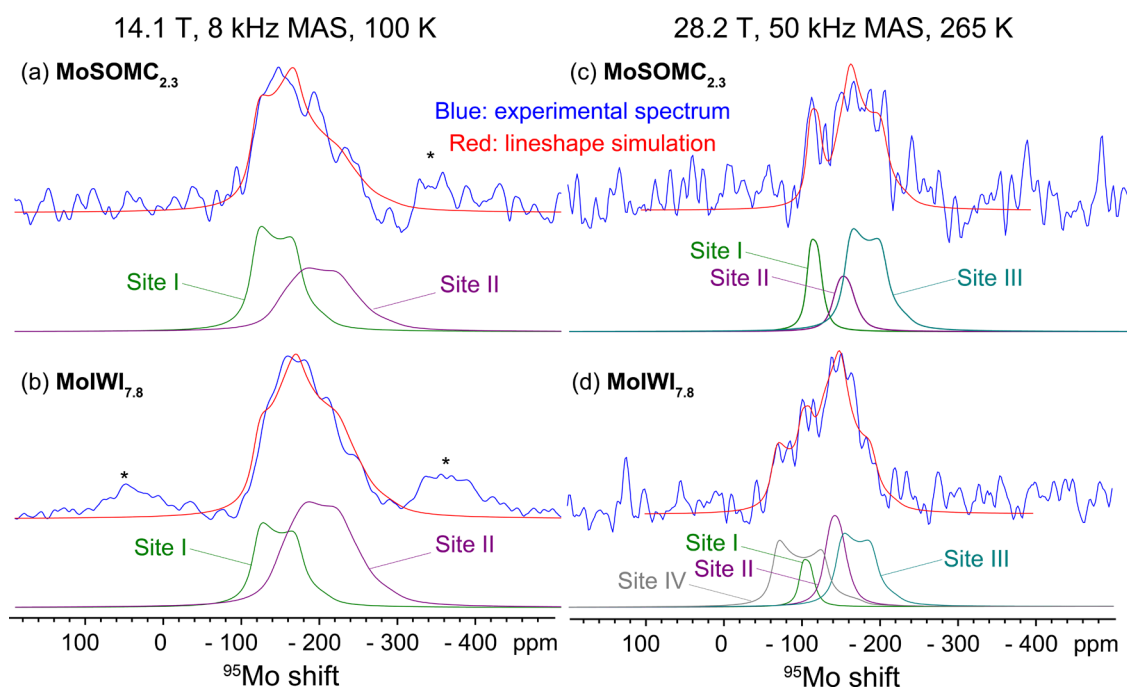


Figure 4. Solid-state ^{95}Mo QCPMG-MAS-NMR reconstructed echo spectra (blue) along with lineshape simulations (red) and spectral deconvolutions of (a, c) $\text{MoSOMC}_{2,3}$ and (b, d) $\text{MoIWI}_{7,8}$ acquired at (a, b) 14.1 T, 100 K, and 8 kHz MAS or (c, d) 28.2 T, 265 K, and 50 kHz MAS. Asterisks indicate spinning sidebands. See Section S4.1 for complete solid-state ^{95}Mo NMR data.

$\text{MoIWI}_{4,8}$, $\text{MoIWI}_{7,8}$, and $\text{MoIWI}_{15,6}$ are modulated by the formation of different types of surface species such as Mo oxide oligomers and particles. The ratio of site I in $\text{MoSOMC}_{2,3}$ to $\text{MoIWI}_{2,5}$ is approximately $\times 2.5$, paralleling the $\times 1.5$ – 2.0 increase in catalyst activity. This indicates that Site I is an easily reduced site that is linked to catalyst activity, particularly at sub-monolayer Mo loadings. The large differences in ^{95}Mo δ_{iso} and C_Q values for Mo sites of nominally the same stoichiometry (i.e. Mo dioxo with two siloxide linkages) suggest significant differences in the local structure of the Mo centers of the (pre)catalysts, which we hypothesize are linked to their reactivity.

Relating Structure, Electronics, and Spectroscopic Parameters of Mo Oxo Surface Sites. To assess the possible origins of these different NMR signatures and establish the specific relations of the geometry, electronic structure, and ^{95}Mo NMR parameters, we turned our attention to first-principles calculations based on density functional theory (DFT). Calculated chemical shielding tensor components (σ_{ii}) are related to experimentally measured chemical shifts (δ_{ii}) by the relation $\delta_{ii} = \frac{\sigma_{\text{ref}} - \sigma_{ii}}{1 - \sigma_{\text{ref}}}$, where σ_{ref} is the chemical shielding of a reference compound. To verify the accuracy of our calculations, calculated parameters were benchmarked on the experimental solution and/or solid-state ^{95}Mo NMR spectra of a reference library of 10 monomeric molecular Mo(VI) mono and dioxo compounds^{44–46} (Section S5). Molecular geometries for the reference compounds were optimized using the B3LYP⁴⁷ functional in combination with the 6-31g(d)⁴⁸ and lan12dz⁴⁹ basis sets for main-group and transition metal elements, respectively. The anisotropic chemical shielding (σ) and electric field gradient (efg) tensors were calculated (Section S6.1) with the ADF 2019 code using revised Perdew–Burke–Ernzerhof functional⁵⁰ in combination with TZ2P and QZ4P⁵¹ basis sets for main-group elements and Mo, respectively, with the all-electron relativistic zeroth-

order regular approximation (ZORA)⁵² in its spin–orbit two-component form. A linear correlation to experimental results (Section S6.2) shows excellent agreement between calculated ^{95}Mo σ_{iso} and measured ^{95}Mo δ_{iso} values (Figure S6.1). Calculated quadrupolar coupling constants were higher than the measured values by 0.2–1.6 MHz (Tables S5.2 and S6.1), which can be attributed to the influence of dynamic averaging of efg tensors as previously observed.^{20,53}

We then sought to understand the relation of NMR parameters (^{95}Mo δ_{iso} and C_Q) of Mo dioxo sites and their local structures by computationally screening their response to ligand geometry and the number and types of coordinating ligands for simple molecular models. Simplified computational models for Mo dioxo surface sites having the structure $[\text{Mo}(\text{O})_2(\text{OSiF}_3)_2]\text{L}_n$ were considered where L = a neutral coordinating ligand (e.g., dimethyl ether) as a model for a surface siloxane moiety and $n = 0, 1,$ or 2 . ($\text{SiO}-\text{Mo}(\text{O})_2-\text{SiO}$) angles (α) were systematically varied (Figure 5a), while all atom positions were relaxed to allow physically meaningful ($\text{Mo}-\text{O}$) distances. The ($\text{O}=\text{Mo}=\text{O}$) angle was generally unaffected, varying only 3° (from 107.6 to 104.6°) when α was changed from 87.5 to 135.0° . Overall, several trends are observed (Figure 5b–d; Section S6.3): increasing the coordination number generally deshields the ^{95}Mo δ_{iso} as does decreasing α . As α is decreased below the relaxed value for the $n = 0$ model (ca. 107°), the ^{95}Mo C_Q increases. In this regime, the addition of neutral coordinating ligands increases C_Q as well. When α is increased above 107° , the C_Q also tends to increase, though, in this regime, adding additional neutral ligands typically decreases C_Q . Similar trends are observed for a range of models of Mo dioxo surface sites, including models bearing neutral silanol or siloxane L ligands and molybdasiloxane rings of different sizes (Section S6.4).

Based on these trends, we can establish the primary differences between the four ^{95}Mo species observed in the

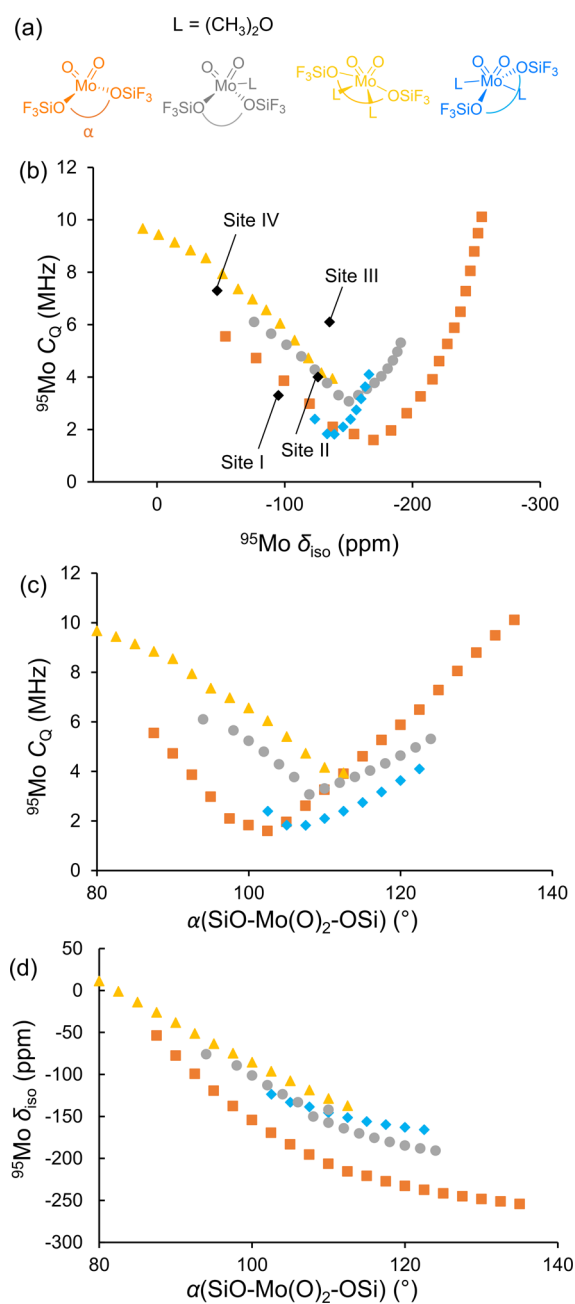


Figure 5. (a) Simplified computational models for Mo dioxo sites with different coordination numbers. (b) $^{95}\text{Mo } C_Q$ vs δ_{iso} , (c) $^{95}\text{Mo } \delta_{\text{iso}}$ vs $\alpha(\text{SiO}-\text{Mo}(\text{O})_2-\text{OSi})$, and (d) $^{95}\text{Mo } C_Q$ vs $\alpha(\text{SiO}-\text{Mo}(\text{O})_2-\text{OSi})$ for models without a neutral coordinating ligand (orange), with one neutral ligand $L = \text{O}(\text{CH}_3)_2$ (gray), or with two neutral ligands in *cis* (yellow) or *trans* (blue) configurations.

different Mo oxo precatalysts. The signal from site I ($\delta_{\text{iso}} \approx -91$; $C_Q \approx 3.3$ MHz), the presence of which appears to be related to catalytic activity, shows a smaller $^{95}\text{Mo } C_Q$ than the other species, suggesting a low-coordinate tetrahedral site. Meanwhile, the relatively deshielded δ_{iso} value indicates an $\alpha(\text{SiO}-\text{Mo}(\text{O})_2-\text{SiO})$ angle of ca. 90° by comparison to the simplified computational models. Thus, we assign site I to a low-coordinate “strained” surface site with an acute ($\text{SiO}-\text{Mo}(\text{O})_2-\text{SiO}$) angle. Site II ($\delta_{\text{iso}} \approx -126$; $C_Q \approx 4.0$ MHz) most likely corresponds to a “relaxed” tetrahedral surface site with one or two coordinated siloxane moieties. Site III ($\delta_{\text{iso}} \approx -135$; $C_Q \approx 6.1$ MHz) does not directly resemble any of the

simplified small models, but its ^{95}Mo NMR parameters are similar to those measured for the silica-supported Mo oxo siloxide $\text{Mo}(\text{O})_2(\text{OSi}(\text{O}^t\text{Bu})_3)_2/\text{SiO}_{2-700}$ ($\delta_{\text{iso}} \approx -150$ and $C_Q \approx 5.0$ MHz; Section S5.5) as well as those calculated for model complexes having coordinated neutral siloxane or silanol ligands (Figure S6.3). The high C_Q and shielded δ_{iso} values of site III thus indicate a high-coordinate surface site with a relatively large $\text{SiO}-\text{Mo}(\text{O})_2-\text{OSi}$ angle and at least one coordinated neutral ligand such as a surface siloxane bridge. The highly deshielded signal from site IV ($\delta_{\text{iso}} \approx -47$; $C_Q \approx 7.3$ MHz), which is only detected for **MoIWI**_{7,8} at 28.2 T because of the large C_Q is most plausibly a hexacoordinate Mo dioxo site, though a small quantity of oxidic nanoparticles or clusters with signals in this region^{37,54,55} may be present at these relatively high Mo loadings and cannot be excluded. Overall, the ^{95}Mo NMR parameters provide highly resolved structural insights into the supported Mo oxo species and show that each of the (pre)catalysts exhibits a distribution of Mo dioxo sites with several different geometries and coordination environments.

Notably, we have recently shown that ^{95}Mo chemical shifts directly probe the electronic structure of homogeneous Mo alkylidyne catalysts for alkyne metathesis,²⁰ responding to the positions of HOMO and LUMO as well as the HOMO–LUMO gap and thereby providing a direct experimentally accessible link to reactivity. Since geometric strain has been invoked in the reactivity of supported Mo oxo catalysts,⁹ we hypothesized that ^{95}Mo chemical shifts can here provide a link between the ligand geometry, positions of frontier molecular orbitals (FMOs) and, correspondingly, reactivity. Indeed, for the simplified model $[\text{Mo}(\text{O})_2(\text{OSiF}_3)_2]$, a strong relation is observed between the calculated LUMO energy and $\alpha(\text{SiO}-\text{Mo}(\text{O})_2-\text{OSi})$ (Figure 6a) as well as $^{95}\text{Mo } \delta_{\text{iso}}$ (Figure 6b). Very similar relations are observed for the five- and six-coordinate models (Section S6.5). As α values are decreased below 115° (increasing strain), the LUMO energy decreases nearly linearly. The HOMO–LUMO gap for these compounds is driven primarily by the decrease in the LUMO energy as the HOMO energy is nearly constant (Section S6.5) as it is localized on the oxo ligands (vide infra), the geometry of which changes very little. A strained geometry around the metal center thus results in decreasing LUMO energy, which is consistent with the higher reducibility of Mo and greater reactivity of the surface species as well as more deshielded ^{95}Mo chemical shifts. Indeed, a similar link between ^{95}Mo chemical shifts and reducibility was recently found for molecular Mo(VI) oxo compounds with different (fluor)alkoxy ligands.⁴⁵ The manifestation of this effect in the ^{95}Mo chemical shifts of surface species provides an experimental link between their geometry, electronic structure, and reactivity, which can be directly accessed and used to assess the performance of heterogeneous catalyst materials.

Orbital Analysis of ^{95}Mo NMR Chemical Shifts and Links to Electronic Structure. The components of the chemical shielding tensor can be decomposed into diamagnetic and paramagnetic as well as spin orbit contributions ($\sigma_{ii} = \sigma_{ii,\text{dia}} + \sigma_{ii,\text{para+SO}}$).⁵⁶ The diamagnetic contribution is typically constant for a given nucleus.⁵⁶ Changes in the chemical shielding arise mostly from $\sigma_{ii,\text{para+SO}}$, which the Ramsey equation⁵⁶ (Figure 7a) relates to the overlap of filled/occupied (Ψ_{occ}) and virtual/vacant (Ψ_{vac}) orbitals that are coupled by the angular momentum operator \hat{L}_i of the principal axis i . Since $\sigma_{ii,\text{para+SO}}$ is inversely proportional to the energy difference

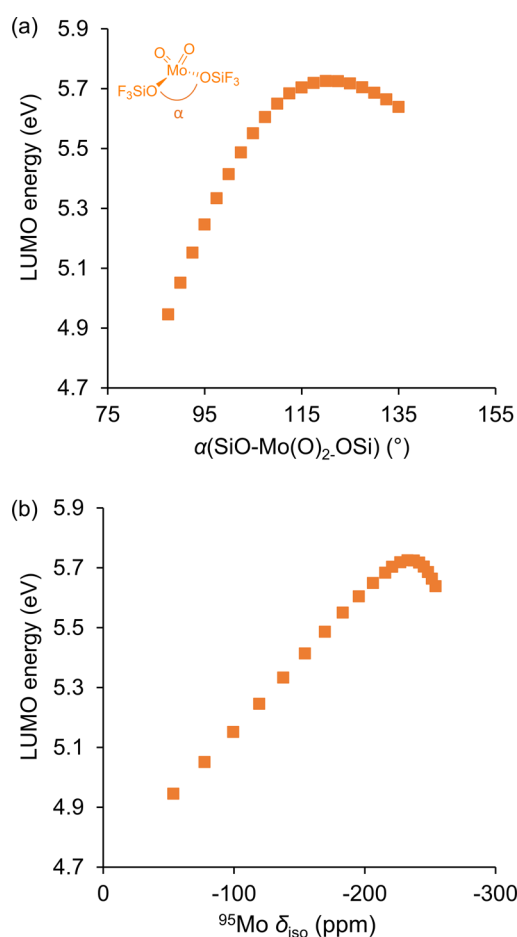


Figure 6. Calculated LUMO energy as a function of (a) $\alpha(\text{SiO-Mo}(\text{O})_2\text{-OSi})$ angle and (b) $^{95}\text{Mo } \delta_{\text{iso}}$ for $[\text{Mo}(\text{O})_2(\text{OSiF}_3)_2]$ models.

between these occupied and vacant orbitals, $\Delta E_{\text{vac-occ}}$, the closer the orbitals are in energy, the greater the deshielding of the corresponding chemical shielding tensor component. Orbital analyses of chemical shift tensor components have been used to understand reactivity patterns of coordination compounds, mostly focusing on the chemical shift/shielding tensors of nuclei in ligand atoms bound to a metal center.^{57–62} Our most recent work on molecular Mo-based alkyne metathesis catalysts showed that orbital analysis of chemical shift/shielding tensors of metal nuclei (i.e., ^{95}Mo) can provide more direct links to the frontier molecular orbitals (FMOs) involved in reactivity.²⁰

In order to relate the local geometry and ^{95}Mo chemical shift tensors in the Mo dioxo complexes discussed above, we performed DFT calculations of a smaller computational model, namely, $[\text{Mo}(\text{O})_2(\text{F})_2]$, where $\alpha(\text{F-Mo}(\text{O})_2\text{-F})$ angles were set to 87.5, 107.5, or 135.0°. This further simplified ligand set was chosen to facilitate orbital analysis. The relation between the geometry and ^{95}Mo chemical shielding tensors follows the same trend as for the $[\text{Mo}(\text{O})_2(\text{OSiF}_3)_2]$ series (Section S6.6) with σ_{iso} becoming more deshielded with decreasing $\alpha(\text{X-Mo-X})$. Also, like the $[\text{Mo}(\text{O})_2(\text{OSiF}_3)_2]$ series, the $^{95}\text{Mo } \sigma_{\text{iso}}$ is largely driven by changes in σ_{11} , which is oriented between the two oxo ligands and defines the z axis (Figure 7b).

Orbital analysis of the ^{95}Mo chemical shielding tensors based on symmetry arguments anchored on group theory reveals the specific relations of geometry, FMOs, and chemical

shift response. From natural chemical shift (NCS) and natural bonding orbital (NBO) analyses (Section S6.7), the occupied natural localized molecular orbitals (NLMOs) that contribute most to the $^{95}\text{Mo } \sigma_{11}$ of $[\text{Mo}(\text{O})_2\text{F}_2]$ (C_{2v} symmetry) are the $\sigma(\text{Mo-O})$ NLMOs followed by $\pi(\text{Mo-O})$ NLMOs (Figure 7c,d and Figures S6.10 and S6.11). Both these contributions to σ_{11} decrease in magnitude with increasing $\alpha(\text{F-Mo-F})$ angle (Figure 7d). Multiple d orbitals contribute to $\sigma(\text{Mo-O})$, specifically $d_{x^2-y^2}$ and d_{yz} ; similarly, d_{xy} and d_{xz} orbitals contribute to $\pi(\text{M-O})$ (Figure 7c). The symmetry of the coupled virtual orbitals can then be deduced using group theory. Considering that \hat{L}_z is of a_2 symmetry in the C_{2v} point group (Table S6.10), orbitals of irreducible representation a_i can only couple to those of representation a_j , while b_i can only couple to b_j with $i = (1,2)$ and $j = (2,1)$. Hence, the occupied orbitals contributing to $\sigma(\text{Mo-O})$ NLMOs, $d_{x^2-y^2}$ (or d_{yz}) with an a_1 (or b_2) symmetry, will only couple to virtual orbitals with an a_2 (or b_1) symmetry, namely, d_{xy} (or d_{xz}). On the other hand, occupied orbitals contributing to $\pi(\text{Mo-O})$ NLMOs, for example, d_{xy} (or d_{xz}) with an a_2 (or b_1) symmetry, will only couple to virtual orbitals with an a_1 (or b_2) symmetry, namely, $d_{x^2-y^2}$ (or d_{yz}). These couplings are depicted in Figure 7e. Note that the HOMO, with a b_2 symmetry (Figure S6.13), does not contribute to the σ_{11} component of the ^{95}Mo chemical shielding tensor since it corresponds to lone pairs on the oxo ligands and has no metal-based character. Although the d_z orbital (a_1 symmetry) would not be expected to contribute to the $^{95}\text{Mo } \sigma_{11}$ because it is oriented along the z axis, it is mixed with other a_1 symmetric orbitals, modulating their contribution as a function of the $\alpha(\text{F-Mo-F})$ angle (see Figures S6.12 and S6.13 and accompanying discussion).

Examining all 17 FMOs (12 occupied, mostly based on ligand p orbitals, and 5 virtual, mostly based on metal d orbitals) as a function of the $\alpha(\text{F-Mo-F})$ angle shows that the occupied orbitals remain very similar in energy (Figure S6.15). On the other hand, the energy of the virtual orbitals varies more significantly and, consequently, chemical shielding is mostly affected by the positions of the virtual orbitals. For the $^{95}\text{Mo } \sigma_{11,\text{para+SO}}$ (Figure 7f), the virtual orbital with an a_2 symmetry (LUMO+1) contributes the most, followed by orbitals with an a_1 symmetry (LUMO and LUMO+3, which have mixed characters). Increasing $\alpha(\text{F-Mo-F})$ brings the fluoride ligands toward the xy plane, leading to a larger overlap between F p orbitals and Mo d_{xy} (a_2) and $d_{x^2-y^2}$ (a_1) orbitals, which increases the energy of the LUMO and nearby virtual orbitals, consequently driving and increasing ^{95}Mo chemical shielding (decreasing the chemical shift). The next contributors are the virtual orbitals with b_1 and b_2 symmetries, namely, LUMO+2 and LUMO+4, respectively. Increasing $\alpha(\text{F-Mo-F})$ decreases the overlap between F and the d_{xz} (b_1)/ d_{yz} (b_2) Mo orbitals, lowering their energy, which results in a marginal increase of their contribution to the overall σ_{11} . Notably, averaging the contributions to virtual a_2 and b_1 orbitals (coupling to filled orbitals with a $\sigma(\text{M-O})$ character) or a_1 and b_2 orbitals (coupling to filled orbitals with a $\pi(\text{M-O})$ character) gives the same contributions obtained from NCS-NBO analysis from filled $\sigma(\text{M-O})$ or $\pi(\text{M-O})$ NLMOs, respectively. These orbital couplings are indicated in Figure 7g.

Overall, the orbital analyses show that the ^{95}Mo chemical shift is mostly driven by the energy of the low-lying virtual orbitals that respond to the position of the anionic X ligands, explaining the strong relation of the LUMO energy and local geometry, hence rationalizing the observed trends. Namely,

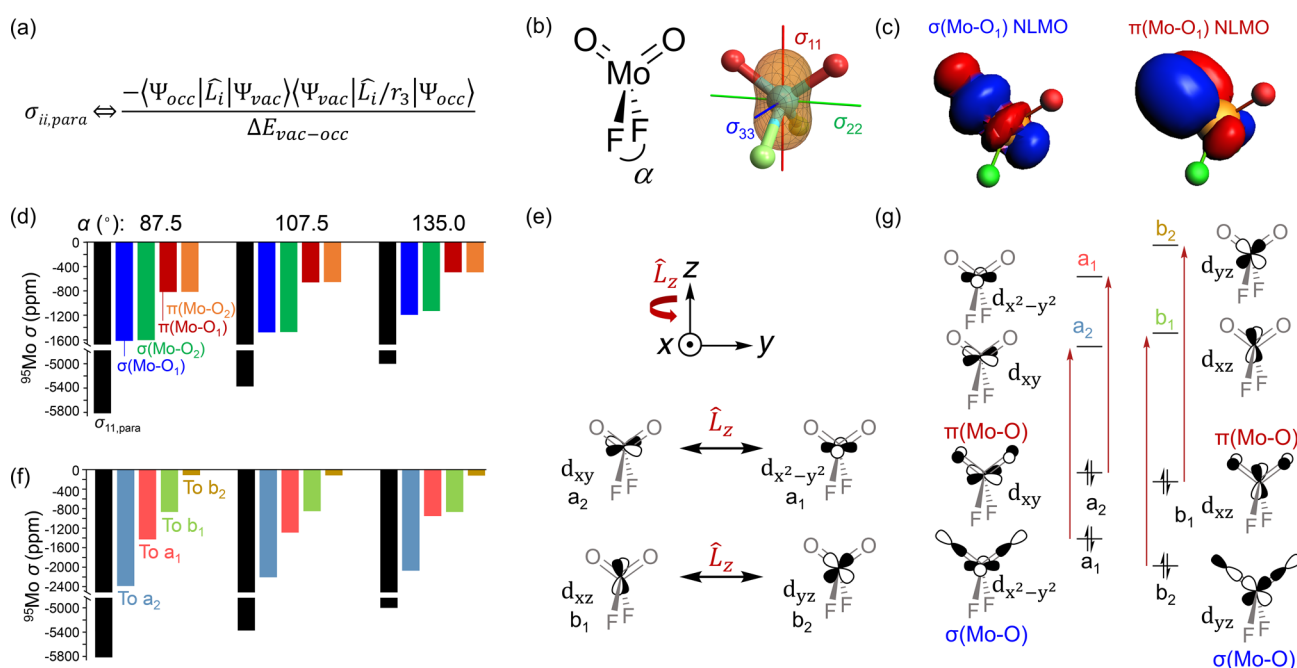


Figure 7. Summary of orbital analysis of ^{95}Mo chemical shielding tensors. (a) Ramsey equation relating chemical shielding to the overlap of occupied and vacant orbitals and the energy difference between these orbitals. (b) ^{95}Mo chemical shielding tensor orientation for $[\text{Mo}(\text{O})_2\text{F}_2]$. (c) Relevant NLMOs. (d) Contributions to the ^{95}Mo σ_{11} for $[\text{Mo}(\text{O})_2\text{F}_2]$ models with different $\alpha(\text{F}-\text{Mo}(\text{O}_2)-\text{F})$ angles arising from the occupied NLMOs shown in c. (e) Orbital couplings relevant to the ^{95}Mo chemical shielding. (f) Contributions of virtual orbitals of given symmetry to the ^{95}Mo σ_{11} for $[\text{Mo}(\text{O})_2\text{F}_2]$ models with different $\alpha(\text{F}-\text{Mo}(\text{O}_2)-\text{F})$ angles. (g) Simplified excerpt of the MO diagram showing the couplings from occupied to virtual orbitals. See Section S6.7 for details of the orbital analysis.

decreasing the $\alpha(\text{X}-\text{Mo}-\text{X})$ angle and increasing strain at the Mo center decreases the energy of low-lying vacant FMOs, resulting in more deshielded (higher chemical shift) ^{95}Mo NMR signatures of more readily reducible and reactive Mo dioxo sites. The prominence of the deshielded ^{95}Mo NMR signal from site I in the solid-state ^{95}Mo NMR spectra of **MoSOMC**_{2,3} is thus linked to the high fraction of reducible Mo sites as well as the higher catalytic activity of this material.

CONCLUSIONS

All Mo-based catalysts discussed in this work contain similar isolated Mo dioxo surface sites according to their XAS signatures but show different catalytic olefin metathesis activities. The activity of these catalysts is related to the intensity of the deshielded ^{95}Mo NMR signal attributed to a specific site I; these sites are particularly abundant in **MoSOMC**_{2,3}, a catalyst prepared via SOMC using highly dehydroxylated silica and a thermolytic molecular precursor.¹⁴ In the corresponding catalyst prepared by impregnation, they are present in a significantly lower amount than in the SOMC-derived catalyst at the same Mo loading. Similar trends are found upon the titration of the amounts of reducible sites with **red-I**, correlating activity, number of reducible sites, and quantity of site I. Notably, detailed DFT analyses indicate that the deshielded ^{95}Mo chemical shifts of site I best match “strained” Mo sites associated with small $\alpha(\text{SiO}-\text{Mo}-\text{OSi})$ angles. Small $\alpha(\text{SiO}-\text{Mo}-\text{OSi})$ angles lead to low-energy LUMOs and thereby increased reducibility, which is consistent with the experimental correlations between activity, reducibility, and NMR signatures. This shows that high olefin metathesis activity of Mo oxo based catalysts requires “strained” tetra-coordinated Mo sites that are easily reduced, which is consistent with the proposal that Mo(VI) alkylidenes,

the key intermediates for olefin metathesis, are formed via reaction of olefins with low-valent Mo(IV) sites that are generated via reduction of the Mo(VI) di-oxo precatalytic sites (Figure 1c).³⁰ The propensity to form more strained sites by SOMC is likely due to the preparation method that involves the use of highly dehydroxylated silica, which itself exhibits a high fraction of strained siloxane bridges,^{63,64} and is carried out in the absence of water that can promote dissolution/precipitation and reorganization of surface species.

We note also that though the relative amounts of reducible sites as measured across the various catalysts differ, for example, by a factor of ca. 6 for **MoSOMC**_{2,3} compared to **MoIWI**_{2,5} with the same Mo loading, these differences are larger than the differences of their catalytic reaction rates, ca. 1.5–2.0, indicating that other factors in addition to reducibility are at play. For example, the presence of Brønsted acid sites, evidenced here by solid-state $^{15}\text{N}\{^1\text{H}\}$ CPMAS NMR of pyridine-adsorbed samples, has been proposed to be involved in generating the active high-valent metal(VI) alkylidenes from low-valent M(IV) species.^{10,30,65,66} As recently shown for both Mo and W-based heterogeneous catalysts, this process is dynamic and can be accelerated by the presence of organic mediator species such as branched olefins, which act as proton shuttles,¹¹ yielding almost 2 orders of magnitude in the increase in catalytic activity for **MoSOMC**_{2,3}. The different propene metathesis enhancement factors observed on the addition of branched promoter olefins for the SOMC ($\times 120$) and classical catalysts ($\times 22$ – 90) show how the dynamic equilibrium of active and inactive Mo sites, which can be altered by the composition of the gas feed, also depends on the strain and reducibility of surface sites, which depend in turn on the synthetic approach. The mutual spatial proximities of reactive (strained) di-oxo Mo(VI) sites and Brønsted acid sites

are also likely key to generating active sites, a process that can be promoted by olefins. Accessing and tuning such parameters will provide further opportunities to improve catalytic performances.

This study also highlights the power of high-field solid-state ^{95}Mo NMR spectroscopy, which is able not only to identify and distinguish various surface Mo sites but also to relate their signatures to specific electronic structures and coordination environments. While Mo K-edge XAS is not able to distinguish significant differences between the various catalysts prepared in this study, the ^{95}Mo NMR signatures of Mo dioxo surface sites are extremely sensitive to their local environments. The ^{95}Mo chemical shifts (δ_{iso}) vary across 200 ppm, depending on the $\alpha(\text{SiO}-\text{Mo}-\text{OSi})$ angles, while the quadrupolar coupling constants (C_Q) provide clear information on the local geometry (tetra-, penta-, and hexa-coordinated sites). Furthermore, our computational analyses also indicate that the ($\text{O}_1=\text{Mo}=\text{O}_2$) angles of the dioxo unit are minimally perturbed by the local environment and geometry (α and coordination number); distinguishing between various di-oxo sites would thus not be possible by Raman spectroscopy, which otherwise can effectively distinguish mono- and di-oxo species.⁶⁷

While the use of multiple complementary characterization techniques is crucial to ascertain the structures of metal (surface) sites, our analyses demonstrate how NMR (like EPR spectroscopy for paramagnetic species) provides unique information on the electronic structure because of the symmetry of the magnetic moment operator, \hat{L}_i . This operator, having the same symmetry as the rotational operator R_i , probes directly the FMOs of metal sites with σ and π -symmetries, linking spectroscopic signatures to site-specific descriptors for reactivity. This motivates further applications of such approaches to understand electronic structures and (re)activity of transition metal sites across functional materials such as heterogeneous catalysts.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.3c02201>.

Experimental section, additional catalyst characterization, catalytic reactivity data, characterization of reference compounds, and additional solid-state NMR and DFT results (PDF)

Cartesian coordinates of all calculated structures (ZIP)

Accession Codes

CCDC 2117644 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Christophe Copéret – Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; orcid.org/0000-0001-9660-3890; Email: ccoperet@ethz.ch

Authors

Zachariah J. Berkson – Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; orcid.org/0000-0002-2157-4172

Ran Zhu – Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Christian Ehinger – Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; orcid.org/0000-0003-2013-7429

Lukas Lätsch – Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; orcid.org/0000-0002-0125-6396

Stefan P. Schmid – Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland

Darryl Nater – Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland

Stephan Pollitt – Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; PSI, CH-5232 Villigen, Switzerland; orcid.org/0000-0002-6589-0134

Olga V. Safonova – PSI, CH-5232 Villigen, Switzerland; orcid.org/0000-0002-6772-1414

Snædís Björgvinsdóttir – Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; orcid.org/0009-0005-5783-4887

Alexander B. Barnes – Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich CH-8093, Switzerland; orcid.org/0000-0003-3748-8508

Yuriy Román-Leshkov – Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0002-0025-4233

Gregory A. Price – Applied Sciences, bp Innovation & Engineering, BP plc, Saltend, Hull HU12 8DS, U.K.; orcid.org/0000-0003-0904-7000

Glenn J. Sunley – Applied Sciences, bp Innovation & Engineering, BP plc, Saltend, Hull HU12 8DS, U.K.

Complete contact information is available at:

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Notes

The authors declare no competing financial interest.

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