

Understanding Control of Speciation of Molybdenum Oxides in MFI Type Zeolites

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1 Understanding Control of Speciation of Molybdenum Oxides in MFI Type Zeolites

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Abstract

Metal oxide-impregnated zeolites are employed in a wide variety of catalytic reactions, including in methane dehydroaromatization (MDA). The most studied catalysts for MDA are Mo carbides supported on H-ZSM-5, formed through carburization of Mo-oxide loaded H-ZSM-5. Complete structural understanding of these materials has not yet been achieved, limiting the potential for rational catalyst design for improved performance. We hereby pursue experimental and theoretical investigations of these catalyst precursors to uncover rational design principles. We employ temperature-programmed oxidation and extended X-ray absorption fine structure experiments, density functional theory calculations, and QuantEXAFS analysis to unveil Mo-oxide speciation in H-ZSM-5. We demonstrate that Mo-oxides exist within these systems as a combination of various motifs and the relative abundance of these species is controlled through tailored preparation methods. The synergies exploited in this work may be leveraged in other related catalysts. The conclusions drawn are applicable to other relevant applications of zeolite-supported metal oxides.

1. Introduction

Zeolites are crystalline (alumino-)silicate nanoporous materials with precise topologies and well-defined pores. Each zeolite possesses a particular pore architecture with specific channel diameters, 8 dimensionalities (1-3D and combinations thereof), cages, and pockets. Substitution of Si sites in the zeolite 4 framework by trivalent elements such as Al leads to a negative charge that is compensated by 5 extraframework cations. During synthesis, common cations are H^+ , Na^+ , or Ca^{2+} , but these cations may be 6 postsynthetically exchanged with other species, including transition metals such as Fe, Co, Ni, and Cu. 7 The specific interaction between the extraframework cation, or cationic metal complex, and the trivalent 8 framework atom, as well as the confinement acquired by the metal cation based on its location within the 9 zeolite pore structure, endows these metal-zeolite composites with unique properties that make them 10 active, selective, and stable catalysts in a variety of industrially and environmentally relevant reactions. 11

These reactions have applications in and beyond oil refining^[1, 2], biomass conversion^[3, 4], gas 12 valorization^[5-8], methanol to hydrocarbon conversion^[9-11], and NO_x selective reduction^[12-16]. 13

To establish rigorous structure-activity relations in metal-zeolite catalysts, it is of utmost importance 14 to be able to characterize the local structure of these dispersed metal cation complexes within zeolite 15 channels. This task has proven to be complicated given both the dispersion of the metal sites and the added 16 complexity derived from the zeolite structure and texture. As with most catalytic materials, the most 17 promising route to obtain rigorous structural characterization of metal-zeolite catalysts is by applying 18

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35 19 various relevant characterization techniques in concert with computational calculations. This integrated

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37 20 approach is especially valuable given that the synthesis techniques employed in preparation of metal-

38 21 zeolite catalysts (by incipient wetness impregnation, ion exchange, or solid-state ion exchange) do not

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40 22 usually allow for strict control of the metal speciation, leading to coexistence of multiple species within

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42 23 the zeolite pores. In this work we demonstrate a strategy to study such systems through combined

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44 24 experimental and computational efforts with focus on the specific example of the Mo/H-ZSM-5

45 25 (framework type MFI) catalysts employed in methane dehydroaromatization (MDA). MDA is a single

47 26 step, non-oxidative reaction that directly converts methane into liquid aromatics, light hydrocarbons, and

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49 27 hydrogen as a co-product. MDA has drawn interest for its potential as a technology capable of
converting

50 methane into transportable liquid products to reduce flaring of natural gas^[5, 6, 17-20].

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29 Molybdenum oxides dispersed within H-ZSM-5 channels are the most effective catalysts known to

MDA. Under the relevant conditions, the starting Mo-oxide species migrate into the zeolite

anchor at Brønsted acidic sites (BAS) to form local anchored Mo-oxides. Upon exposure to

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3 1 methane under reaction conditions, the anchored Mo-oxides reduce and carburize to form Mo carbides

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5 2 and oxycarbides, which are generally accepted to be the active centers for MDA, although the details of

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7 3 the reaction mechanism are yet unclear. Presently, there is debate on
whether the MDA reaction proceeds

8 ^[6], where the carbidic Mo centers activate methane to produce C₂H_x

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4 via a bifunctional mechanism

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5 intermediates that subsequently undergo aromatization to benzene on the BAS of the zeolite, or a

monofunctional mechanism^[6, 21], where the carbidic Mo is responsible for both the methane activation and also CH_x species aromatization to benzene. The exact Mo speciation at different stages of MDA also remains a point of debate in literature. Understanding the true nature of the Mo species throughout the

entire catalyst life cycle will help elucidate the reaction mechanism for MDA and in turn facilitate rational design of more stable, commercially viable catalysts. Starting supported Mo-oxides have been reported to

+ monomers^[5, 18, 22-27], MoO₂²⁺ monomers^[5, 18, 22, 23, 26-32], or Mo₂O₅²⁺ dimers^[5, 17, 22, 24, 25, 27, 29, 11] be MoO₂OH

^[31-37]. Gao et al.^[18, 26] studied the identity and anchoring site of the initial Mo-oxide monomer structures

by combining density functional theory (DFT) with multiple spectroscopic techniques such as in situ

Raman spectroscopy and in situ UV-vis to report the MoO₂OH⁺ and MoO₂²⁺ structures. On the other

hand, using Raman and X-ray absorption spectroscopy (XAS), together with quantification of water

formed during a temperature-programmed oxidation of the catalyst precursors, existence of Mo₂O₅²⁺

dimeric species formed from condensation of two anchored MoO₂OH⁺ monomers was suggested^[22, 25].

Herein we analyze closely the speciation of the anchored Mo-oxides in the starting Mo/H-ZSM-5 MDA

catalysts to clarify the differences observed in the literature regarding these structures.

One important factor that could explain discrepancies in proposed Mo-oxide structures is the synthesis technique employed in the preparation of the Mo/H-ZSM-5 catalysts. Groups reporting the presence of a $\text{Mo}_2\text{O}_5^{2+}$ dimer generally prepare the catalysts by “physical mixing” where MoO_3 powder and H-ZSM-5 are first mixed and ground, and then calcined^[22]. The calcination step is crucial to enable the MoO_3 phase to first spread over the external zeolite surface forming MoO_x moieties that upon further heating above the sublimation point migrate into the zeolite channels where they anchor at the BAS. Alternatively, research groups reporting presence of anchored MoO_2^{2+} monomers often employ incipient wetness impregnation to incorporate Mo onto the zeolite. This is done by adding a precisely measured volume of an aqueous solution of the Mo-oxide precursor (usually ammonium heptamolybdate tetrahydrate (AHM)) to the H-ZSM-5 support. The solution is added dropwise until reaching the incipient wetness point. The fact that groups preparing catalysts by these different synthesis techniques have generally presented evidence for different Mo-oxide speciation inevitably leads to questions of whether differences in the

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chemistry involved in the synthesis procedures subsequently affect the metal oxide speciation. We have not been able to identify in the published MDA literature any work that has contrasted catalyst structures employing the different synthesis techniques.

To deconvolute the discrepancy between conflicting reports of Mo-oxide structure on Mo/H-ZSM-5, in this work we investigate the MoO_x speciation as a function of the synthesis technique by exploring catalysts synthesized by the two most employed methods in the literature, physical mixing of MoO_3 with H-ZSM-5 and incipient wetness impregnation of Mo-oxide precursors on H-ZSM-5. We employ a

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8 combination of experimental and computational techniques to evaluate the speciation of MoO_x on H-
9 ZSM-5. We have characterized the stoichiometry of the anchored Mo-oxides in the catalysts prepared by
10 both techniques indirectly via temperature-programmed calcination of Mo/H-ZSM-5 precursors under
11 oxidative conditions while quantifying the water evolution resulting from the reaction of the molybdenum
12 oxide precursors (we will refer to these as temperature-programmed oxidation, TPO, experiments). The
13 quantity of water produced in the process can aid in determining the stoichiometry of the anchored Mo
14 oxides. We also report direct measurements of the structure of the molybdenum species using operando
15 XAS. We have monitored the average local electronic structure, X-ray absorption near-edge structure
16 (XANES), of the Mo species as they evolve from the precursors to the anchored species during the
17 temperature-programmed oxidation while monitoring the sample temperature and water produced during
18 [38, 39], and the TPO.

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evolution of species during the TPO. Local atomic structure, extended X-ray absorption fine structure

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ZSM42

5 to assess the viability of specific structures. These calculations provide atomistic characterization of the
nature and location of these motifs and enable comment on their thermodynamic viabilities. We include
in this set of calculations evaluation of anchoring possibility of Mo-oxides in proximity of BAS without
direct coordination, identifying viable motifs not previously considered in the literature. We combine our
DFT-based structure models with our XAS-measured spectra through QuantEXAFS analysis^[40] to identify
which specific structures among those we have computed best agree with our measured spectra and how
the structures that best agree vary in motif as a function of metal loading and catalyst preparation method.
Through this combined theoretical and experimental investigation, we conclude that specific motifs of

Mo-oxide catalyst precursors may be promoted or inhibited through system choice and preparation.

Furthermore, the strategy we develop here may be extended to other transition metal-zeolite systems involving presence of dispersed metal-oxides within zeolite channels.

2. Methods

2. 1. Experimental Methods

2.1.1. Catalyst preparation – Physical Mixing & Incipient Wetness Impregnation

The H-ZSM-5 support was prepared by calcining NH_4 -ZSM-5 (Si/Al = 15 and 40, Zeolyst

International) at 500 °C for 6 h. Each of two methods, physical mixing (PM) and incipient wetness

impregnation (IWI), were used to prepare two sets of Mo/H-ZSM-5 catalysts. For PM catalysts, mixtures

of MoO_3 (Sigma Aldrich, 99.9%) and H-ZSM-5 were ground by hand in an agate mortar and pestle for

approximately 0.5 h, reducing the mixture to a powder to ensure maximum contact between the Mo-oxide

and the H-ZSM-5 support. For IWI catalysts, first the incipient wetness point for a certain mass of H-

ZSM-5 was first determined with water. For this, water was added drop by drop to the H-ZSM-5 until

reaching the incipient point whereby the zeolite was wet but did not possess any supernatant water. The

incipient point volume was then used to calculate the volume of aqueous solution of ammonium

heptamolybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, Sigma Aldrich) to be added to the H-ZSM-5 support

for the different catalyst samples. After impregnation, the samples were dried overnight at ambient

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procedures employed previously in the literature

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. For PM catalysts, the as-prepared catalysts were calcined to 350 °C, held for 2 h, and ramped to 700

°C all at 10 °C min⁻¹. For IWI catalysts, the as-prepared catalysts were calcined to 200 °C, held for 3 h, ramped to 500 °C, held for 2 h, all at 10 °C min⁻¹. **Table 1** details the established nomenclature for the

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Mo/H-ZSM-5 samples used in this study. The nomenclature uses the following format: A -Mo/Z- B (C),

where A denotes the nominal Mo/Al ratio in the catalyst tenfold, B denotes the synthesis technique (PM vs. IWI), and (C) denotes the Si/Al ratio of the support.

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Table 1. Nomenclature of prepared Mo/H-ZSM-5 samples reflecting metal loading, synthesis method.

Nomenclature	Mo wt. %	Nominal Mo/Al Ratio	Mo Precursor
1-Mo/Z-PM (15)	1	0.11	MoO ₃
3-Mo/Z-PM (15)	3	0.34	MoO ₃
4-Mo/Z-PM (15)	4	0.45	MoO ₃
1-Mo/Z-PM (40)	0.4	0.11	MoO ₃
3-Mo/Z-PM (40)	1.2	0.34	MoO ₃
4-Mo/Z-PM (40)	1.6	0.45	MoO ₃
1-Mo/Z-IWI (15)	1	0.11	AHM*
2-Mo/Z-IWI (15)	2	0.22	AHM
3-Mo/Z-IWI (15)	3	0.34	AHM
4-Mo/Z-IWI (15)	4	0.45	AHM

* AHM = Ammonium Heptamolybdate Tetrahydrate

2.1.2. Quantitative Temperature-Programmed Oxidation (TPO)

Temperature-programmed oxidation of the Mo/H-ZSM-5 precursors (H-ZSM-5 with MoO₃ for PM

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33 4 samples, and H-ZSM-5 with ammonium heptamolybdate tetrahydrate for IWI samples) was performed in
34 5 a fixed-bed quartz reactor (8 mm i.d.) at atmospheric pressure and varying temperature programs for the
35
36 6 different catalyst types as described in **Table 2**. The reactor was charged with 0.3 g of catalyst powder
37
38 7 held in place by quartz wool. The catalyst precursors were heated to reaction temperature at
a rate of 10
39 ⁻¹ under a flow of 20% O₂ in Ar at a flow of 50.0 ml min⁻¹ and at different temperature profiles for
40 8 °C min
41 9 catalysts prepared via different synthesis methods. Evolution of H₂O signals (m/z = 18)
during the TPO 42
43 10 experiment was monitored with a MKS Cirrus 3 atmospheric gas analyzer.
44

45 Table 2. Temperature profiles employed in TPO of Mo/H-ZSM-5 prepared with different synthesis methods.

46 Temperature Profile Segment	47 Physical Mixing (PM)	48 Incipient Wetness Impregnation (IWI)
49 1.	25 to 350 °C (10 °C min ⁻¹)	25 to 200 °C (10 °C min ⁻¹)
50 2.	hold 2 h	hold 2 h
3.	350 to 700 °C (10 °C min ⁻¹)	200 to 500 °C (10 °C min ⁻¹)
4.	-	hold 2 h
5.	-	500 to 700 °C (10 °C min ⁻¹)

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XRD patterns were recorded at room temperature on a Rigaku Ultima III PXRD diffractometer using Cu K α radiation. The instrument was operated at 40 kV and 44 mA, and the samples were scanned at a rate of 0.5 °/min.

2.1.4. X-Ray Absorption Spectroscopy (XAS)

X-ray absorption spectra of the as-prepared and the calcined (after TPO) catalysts were recorded at the Stanford Synchrotron Radiation Lightsource (SSRL) at beamline 9-3 using a cryogenically cooled double crystal Si (220) monochromator and pair of Rh-coated collimating and focusing mirrors located before and after the monochromator, respectively, for harmonic rejection. The storage ring was operated at 3 GeV with a ring current of 500 mA in top-off mode. The beam spot on the sample was fixed to 0.5 mm $\times$ 0.5 mm. The XANES and EXAFS spectra were recorded at the Mo K-edge (20000.0 eV) in transmission geometry mode using argon-filled ion chambers. A spectrum of Mo foil was simultaneously acquired and used for energy calibration. XAS spectra were collected in continuous scanning mode with a spectrum collected every 90 seconds. Operando data were conducted with the catalyst particles (125 – 180 μ m) placed inside a quartz reactor tube (2.6 mm i.d. $\times$ 3 mm o.d.)^[42] forming approximately a 1 cm long bed.

For PM catalysts, the as-prepared catalysts were heated to 350 °C, isothermally held until no further

⁻¹ in a 10 sccm flow of 20% O₂/He. spectral changes were observed, and ramped to 700 °C all at 10 °C min

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For IWI catalysts, the as-prepared catalysts were heated to 200 °C, isothermally held until no further spectral changes were observed, ramped to 400 °C, held until no further spectral changes were observed, then ramped to 700 °C all at 10 °C min⁻¹ in a flow of 10 sccm of 20% O₂/He. The composition of the effluent gas from the experimental cell was monitored using a Hiden QGA mass spectrometer.

2.1.5. XAS Analysis

Transient XAS data and XANES spectra were processed (energy calibrated, normalized, interpolated to a common energy grid) and correlated to the mass spectrometer data using CatXAS^[43]. The normalized data [38, 39]. The data

XANES spectra were analyzed using PCA and MCR-ALS spectral deconvolution codes range used during the PCA and MCR-ALS analysis was 19,925-20,250 eV with non-negative spectra and non-negative concentration constraints applied during the MCR-ALS analysis.

Steady-state EXAFS data were processed using Athena and QuantEXAFS^[44, 40]. Athena was used for energy calibration, normalization, merging of spectra to improve signal-to-noise, and EXAFS extraction.

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2.2. Computational Methods

2.2.1. Calculations Details

Fully periodic DFT calculations were performed with a planewave basis set within the Vienna ab initio

[45] (VASP) to study the speciation of Mo-oxide structures within H-ZSM-5. All spin10 4
simulation package

polarized DFT calculations used projector augmented wave pseudopotentials^[46] and the generalized
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6 gradient approximation of Perdew, Burke, and Ernzerhof (PBE)^[47]. The planewave basis set cutoff
energy

7 was 700 eV, and the reciprocal-space integration of the Brillouin zone was sampled at Γ ($1 \times 1 \times 1$

8 Monkhorst-Pack grid). The atomic positions were optimized until interionic forces were less than 0.03

9 eV/Å in all Mo-oxide/H-ZSM-5 structures.

2.2.2. Models of Mo-oxides/H-ZSM-5 (Model details)

To generate models of MoO_x species supported by H-ZSM-5, we began by optimizing the ZSM-5 unit
cell geometry using DFT, starting from a structure obtained from the International Zeolite Association

(IZA) database^[48]. The ZSM-5 unit cell contains 288 atoms: 96 Si atoms and 192 O atoms. In ZSM-5,

each Si⁴⁺ ion is charge-balanced by two O²⁻ ions, and each Si⁴⁺ ion is coordinated tetrahedrally by four

15 O²⁻. Isostructural substitution of
one Si⁴⁺ ion by an Al³⁺ ion creates a local
charge of -1, which is balanced

+ ion) bound to an oxygen ion coordinated
16 by introducing a charge-
compensating Brønsted acidic proton (H

17 to the Al³⁺ species to generate
H-ZSM-5. The ZSM-5 unit cell contains
12 chemically/coordinatively

distinct tetrahedral sites (T-sites). H-ZSM-5 can be synthesized in various Si/Al ratios wherein a fraction

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19 of the Si is substituted with Al and a charge-compensating proton^[49-51]. Models of MoO_x/H-ZSM-5
[18, 22, 26] within the DFT-optimized unit cell

20 structures were constructed with a variety of proposed motifs

21 of H-ZSM-5. To select motifs for Mo-oxide speciation at the initial stages of methane

22 dehydroaromatization, the three most frequently spectroscopically evidenced proposed motifs of Mo-

[18], MoO₂OH⁺ [18, 26], MoO₂²⁺ [18, 29], and Mo₂O₅²⁺ [22, 29], were considered. In general, 23 oxides in the
literature

24 we categorize MoO_x species into two main categories: "Mo monomer" and "Mo dimer" species. MoO_x

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25 species are proposed to anchor in the vicinity of Al-atom framework sites, with isolated Al sites allowing

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26 formation only of MoO₂OH⁺ Mo monomer species and two Al
sites near one another additionally

27 ²⁺ Mo monomer species and Mo₂O₅²⁺ Mo dimer species.

28 facilitating existence of both MoO₂

29 The electronic structure and stability of the MoO₂OH⁺ monomer motif anchored on each of the 10

isolated symmetrically unique Al-substituted T-sites around a single 10-member ring in the straight

30 channel of H-ZSM-5 were explored, with the previously published DFT-calculated geometry of

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3 1 MoO_2OH^+ used to initialize calculations^[1]. To date, studies of Mo-oxides anchored in zeolites have
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5 2 focused on anchoring at expected strongly binding acidic sites^[18, 22, 26, 28, 52]. We have considered these
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5 well as the potential for these oxides to anchor elsewhere in the zeolite to investigate the viability of such

anchoring motifs. Because structures with greater separations between the Mo and Al^{3+} are not expected to be thermodynamically favored, we have limited this study to two complementary investigations: either Al^{3+} at T-site 8 with the other varying between all unique T-sites within the 10168 the Mo-oxide or the Al member ring. The various structural arrangements of siting both the MoO_2OH^+ and the Al^{3+} within the zeolite in this work are illustrated in **Figure 1**. The energetics of these structures represented as a matrix $^{+}$ species anchored atop the Al-substituted Si sites as the diagonal 11 are provided in **Figure 9** with MoO_2OH 12 elements of this matrix. The elements not along the diagonal of this matrix represent the possibility of anchoring of the Mo monomer atop Si sites near to or distant from the Al atom inside the zeolite's

14 channels, with distance from the diagonal representing a greater coordinative distance between Al site and

⁺ anchoring site around the 10-member straight channel ring of H-ZSM-5. Inclusion of these 15 MoO₂OH

16 motifs in our structure database allows for assessment of whether these species may be likely contributors

to observed EXAFS spectra.

We have also studied the other Mo-oxide motifs to exist within H-ZSM-5, noting that these motifs,

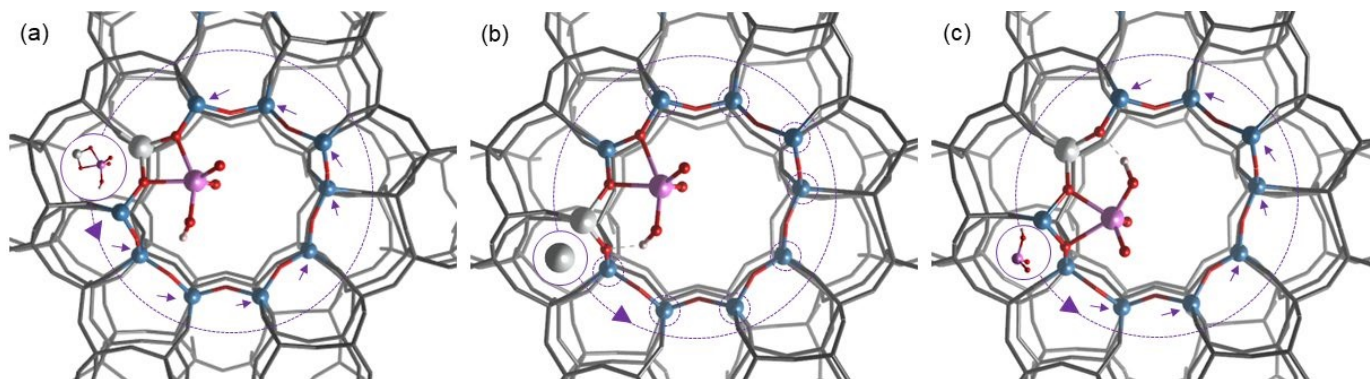


Figure 1. Schematic of: (a) MoO₂OH⁺ monomer anchored atop the Al atom-substituted T-site demonstrating 49 potential T-sites for “atop” anchoring. (b) MoO₂OH⁺ monomer anchored at T-site 8, demonstrating potential other T-sites for Al substitution. (c) MoO₂OH⁺ monomer anchored adjacent to the Al-substituted T-site demonstrating potential for anchoring both near to and distant from the Al-substituted T-site. Color scheme: silicon (blue), oxygen (red), aluminum (silver), molybdenum (magenta), hydrogen (white), non-specific framework (grey).

MoO₂²⁺ and Mo₂O₅²⁺, each require two Al³⁺ sites and two acidic protons to exist in proximity to one another within the H-ZSM-5 pore to anchor to the H-ZSM-5 framework. Consistent with previous studies

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of these motifs, the possible double Al-atom framework sites in H-ZSM-5 were considered as Al-O-Si-OAl (Next-Nearest-Neighbor, NNN), and Al-O-(Si-O)₂-Al (Next-Next-Nearest-Neighbor, NNNN)^[14, 16, 19], and anchoring of this second type of Mo monomer (MoO₂²⁺) as well as the Mo dimer (Mo₂O₅²⁺) on 8

4 candidate double Al sites inside the straight and sinusoidal channels of H-ZSM-5 were investigated.

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9 6,9; 6,6; 3,12; 3,3; 1,10; 1,1, where these pairs of numbers denote the T-sites at which the Al³⁺ cations are

sited, following nomenclature in **Figure 8 (a)**) inside the straight and sinusoidal channels of H-ZSM-5. It

²⁺ species, the anchoring site of the Mo atom is not fully should be noted that for some of the MoO₂

specified by knowing at which T-sites Al atoms are substituted, necessitating the nomenclature described

subsequently for uniquely identifying these structures. For Mo₂O₅²⁺ dimers, we have additionally

considered the possibility that the larger structure may be anchored at double Al sites (3,7; 3,8; 2,8; and

2,7) with greater coordinative separation (next-next-next-nearest-neighbor, NNNNN, or “fourth nearest-neighbor”, for instance). In total, 42 models of MoO₂OH⁺, 8 models of MoO₂²⁺, and 12 models of Mo₂O₅²⁺

were considered in this work, with differences between models of like stoichiometry being the T-sites at

³⁺ is substituted within the framework. To which they are anchored as well as the T-sites at which Al

uniquely identify each of the 62 structures, we introduce the following nomenclature system:

For MoO₂OH⁺ monomers, we use MoO₂OH⁺-*A*, Al *B*, where *A* denotes the anchoring site of Mo-oxide and *B* denotes the Al-substituted T-site.

²⁺ monomers, we use $\text{MoO}_2^{2+}\text{-}A\text{-}B$ (Al C,D), where A and B denote the sites between which

For MoO_2

the Mo atom is anchored and C and D denote the Al-substituted T-sites.

For $\text{Mo}_2\text{O}_5^{2+}$ dimers, we use $\text{Mo}_2\text{O}_5^{2+}\text{-}A,B$ (Al C,D), where A and B denote the sites atop which the

Mo is bidentately anchored and C and D denote the Al-substituted T-sites.

Adsorption Energetics of Mo-oxide in H-ZSM-5

Binding energies of MoO_x species in H-ZSM-5 were calculated to investigate their thermodynamic

viabilities; the same theory level as for geometry optimization has been applied in these calculations. We have investigated the binding energies of Mo-oxide species referenced to MoO_3 in the gas phase. While

MoO_3 in the gas phase is expected to be thermodynamically unfavored and therefore lead to highly

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exothermic values for anchoring of MoO_x species within H-ZSM-5, we focus our discussion on the relative

energetics between these species such that this reference choice has no bearing on the conclusions drawn.

To calculate the reference energy of MoO_3 and H_2O , an isolated MoO_3 or H_2O unit was simulated in a

$20 \times 20 \times 13.5$ Å box such that interaction between periodic images of the molecules does not contribute

significantly to energetics. For the reference energy of the H_2O molecule, corrections to the potential to

account for the permanent electrostatic dipole of H_2O were included.

The adsorption energy of the Mo monomer anchored at a single Al-atom framework site was

calculated using:

$$\Delta EE = EE_{\text{HH-ZZZZZZ-5+ZZMMO}_2\text{OOHH}^+} - EE_{\text{HH-ZZZZZZ-5}} - EE_{\text{ZZMMO}_3} \quad (1)$$

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where $EE_{HH-ZZZZZ-5+ZZMMO_2O_2OH^+}$, $EE_{HH-ZZZZZ-5}$, and EE_{ZZMMO_3} denote the energies of H-ZSM-5-plus-MoO₂OH⁺

complex, bare H-ZSM-5, and MoO₃, respectively. A negative ΔEE in this convention corresponds to an exothermic adsorption.

In a similar calculation, the adsorption energetics of the Mo monomer anchored at double Al site was calculated as follows:

$$\Delta EE = EE_{HH-ZZZZZ-5+ZZMMO_2}^{2+} + EE_{HH_2O} - EE_{HH-ZZZZZ-5} - EE_{ZZMMO_3} \quad (2)$$

where $EE_{HH-ZZZZZ-5+ZZMMO_2}^{2+}$, $EE_{HH-ZZZZZ-5}$, and EE_{HH_2O} denote the energies of H-ZSM-5-plus-MoO₂²⁺ complex,

bare H-ZSM-5 containing two Al atoms, and water, respectively.

Finally, to study the stability of the Mo dimer, equation (3) was employed.

$$\Delta EE = EE_{HH-ZZZZZ-5+ZZMM_2O_5}^{2+} + EE_{HH_2O} - EE_{HH-ZZZZZ-5} - 2 \times EE_{ZZMMO_3} \quad (3)$$

where $EE_{HH-ZZZZZ-5+ZZMM_2O_5}^{2+}$ and $EE_{HH-ZZZZZ-5}$ denote the energies of H-ZSM-5-plus-Mo₂O₅²⁺ complex and

bare H-ZSM-5 containing two Al atoms, respectively.

In all cases above, we have referenced energies against one particular H-ZSM-5 structure. In reality, for a given Al siting arrangement with N Al sites according to Lowenstein's rule, there are 4^N unique

24 sitings of acidic protons, some of which are more favorable than others. We have investigated the
 25 magnitude of the effect of proton siting and found it to be small relative to an arbitrary H-ZSM-5 model.
 26 We computed the energy of the H-ZSM-5 structures with the charge-compensating proton bound to each
³⁺ cation, which we used to calculate the Boltzmann
 of the four unique oxygen atoms coordinated to the Al
 average energy (for this we have used the reaction operating temperature of $T = 973.15$ K) using equation
 (4). The H-ZSM-5 structure energies were predicted to range from 6.6 kJ mol^{-1} less stable to 2.5 kJ mol^{-1}
 more stable than the Boltzmann average for a single Al-substituted T-site. To study effects of Boltzmann

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averaging on H-ZSM-5 with two Al atoms, we consider H-ZSM-5 with Al substituted at T-sites 3 and 12,
 a NNN (Al-O-Si-O-Al) arrangement which we expect to be the upper bound of deviation from the single-
 Al case due to proximity of the Al^{3+} cations. We considered the 16 chemically unique arrangements for

$^{-1}$ less stable to 7.7 kJ mol^{-1} more stable
 proton siting and calculated
 energies ranging from 55.7 kJ mol^{-1}

than the Boltzmann average. We
 note that the system predicted to be ~ 56
 kJ mol^{-1} less stable for siting of

acidic protons is not representative of the typical systems and features acidic protons sited in proximity to
 one another with NNN Al siting and would not be expected to contribute with a high probability to
 observed states.

$$E = \sum_i \frac{E_i}{\sum_j E_j} \exp\left(\frac{E_j - E_i}{k_B T}\right) \quad (4)$$

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where EE_{ii} and ΔEE_{ii} denote the energies of H-ZSM-5 configuration i , and the relative energy of

configuration i to the ground-state configuration, respectively.

2.2.3. DFT-based EXAFS analysis (QuantEXAFS)

The EXAFS data were analyzed with the QuantEXAFS^[40] workflow that uses the X-ray Larch package^[53].

QuantEXAFS is an automated workflow for EXAFS analysis that uses a library of DFT-optimized

structures to generate feff.inp files and model the EXAFS data. The code uses Seaborn and Matplotlib for

plotting the fitting results. Assuming the database of DFT-optimized structures was exhaustive, the

coordination numbers were ‘fixed’ in EXAFS analysis and were not included as a fit parameter unlike the

conventional method. Additionally, all the scattering paths generated using FEFF were categorized based

on distance-dependent variables (σ_i^2 and α_i) and used in the fit. Unique values of D-W factors (σ_i^2) and α_i

(fixed error correction allowed in DFT-generated bond distances) were generated for each category of

paths and used in the model.

3. Results

3.1. Quantitative Temperature-Programmed Oxidation

We performed TPO to quantify evolution of H₂O in catalysts to elucidate the speciation of Mo-oxides

in H-ZSM-5, consistent with previous approaches by Iglesia et al.^[22] Anchoring of Mo-oxides on zeolitic

²⁺ dimer on double BAS leads to desorption of H₂O. Nominally (**Figure 2**), the formation of: (i) a Mo₂O₅

Al-atom sites yields one H₂O molecule (H/Mo = 1); (ii) a MoO₂²⁺ monomer on double Al-atom sites yields one H₂O molecule (H/Mo = 2); and (iii) a MoO₂OH⁺ monomer on a single Al-atom site yields no H₂O

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Page 13 of 41

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3 1 molecules ($H/Mo = 0$). Thus, calculating the atomic H/Mo ratios by H_2O quantification during TPO can 4
5 reveal structural information about the anchored Mo-oxides.

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8 3 3.1.1. H_2O evolution on Mo/H-ZSM-5 prepared by physical mixing (PM)

9 4 We investigated H_2O evolution during TPO of physically mixed Mo/H-ZSM-5 (Mo/Z-PM in **Table**

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11 5 1) using the temperature profile in **Table 2** for PM samples. **Figure S1 (a)** shows the H_2O desorption

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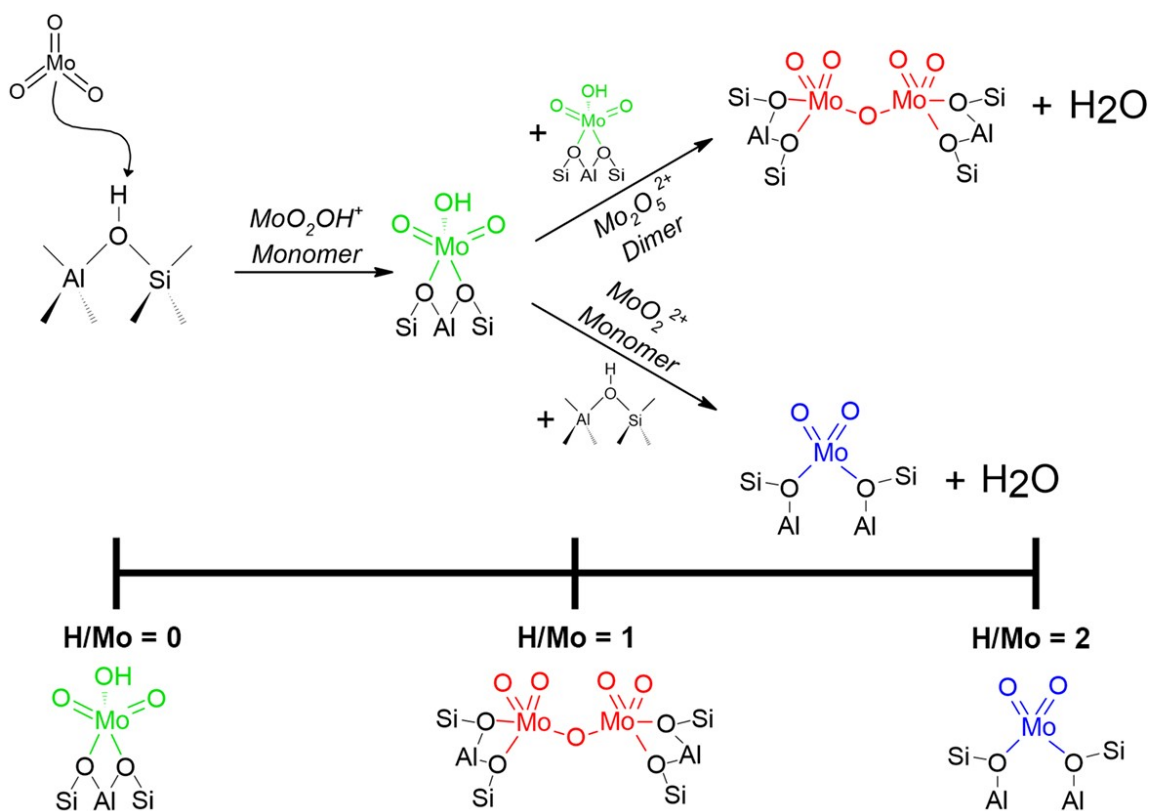


Figure 2. Mechanisms leading to different anchored Mo-oxide species, along with nominal H/Mo ratios from TPO.

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9 eventually leading to migration of MoO_x species into zeolite channels. Subsequently, they can exchange

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49 10 onto zeolitic BAS to form anchored Mo-oxides depicted in **Figure 2**. The formation of H₂O due to 50
11 anchoring is evidenced in TPO (**Figure S1 (a)**) by the distinct peak between 350 and 700 °C. Therefore, 12
analyses of desorbed H₂O from metal oxide anchoring in PM samples were performed within this range.
13 **Figure 3 (a)** shows the H₂O desorption rates above 350 °C during TPO of Mo/Z-PM (15) catalysts 14 with
varying Mo loadings (Mo/Al = 0 – 0.45). H₂O formed during TPO of bare H-ZSM-5 (Mo/Al = 0) at

these elevated temperatures has been attributed to the condensation of two neighboring BAS in the presence of O_2 , resulting in the formation of extraframework Al_2O_3 (i.e., framework dealumination)^[22].

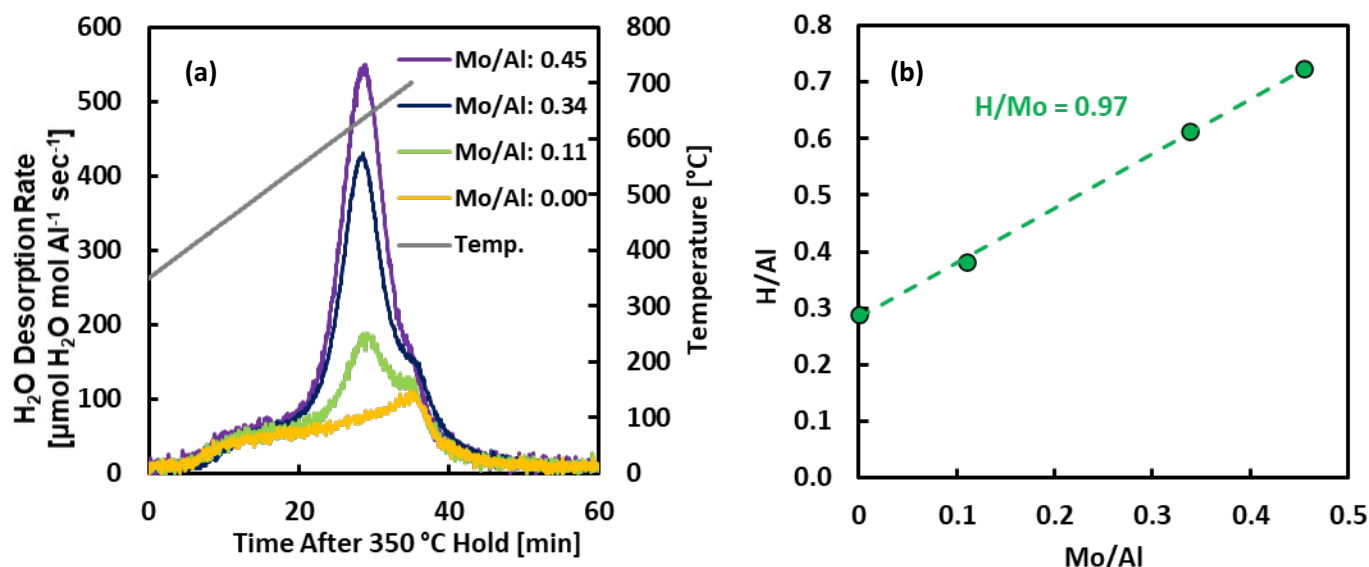


Figure 3. (a) Desorption rate of H_2O per mol Al with varying Mo loadings in Mo/Z-PM (15) catalysts from 350 to 700 $^{\circ}C$ at 10.0 $^{\circ}C min^{-1}$. (0.3 g, 100 $cm^3 min^{-1}$, 20% O_2/Ar); integrated areas were calculated to quantify H/Al ratios. Solid gray line represents the PM temperature program as described in **Table 2**; (b) Ratio of H/Al from desorbed H_2O during TPO of Mo/Z-PM (15) catalysts as a function of Mo loading.

The amount of H_2O formed above 350 $^{\circ}C$ increases with Mo loading, with a peak H_2O desorption rate at 630 $^{\circ}C$. **Table 3** details the atomic ratios calculated from integration of the H_2O desorption curves (H/Al) for each Mo loading (Mo/Al) to determine the stoichiometry of Mo exchanging onto BAS (H/Mo). H_2O contributions from dealumination were accounted for by subtracting H/Al of the bare H-ZSM-5 from H/Al in Mo/H-ZSM-5 catalysts (denoted as the H/Al_F column in **Table 3** where Al_F refers to framework Al) assuming that the extent of dealumination is equal in both Mo-containing and bare H-ZSM-5. Plotting the

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4 9 desorbed H₂O per Al site as a function of Mo/Al shows that approximately one proton is exchanged per
5 10 anchored Mo (H/Mo = 0.97) (**Figure 3 (b)**) which closely corresponds to the expected value if only 11
6 dimeric species, Mo₂O₅²⁺, were formed (H/Mo = 1), suggesting that a prevalence of dimeric anchored 12 Mo-
7 oxides exists within physically mixed Mo/H-ZSM-5 catalysts.

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15 7 Similar measurements were performed on Mo/Z-PM catalysts using a lower acidity H-ZSM-5 support

16 8 (Si/Al = 40). Analysis of the corresponding H₂O evolution curves (**Figure S2** and **Table S2**) between 350

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18 9 °C and 700 °C in Mo/Z-PM (40) at the same Mo/Al ratios (0 – 0.45) yields a lower ratio of H/Mo = 0.77,

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20 10 suggesting a decrease in the formation of the dimeric Mo-

oxides. This is reasonable given that the

21 + structures being near enough to form the dimer is decreased

on a

22 11 probability of two anchored MoO₂OH

23 12 support with fewer BAS.

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Table 3 H₂O quantification from TPO of Mo/Z-PM (15) catalysts above 350 °C. ^a H/Al=

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values were obtained by subtracting the H/Al of the bare H-ZSM-5 from the H/Al^b measured for each Mo-containing catalyst. H/Mo values were obtained by dividing H/Al_F by the corresponding Mo/Al ratio.

Catalyst	Nominal Mo loading [wt.%]	Nominal Mo/Al	H/Al	H/Al _F ^a	H/Mo ^b
H-ZSM-5	0	0	0.29	0	-
1-Mo/Z-PM (15)	1	0.11	0.38	0.09	0.86
3-Mo/Z-PM (15)	3	0.34	0.61	0.32	0.96
4-Mo/Z-PM (15)	4	0.45	0.72	0.44	0.96

3.1.2. H₂O evolution on Mo/H-ZSM-5 prepared by incipient wetness impregnation (IWI)

We investigated H₂O evolution during TPO of Mo/H-ZSM-5 prepared by incipient wetness impregnation (Mo/Z-IWI from **Table 1**) using the temperature profile in **Table 2** for IWI samples. **Figure 8**

4 **S1 (b)** shows the H₂O desorption profile of a Mo/Z-IWI catalyst over the entire temperature range of TPO.

5 Similar to Mo/Z-PM in **Figure S1 (a)**, an initial intense H₂O signal was observed attributed to moisture,

6 followed by two more peaks at higher temperatures which we assign to H₂O formed from Mo-oxide

7 anchoring. Thus, analyses of H₂O evolution in IWI samples at different Mo loadings were performed

8 between 200 – 500 °C and 500 – 700 °C, as shown in **Figure 4**. Additionally, to account for H₂O

9 contributions from the AHM precursor, we quantified H₂O formed during TPO of pure AHM between

10 200 – 500 °C (Detailed in **Figure S1 (c)** and **Table S1**) and subtracted the corresponding amounts from

11 H/Al in Mo/H-ZSM-5 catalysts in this range (**Table 4**). A significant H₂O signal remains in the samples

12 even after subtracting contributions from AHM, which we attribute to anchoring of Mo-oxides at much

13 lower temperatures (~400 °C) than in Mo/Z-PM catalysts (~650 °C).

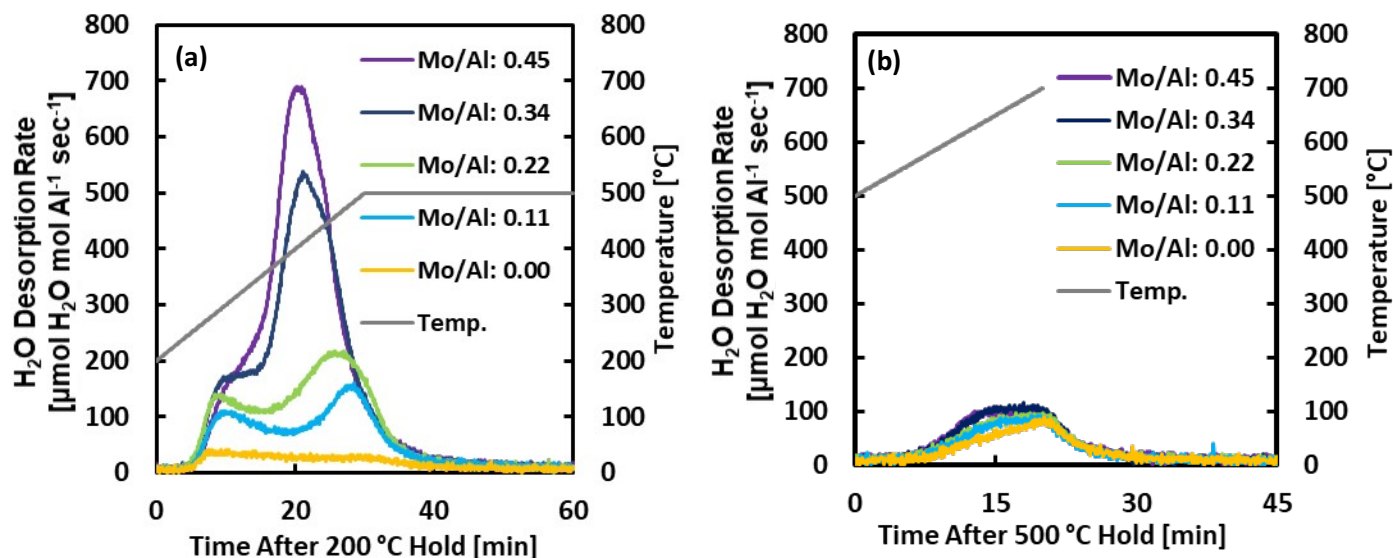


Figure 4. (a) Desorption rate of H₂O per mol Al with varying Mo loadings of Mo/Z-IWI (15) from 200 to 500 °C at 10.0 °C min⁻¹. (b) Desorption rate of H₂O per mole of Al with varying Mo loadings of Mo/Z-IWI (15) from 500 to 700 °C at 10.0 °C min⁻¹. Solid gray line represents the corresponding temperature program as described in Table 2.

Anchoring at a lower temperature with IWI catalysts is feasible if we consider that the chemistry of

the Mo precursor, ammonium heptamolybdate tetrahydrate (AHM, (NH₄)₆Mo₇O₂₄·4H₂O) in aqueous solution differs from MoO_x species originating from MoO₃ crystallites at higher temperatures, as is the case with Mo/Z-PM catalysts. According to Barath et al.^[54], an ionic equilibrium ($\text{Mo}_7\text{O}_{24}^{6-} + 4\text{H}_2\text{O} \leftrightarrow$

$7\text{MoO}_4^{2-} + 8\text{H}^+$) occurs when AHM is dissolved in water. We postulate that sufficiently small, aqueous

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3 1 MoO_4^{2-} ions are able to diffuse into the zeolite channels during IWI and remain there after drying, thereby
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5 2 eliminating the need to reach elevated temperatures required for MoO_3 sublimation and migration when
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7 3 using the PM method. Thus, IWI would enable Mo anchoring between 200 – 500 °C. H_2O quantification
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9 4 of catalysts within this range (**Table 4**) and plotting the corresponding H/Al as a function of Mo loading
10 5 (**Figure 5**) yields $\text{H}/\text{Mo} = 1.6$. This non-integer value suggests not only a difference in Mo-oxide
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12 6 speciation compared to PM catalysts (perhaps some presence of MoO_2^{2+} monomers), but also species
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14 7 heterogeneity in IWI catalysts.

15 ^a Total H/Al from 200–500

16 Table ^b H/Al contributions from AHM from 200 – 500 °C at each Mo/Al. 4. H_2O quantification from TPO of Mo/Z-IWI (15)
catalysts from ^c (H/Al 200) ₁— values were obtained by subtracting (H/Al) 500 °C & 500 – 700 °C. _{AHM} from

17 °C. ^d (H/Al_F)₁ values were obtained by subtracting (H/Al)₁ of bare H-ZSM-5 from (H/Al)₁ of the Mo-containing catalysts from 18
(H/Al). ^e (H/Mo)₁ values were obtained by dividing (H/Al_F)₁ by the corresponding Mo/Al ratio. ^f Total H/Al from 500 – 700 19 200°C. –
500 °C. ^g (H/Al_F)₂ values were obtained by subtracting (H/Al)₂ of bare H-ZSM-5 from that of Mo-containing catalyst from 500 – 700 20
°C. ^h (H/Mo)₂ values were obtained by dividing (H/Al_F)₂ by the corresponding Mo/Al ratio.

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Catalyst	Mo loading [wt.%]	Nominal Mo/Al	H/Al ^a	(H/Al) _{AHM} ^b	(H/Al) ₁ ^c	(H/Al _F) ₁ ^d	(H/Mo) ₁ ^e	(H/Al) ₂ ^f	(H/Al _F) ₂ ^g	(H/Mo) ₂ ^e
H-ZSM-5	0	0	0.09	0	0.09	0	-	0.15	0	-
1-Mo/Z-IWI (15)	1	0.11	0.30	0.05	0.25	0.16	1.46	0.20	0.05	0.46
2-Mo/Z-IWI (15)	2	0.22	0.50	0.09	0.41	0.32	1.43	0.17	0.02	0.11
3-Mo/Z-IWI (15)	3	0.34	0.85	0.14	0.71	0.62	1.82	0.21	0.06	0.19
4-Mo/Z-IWI (15)	4	0.45	0.93	0.19	0.75	0.66	1.45	0.20	0.06	0.12

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34 9 Quantification of desorbed H_2O between 500 – 700 °C shows little H_2O formation across Mo loadings.

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XAS analysis of Mo/Z-IWI (15) catalysts, shown in the next section, shows no appreciable change in local

Mo structure within this temperature range, suggesting that most of the Mo-oxide anchoring occurs during the lower temperature range of 200 – 500 °C. We surmise that H₂O contributions between 500 – 700 °C can be attributed to either dealumination or formation of minor amounts of aluminum molybdate. X-ray diffraction of Mo/H-ZSM-5 catalysts after TPO was also performed to ensure Mo dispersion into zeolite channels after TPO. The diffraction patterns shown in **Figure S3** indicate that, other than diffraction peaks from H-ZSM-5, no other peaks from any Mo-containing phases were detected in the catalysts. This suggests that the Mo species did not form any crystalline phases on the zeolite's external surface.

The quantitative TPO results point to a difference in the distribution of Mo-oxide species as a function of the synthesis method. The slopes of the H/Al versus Mo/Al plots obtained from H₂O quantification yield non-integer values of H/Mo that vary depending on synthesis method, implying coexistence of distinct Mo-oxide species of different distributions. Physically mixed catalysts (H/Mo = 0.97) suggest a prevalence of dimeric Mo₂O₅²⁺, whereas IWI catalysts (H/Mo = 1.6) suggest a distribution of Mo-oxide

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species, with potentially some presence of monomeric MoO₂²⁺. We point out that while the PM synthesis method involves a solid-state introduction of MoO_x into H-ZSM-5 using the MoO₃ solid precursor, in the

IWI method the Mo precursor, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, is dissolved in a liquid state prior to calcination. We

posit that this synthesis-dependent difference in speciation is caused by the different chemistries involved in the different mechanisms for migration of the Mo species inside the zeolite channels as a consequence of the different speciation of the starting Mo precursors (MoO_3 versus $(\text{Mo}_7\text{O}_{24})^{6-}$). To test this hypothesis, we performed operando XAS measurements as described in the following section.

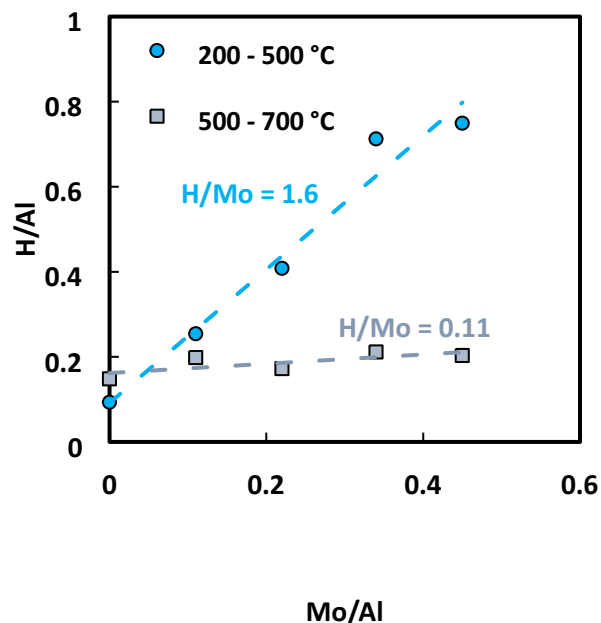


Figure 5. Ratio of H/Al from desorbed H_2O during TPO of Mo/Z-IWI (15) as a function of Mo loading. Circle points correspond to H_2O formed between 200 – 500 °C, square points correspond to H_2O formed between 500 – 700 °C.

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3.2. Monitoring local electronic structure of Mo species during calcination by operando XANES

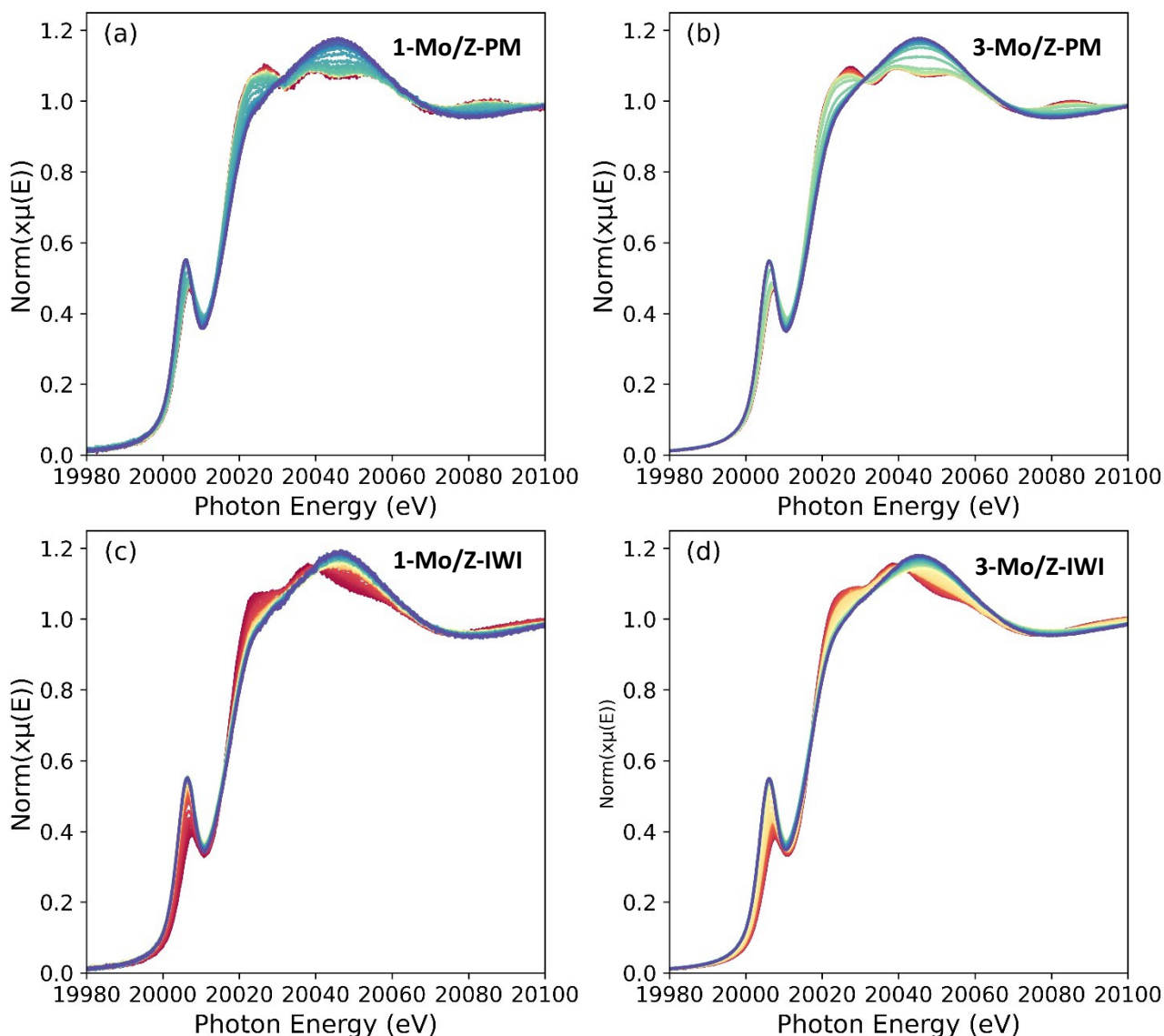


Figure 6. Operando Mo K-edge XANES spectra of pre-catalysts undergoing TPO employing the corresponding temperature profiles for PM and IWI catalysts as shown in **Table 2**. (a) 1-Mo/Z-PM; (b) 3-Mo/Z-PM; (c) 1-Mo/Z-IWI; (d) 3-Mo/Z-IWI. Si/Al = 15 in all catalysts. Color gradient from red to blue corresponds to a temperature change from room temperature, approximately 20 °C, to 700 °C, respectively.

To analyze possible differences in the Mo-oxide local structures from different anchoring pathways associated with differently synthesized catalysts, we performed operando Mo K-edge XANES measurements of the catalysts during TPO. **Figure 6** shows the evolution of 1 & 3-Mo/Z-PM (15) and 1

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6 & 3-Mo/Z-IWI (15) catalysts using the corresponding TPO temperature profiles shown in **Table 2**. The
pre-edge feature of both sets of catalysts grows increasingly pronounced with temperature (with a final
8 pre-edge energy at 20,005 eV), indicating a change in the local geometry of the Mo structure to a
more

tetrahedral character. The initial XANES spectra of the four samples pre-TPO, **Figure S4 (a)**, show that the starting Mo species are dependent on the Mo precursor used in synthesis, MoO₃ or AHM. By the end of the TPO experiments however, XANES spectra detailed in **Figure S4 (b)** show that the Mo species exhibit the same average electronic structure across the four samples, regardless of synthesis technique and Mo loading.

Principal component analysis (PCA) and multivariate curve resolution-alternating least squares algorithm (MCR-ALS) were used to identify the number of dominant spectral signatures that make up the XANES data during the TPO. These a priori analysis methods identify how spectra evolve over time/temperature, identify similar spectral features in datasets, and can be used to identify potentially hidden or minority features. To best resolve subtle differences in the four datasets, all XANES spectra of the four samples were analyzed simultaneously. The scree plot of the PCA (**Figure S5 (a)**) showed that all four XANES spectra can be described with three components, constituting 99.999% of all spectra in the dataset. The first five eigenspectra generated in the PCA (**Figure S5 (b)**) show that the predominant spectral differences occur around the pre-edge peak and white line, which is expected because the largest changes observed in the XANES spectra (**Figure 6**) occur in this region. When comparing how the first three eigenspectra (i.e., components) are correlated as a function of XANES spectra during the TPO, the score plot in **Figure S5 (c)** shows that the four samples start in two distinct regions with the final spectra being clustered in a third region. The initial two groupings, representing the XANES spectra corresponding to the initial as-prepared samples (**Figure S5 (c)**) differentiate the samples by the method of synthesis (physical mixing with MoO₃ or incipient wetness impregnation with AHM). This matches

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the grouping observed in the initial XANES spectra of each sample (**Figure S4 (a)**). The clustering of the eigenspectral components at the end of the TPO for the four samples show that the end states are near identical (**Figure S5 (c)**), indicating that the Mo species in both PM- and IWI-prepared catalysts appear to converge to a distinct final state over the course of TPO, matching the same observation in the end state XANES spectra, **Figure S4 (b)**. While PCA can deconvolute the spectra into their major components, interpretation of the eigenspectra is difficult, leading to use of the approximate deconvolution results from the MCR-ALS analysis guided by PCA results to determine speciation and species evolution during the TPO.

A three-component MCR-ALS spectral deconvolution was performed based upon three principal components from the knee of the PCA scree plot. The eigenspectra from the MCR-ALS deconvolution are plotted in **Figure S6** and will be discussed further below. The concentration of each eigenspectrum in

each XANES spectrum, along with the simultaneous evolved H₂O ($m/z = 18$) signal from the mass spectrometer, is plotted as a function of temperature in **Figure 7**. PM- and IWI-prepared catalysts initially have different eigenspectral compositions at the start of the TPO based on synthesis method, consistent with the as-prepared XANES spectra and PCA analysis. As the temperature increases to 700 °C, all four

samples transition from their initial eigenspectral compositions to a uniform final eigenspectral composition. This uniform composition is consistent with the XANES spectra collected at 700 °C and the composition of PCA components for the corresponding spectra.

The eigenspectra generated in the MCR-ALS analysis were normalized and compared to XANES spectra of bulk Mo compounds (**Figure S6**). Eigenspectrum #1, the component that represented the final state post-TPO for all samples, did not appear to match any known oxidic Mo compound we referenced. This may be interpreted as heterogeneity in the structure of the anchored Mo-oxides, seeing as multiple different spectra could contribute to produce a unique spectrum. Eigenspectrum #2, the dominant component of the as-prepared physically mixed samples, is a close match to XANES spectra of MoO₃. Finally, eigenspectrum #3, the dominant component of the as-prepared incipient wetness impregnated samples, is a close match to the XANES spectra of AHM. The similarities of the two eigenspectra, and a priori analysis result, to the XANES spectra of the appropriate precursors for each synthesis methods (PM or IWI), along with a unique third eigenspectrum that represents the common end state supports that the three-component analysis is sufficient to describe the evolution of the Mo in each pre-catalyst.

During TPO, the temperature at which the conversion from the initial eigenspectral composition to the final composition occurs is different based on the synthesis method/precursor of the catalyst as shown in **Figure 7**. Mo/Z-PM (15) catalysts show that significant change in the composition of XANES spectra occurs between 400 – 500 °C (**Figure 7 (a) & (b)**), where the final state component (eigenspectrum #1) increases as the MoO₃-like component (eigenspectrum #2) decays. Here, we can see that the initial MoO₃ precursor requires elevated temperatures to decompose before mobilizing into zeolite channels and exchanging onto zeolitic BAS, consistent with reports from literature^[22]. This change is independent from

(eigenspectrum #3) before also disappearing at elevated temperatures (**Figure 7 (d)**), consistent with decomposition of the heptamolybdate species into smaller Mo-oxide species and subsequent dispersion of these Mo-oxides above 300 °C^[55]. However, because the conversion into the final state begins at a lower

temperature prior to noticeable MoO₃ eigenspectral character emergence, we interpret this as further evidence that IWI allows aqueous MoO₄²⁻ ions to diffuse into and remain within zeolitic channels during catalyst synthesis, enabling anchoring at a lower temperature and underlining the clear difference in anchoring mechanism between PM- and IWI-prepared catalysts. Overall, the change in the Mo electronic structure at different temperatures for PM or IWI samples is consistent with quantitative H₂O evolution studies, confirming that the H₂O desorption beyond moisture is concomitant with Mo structural change.

However, it appears that most of the mobility and anchoring of Mo in the IWI catalysts occurs at a lower

temperature, coinciding with the initial removal of moisture from the zeolite, whereas Mo in the PM catalysts are mobile only at higher temperatures, well after the last detected moisture-attributed water was removed. This analysis of operando XANES data is not sensitive enough to distinguish the subtle structural differences between the various Mo-oxide species formed after TPO as a function of synthesis method and Mo loading, but it does underpin the clear difference in the temperature at which the different Mo precursors mobilize and anchor on zeolitic BAS.

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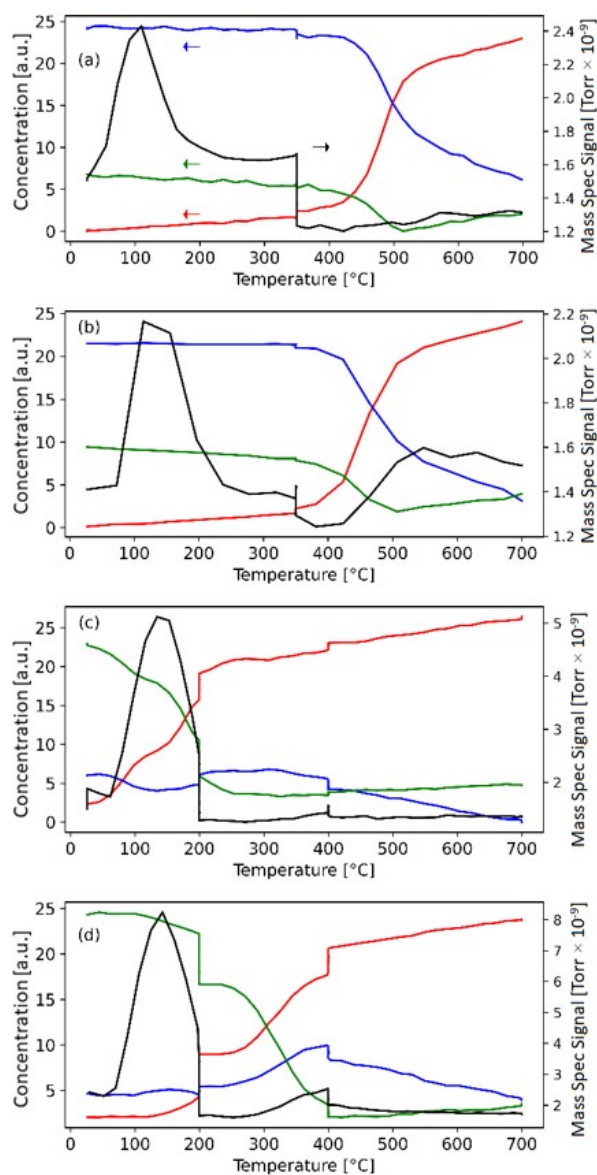


Figure 7. Eigenspectra concentrations (red, blue, green) of XANES spectra recorded at the Mo K-edge during the TPO and the mass spectrometer water signal ($m/z = 18$), black, as a function of temperature for a) 1-Mo/Z-PM (15), b) 3-Mo/Z-PM (15), c) 1-Mo/Z-IWI (15), and d) 3-Mo/Z-IWI (15). Red line: concentration of eigenspectrum #1 (post-TPO-like), Blue line: concentration of eigenspectrum #2 (MoO_3 -like), Green line: concentration of eigenspectrum #3 (AHM-like).

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2 While quantitative H₂O evolution studies elucidate the varying stoichiometric interactions of Mo with 3
zeolitic BAS associated with the anchoring process and operando TPO XANES experiments elucidate the
4 evolution of the Mo species, these data do not provide direct structural information due to lack of

Page 24 of 41

sensitivity (XANES) or ability to determine structure (mass balances from TPO). Therefore, we employ
DFT-assisted EXAFS analysis (QuantEXAFS^[40]) to understand the local coordination environment of Mo atom(s).
Next, we discuss the DFT calculations that were used to atomistically characterize and assess the 8
9 4 viability of these various motifs. The structures predicted through these calculations form the database of
10 5 62 structures which we use for comparison with our experimentally measured EXAFS spectra through
11
12 6 QuantEXAFS analysis.

14 7 3.3. DFT Calculations of Anchored Mo-oxide Species

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16 8 Discussion on Mo-oxide species' structures within H-ZSM-5 has been the subject of many theoretical
17 9 papers; however, most studies have focused on cluster models^[18, 29, 56, 57] rather than studying the anchored
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Mo-oxides within bulk H-ZSM-5. In this work, various MoO_x motifs were studied within the fully periodic H-ZSM-5 unit cell (with lattice constants $a = 20.14 \text{ \AA}$, $b = 20.39 \text{ \AA}$, and $c = 13.53 \text{ \AA}$; 0.33%, 2.34%, and 0.85% larger than experiment^[48, 58]). We have considered a range of Al-substituted T-sites as well as qualitative motifs (monomeric and dimeric MoO_x species) in this analysis. MoO_x nanostructures anchored on a single (a) and double Al-atom site (b,c) are shown in **Figure 8**.

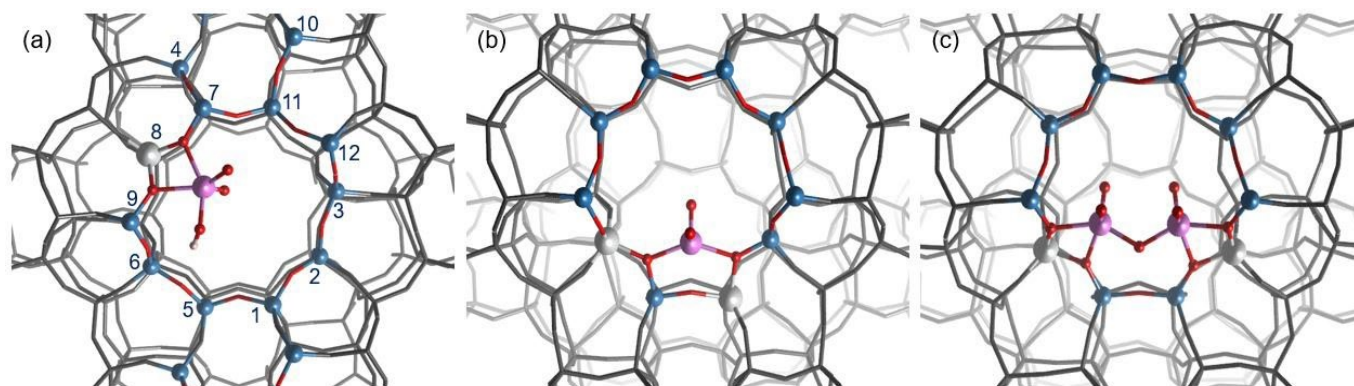


Figure 8. Overview of qualitatively distinct catalyst precursor structural motifs: (a) Isolated MoO_2OH^+ monomer structure anchored on a single Al-atom framework site. T-sites 1-12 are labeled with corresponding numbers for reference. (b) Isolated MoO_2^{2+} monomer structure anchored on double (next-nearest neighbor, NNN) Al-atom $^{2+}$ framework site. (c) Isolated Mo_2O_5 dimer anchored on double (next-next-nearest neighbor, NNNN) Al-atom framework site. Color scheme: silicon (blue), oxygen (red), aluminum (silver), molybdenum (magenta), hydrogen (white), non-specific framework (grey).

3.3.1. Structures of Mo-oxides in H-ZSM-5

- MoO_2OH^+ structure anchored on single Al-atom framework site

The structure of a geometrically optimized Mo monomer anchored on a single Al-atom framework site (T-site 8) is shown in **Figure 8 (a)**. In the MoO_2OH^+ monomer structure, Mo is bidentately coordinated to the framework through two framework oxygen atoms ($\text{Mo}-\text{O}_\text{F}$ bond length 2.16 – 2.35 Å, $\text{O}-\text{Mo}-\text{O}$ angle 67 – 69° among structures studied). These structures also feature two terminal $\text{Mo}=\text{O}$ double bonds (1.71 – 1.72 Å) and an $\text{O}=\text{Mo}=\text{O}$ bond angle (107 – 109°). These results agree with previous literature reports by Podkolzin and co-workers^[18, 26].

⁺ monomers have focused on anchoring either on the T-site

Previous literature reports on MoO_2OH

[5, 18, 22, 23, 25, 26, 29, 56], noting that the latter leads to substituted by the Al atom or on external Si atom sites

the formation of a less stable (more weakly anchored) monomer. In this work, we also assessed the

viability of MoO_2OH^+ anchored at T-sites distant from the Al-substituted T-sites. In this outlook, all

⁺ monomer anchoring sites. Our

11 unique Si or Al sites
within H-ZSM-5 are accessible as
MoO₂OH

12 exploration of this two-
dimensional space of Al siting and
MoO₂OH⁺ siting is represented as
a matrix in

Figure 9. We have considered only some elements of the matrix in **Figure 9**, computing structures of all
diagonal elements (motifs illustrated in **Figure 1 (a)**), all structures with the MoO₂OH⁺ anchored atop T-
site 8 with the Al sited at each T-site around the 10-member ring (motifs illustrated in **Figure 1 (b)**), and
all structures with the Al atom sited at T-site 8 with the MoO₂OH⁺ anchored at each T-site around the 1030
member ring (motifs illustrated in **Figure 1 (c)**). We have additionally considered first-order off-diagonal
elements of this matrix where one Mo-O_F-Al coordination exists but where anchoring is not atop the Al-
substituted T-site. These detailed structures are summarized in **Tables S3-S6**. In these studies we have
focused on structures around one 10-member ring in the straight channel of H-ZSM-5. All MoO₂OH⁺
structures studied were structurally similar regardless of anchoring environment. One parameter of note,
the average Mo-O_F bond length, increased in the monomers anchored further from the Al, an observation
consistent with the expected weaker anchoring of the Mo-oxide away from the Al³⁺ cation. We
additionally note that the Brønsted acidic proton that is abstracted from the framework BAS during

25 anchoring of MoO₃ to
form MoO₂OH⁺ charge-stabilizes
the Al³⁺ cation against the
formula 4- charge

⁺ is anchored in a motif that has a
26 contributed by the
oxygen atoms of the framework.
When the MoO₂OH

27 direct Mo-O_F-Al
coordination, the cationic
character of the anchored Mo-
oxide stabilizes the charge

imbalance. In motifs where the MoO₂OH⁺ anchors in a way that does not share a direct Mo-O_F-Al
coordination, the hydroxyl group of MoO₂OH⁺ points toward one of the Brønsted basic oxygen sites in
the framework coordinated to the Al³⁺ cation.

- MoO₂²⁺ structure anchored on double Al-atom framework site

On a site with two proximal acidic protons charge-compensating the net negative charge resulting from two framework Al^{3+} cations, the MoO_x stoichiometry of an anchoring monomer should be MoO_2^{2+} .

This MoO_2^{2+} motif is shown in **Figure 8 (b)**. Because of Löwenstein's rule on Al siting and Al-Al distance

$^{2+}$, the only viable double Al-atom sites in the 10-member ring are NNN constraints for anchoring MoO_2

and NNNN arrangements. Examples of these structures are shown in **Figure S7**. In each of the eight

MoO_2^{2+} structures, the Mo atom is roughly tetrahedrally coordinated, with two terminal $\text{Mo}=\text{O}$ bonds

(length 1.70 Å) and a $\text{O}=\text{Mo}=\text{O}$ bond angle of $106 - 107^\circ$. On the $\text{Al}-\text{O}-(\text{Si}-\text{O})_2-\text{Al}$ (NNNN) anchoring

site, Mo is bidentately anchored to two framework oxygen atoms ($\text{Mo}-\text{O}_\text{F}$) with bond distances of 2.07 –

2.10 Å and $\text{O}_\text{F}-\text{Mo}-\text{O}_\text{F}$ angles of $135.4 - 135.8^\circ$. Comparing the $\text{Al}-\text{O}-(\text{Si}-\text{O})-\text{Al}$ -coordinated (NNN) 18

structures to the NNNN-coordinated structures, the distance between Mo and framework oxygen ($\text{Mo}-$

O_F), and the bond angle slightly increased to 2.10 – 2.14 Å and $140.1 - 140.5^\circ$, respectively. This

observation could be attributed to the Mo monomer being more symmetrical when anchored at NNNN

sites and acidity being more potent^[29]. The calculated geometries for MoO_2^{2+} -7-11 (Al 8,12) agree with

previous studies^[18, 26]. For the MoO_2^{2+} -9-9 (Al 6,9) structure, the Mo-O_F bond length of 2.10 Å is shorter

^[29]. In comparison with experimental data on 15 than the 2.12, 2.37 Å reported in other DFT studies

16 comparable motifs in the literature^[28] (Mo-O_F: 1.85 Å and Mo=O: 1.69 Å), the Mo-O_F bond lengths in

our models (2.07 – 2.14 Å) are considerably larger, but the Mo=O bond length (1.70 Å) agrees well. It is expected that bond lengths of the functional employed in this work will generally lead to slightly longer bond lengths relative to experiment, although often not by more than a handful of percent (~2 – 4%) so we find reasonable but not exceptional agreement between our structures and experimental measurements attributed to this motif. Summarized structural details for the MoO_2^{2+} species in this work are provided in **Table S7**.

- $\text{Mo}_2\text{O}_5^{2+}$ structure anchored on double Al-atom framework site 25 sites inside straight and sinusoidal channels of H-ZSM-5, we considered all of the pairs of Al-substituted $^{2+}$ monomers plus additional sites to further represent the diversity of 26 T-sites used in our study of MoO_2

structures available to the larger dimers (motif illustrated in **Figure 8 (c)**). A subset of these motifs is

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50 28 illustrated in **Figure S8**. Geometric descriptors for the 12 Mo dimer structures studied are reported in **Table S8**. The Mo dimers we observe are consistent with those reported by Bao and co-workers^[29], wherein the Mo atoms are each bidentately coordinated to two framework oxygens (Mo-O_F), and the MoO-Mo bridge forms an obtuse angle pointed toward the channel center. This motif is qualitatively distinct

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3 1 from the proposed structure by Iglesia and co-workers^[25], where each Mo atom connects with one

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5 2 framework oxygen atom and the Mo-O-Mo bridge's obtuse angle instead points toward the channel wall.

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3 This qualitative discrepancy between the predicted Mo₂O₅²⁺ species and experimentally determined

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^[29]. Each Mo in this dimer published structure is consistent with the observations of Bao and co-workers

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5 motif is qualitatively trigonal bipyramidal in its coordination and the overall structure is roughly

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10 previous DFT studies^[29]. The
obtained Mo-O bond distance in the Mo-
O-Mo bridge is 1.87 – 1.94 Å,

[25], but which agrees well with the Mo-O
11 which is slightly larger than the
experimental value of 1.84 Å

12 bond distance of the previous
DFT calculations (1.91 Å)^[29]. The
calculated Mo-Mo distances in our model,

13 3.33 – 3.54 Å, are smaller than the previous experimental studies by Iglesia and co-workers^[25] (3.7 Å) but
14 agree well with the theoretical studies by Zhou et al.^[29] (3.57 Å). Finally, the Mo-Al distance in our DFT-

15 optimized geometry varies from 2.98 – 3.63 Å; this longer Mo-Al distance (one Al-Mo distance is ~3 Å

16 and the other is ~3.6 Å) in dimer motifs anchored at NNN Al sites (Al-O-Si-O-Al arrangement) agrees
17 well the experimentally determined value data of 3.6 Å^[25] while it is considerably greater than the DFT-

18 calculated distance for a comparable NNN motif of 3.20 Å (with Al substituted at T-sites 6 and 9) by Zhou

19 et al.^[29]. The overall discrepancies between our calculated values and experimental reports is unsurprising

20 due to the qualitative differences between our predictions and the experimentally proposed motif.

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lculations^[18, 29]
show
good
overall
agreement. Our
data are
reported in
**Table
S9.**

3.3.2. Energetics of Mo-oxides in H-ZSM-5

In addition to predicting structures, we computed the binding energies for each structure as described in the methods section in the supporting information (SI). We have used these binding energies as a basis for evaluating the relative thermodynamics of these structures to compare candidate structures within a given motif. The binding energies of the various MoO_2OH^+ monomers are presented as a heat map in **Figure 9**. For instance, MoO_2OH^+ -8, Al 8 (**Figure 1 (a)**), a motif with Mo anchored atop the Al-substituted T-site, is predicted to be 60 kJ mol^{-1} more stable than MoO_2OH^+ -9, Al 8 (**Figure 1 (c)**) which features only one Mo-O_F-Al coordination. The same atop-anchoring motif of Mo, MoO_2OH^+ -8, Al 8, is 167 kJ

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mol^{-1} more stable than MoO_2OH^+ -8, Al 2, a structure with the Al and Mo coordinatively separated by four T-sites. In general, greater coordinative distance between the Al site and the site at which MoO_2OH^+ is anchored results in a decrease in predicted binding energy. Therefore, for a given Al siting, it is more likely that Mo will anchor near to the Al and we expect these species to dominate observed structures.

While we do expect the “conventional” MoO_2OH^+ monomers anchored atop the Al-substituted T-site to contribute to the Mo-oxide mixture, we note that that some structures that share only one Mo-O_F-Al

$^{-1}$ less stable than the atop motifs with two such coordinations, coordination are only $10 - 30 \text{ kJ mol}$

corroborating that these species are very likely to be observed in significant population. Generally,

differences in binding energies of MoO_2OH^+ monomers could be attributed to two factors: intrinsic T-site anchoring preferences and the coordinative separation between the Al-substituted T-site and the Mo monomer anchoring site. Al siting is static from synthesis; therefore, only a small set of the predicted structures will actually be realizable at a given Al-substituted T-site in a real material. In a real sample, it is likely that some distribution of these (and similar) species would coexist with other oxide speciations (MoO_2^{2+} monomers and $\text{Mo}_2\text{O}_5^{2+}$ dimers), for which we discuss the energetics next.

		Mo oxide T-site									
		1	5	6	9	8	7	11	12	3	2
Al atom T-site	1	-281	-251			-136					
	5	-244	-284	-247		-189					
	6		-250	-291	-236	-192					
	9			-259	-271	-258					
	8	-143	-192	-197	-231	-291	-260	-191	-156	-147	-138
	7					-253	-297	-255			
	11					-202	-252	-298	-230		
	12					-186		-270	-280	-262	
	3					-144			-242	-299	-271
	2					-124				-247	-302

Figure 9. Binding energies (kJ mol^{-1}) of MoO_2OH^+ monomers anchored at single Al atom site (T-site indexing shown in **Figure 8 (a)**). These data are also presented tabularly in **Table S10**.

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3 1 Table 5 DFT-calculated binding energy of isolated MoO₂²⁺ monomer oxide species anchored on a double Al-atom
5 2 framework site.

Model characteristic	Structure	Anchoring site type	Channel type	Binding energy (kJ mol ⁻¹)
Mo monomer on double Al-atom site	MoO ₂ ²⁺ -7-11 (Al 8,11)	NNN	Straight	-187
	MoO ₂ ²⁺ -7-11 (Al 8,12)	NNNN	Straight	-153
	MoO ₂ ²⁺ -9-9 (Al 6,9)	NNN	Sinusoidal	-226
	MoO ₂ ²⁺ -9-9 (Al 6,6)	NNNN	Sinusoidal	-182
	MoO ₂ ²⁺ -12-12 (Al 3,12)	NNN	Sinusoidal	-220
	MoO ₂ ²⁺ -12-12 (Al 3,3)	NNNN	Sinusoidal	-188
	MoO ₂ ²⁺ -10-10 (Al 1,10)	NNN	Sinusoidal	-215
	MoO ₂ ²⁺ -10-10 (Al 1,1)	NNNN	Sinusoidal	-185

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4 **Table 5** provides the
DFT-calculated binding
energies of MoO₂²⁺ motifs
anchored on double Al

2+ species to anchor at Al-Al
5 framework sites. As
shown in **Table 5**, there is a
weak preference for MoO₂

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6 pairs in the NNN (Al-Si-O-Si-Al) arrangement. It should be noted that intrinsic Al siting in the H-ZSM-5

is responsible for part of the observed binding energy differences: more stable Al siting generally leads to weaker binding of an external species. The NNNN (Al-(Si-O)₂-Al) arrangement serves as a less

favorable anchoring site for MoO₂²⁺; the two Al³⁺ are sited farther away from one another, and bonding of Mo to two O_F induces a greater distortion in the framework than in NNN motifs.

Table 6. DFT-calculated binding energy of isolated Mo dimer oxide species anchored on a double Al-atom framework site.

Model	characteristic	Structure	Anchoring site type	Channel type	Binding energy (kJ mol ⁻¹)
Mo ₂ O ₅ ²⁺ -8,12 (Al 8,11)	NNN	Straight	-491		
Mo ₂ O ₅ ²⁺ -8,12 (Al 8,12)	NNNN	Straight	-552		
Mo ₂ O ₅ ²⁺ -6,6 (Al 6,9)	NNN	Sinusoidal	-487		

Mo ₂ O ₅ ²⁺ -6,6 (Al 6,6)	NNNN	Sinusoidal	-546		
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Mo monomer on double Al-atom site	Mo ₂ O ₅ ²⁺ -3,3 (Al 3,12)	NNN	Sinusoidal	-549	
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Mo ₂ O ₅ ²⁺ -3,3 (Al 3,3)	NNNN	Sinusoidal	-606		
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Mo ₂ O ₅ ²⁺ -1,1 (Al 1,10)	NNN	Sinusoidal	-496		
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Mo ₂ O ₅ ²⁺ -1,1 (Al 1,1)	NNNN	Sinusoidal	-562		
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Mo ₂ O ₅ ²⁺ -3,7 (Al 3,7)	NNNN	Straight	-568		
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Mo ₂ O ₅ ²⁺ -3,7 (Al 3,8)	NNNNN	Straight	-486
Mo ₂ O ₅ ²⁺ -2,8 (Al 2,8)	NNNNNN	Straight	-446
Mo ₂ O ₅ ²⁺ -3,11 (Al 2,7)	NNNNNN	Straight	-496

Table 6 provides the DFT-calculated binding energies of the Mo₂O₅²⁺ dimers anchored on different double Al framework sites. As shown in **Table 6**, Mo₂O₅²⁺ interacts more favorably with NNNN (Al-(Si-[²⁹]. We do O)₂-Al) arrangements of Al substitutions, in agreement

not expect these energetics to affect speciation because Al siting distributions arise during zeolite

synthesis, anchoring of the monomer precursor species (MoO_2OH^+) happens independently, and

formation of the $\text{Mo}_2\text{O}_5^{2+}$ dimer can be regarded as irreversible and possible if two monomers exist in

appropriate proximity to one another. Thus, the main utility of the energies here is in demonstrating that

these dimers may at least be thermodynamically competitive with the MoO_2OH^+ monomer species.

We note that the energies computed for all motifs and the comparisons between them often rely on

zeolites with different Al sitings, limiting the utility of directly comparing some reported energies.

Moreover, the irreversibility of formation/anchoring/interconversion of MoO_x species as shown in **Figure**

2 (due to disproportionation of H_2O) is expected to result in kinetic trapping, and therefore global

thermodynamic minima are not expected to be explored. Nonetheless, comparing relative energetics of

species of like motif with similar Al sitings can be useful in building insights into which species are most

probable to observe, and the database of structures we have built through this study forms a strong basis

for comparison to experimentally measured spectral data. To corroborate our computational DFT investigations, experimental TPO measurements, and operando XAS spectroscopy, we employ theory-

guided X-ray absorption spectroscopy (QuantEXAFS) to evaluate the speciation of isolated Mo-oxides on

H-ZSM-5 prepared via different synthesis techniques (PM vs. IWI) and Mo loadings (1, 3 wt.%) by

mapping the experimental XAS spectra to the model spectra from DFT-predicted structures.

3.4.

QuantEXAFS/DFT: Active Site Identification

[40] was employed to compare
Theory-guided X-ray
absorption spectroscopy
analysis (QuantEXAFS)

our DFT-predicted Mo-
oxide structures to
experimentally measured
EXAFS spectra to aid in our
analysis

of Mo-oxide speciation in our TPO experiments. QuantEXAFS combines the systematic DFT calculations
of potential stable MoO_x structures with automated analysis of EXAFS data with the aim of determining
the location and motif of the Mo-oxides in H-ZSM-5. In this study using QuantEXAFS, we have analyzed
four samples differing in synthesis technique (IWI and PM), and Mo loading (1 wt.% and 3 wt.%) with H-
ZSM-5 of consistent acidity at Si/Al = 15.

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While our DFT calculations have demonstrated that each of the three qualitatively distinct Mo-oxide
motifs is thermodynamically reasonable, our commentary thus far on which species we expect to observe
has been based on interpretation of TPO results, which provides indirect evidence of Mo-oxide local
structures. By using our DFT-predicted structures as a database for comparison to our experimentally
measured EXAFS spectra, we demonstrate that the measured spectra are consistent with the spectra that

could arise from the distinct motifs represented among our model structures. **Figure 10** shows the experimentally measured Mo K-edge EXAFS data, which we additionally note exhibit distinct characteristics between different Mo loadings and/or preparation methods, suggesting that the spectral differences observed may be attributed to both metal loading and catalyst preparation method.

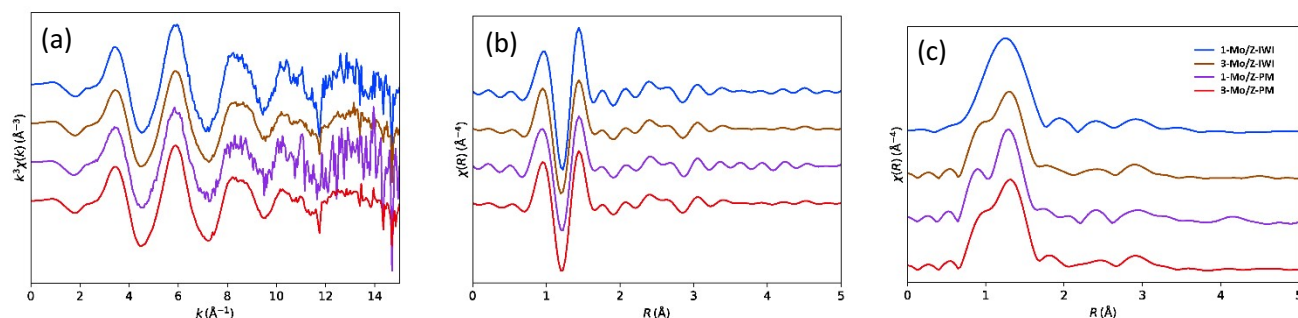


Figure 10. Experimental EXAFS data, (a) k -space (2.0–14.0 $\text{\AA}^{-1}$), R -space (b) imaginary part, and (c) magnitude (0.5–5.0 $\text{\AA}$).

For 1-Mo/Z-IWI (15), we find that the structures that best fit are all MoO_2OH^+ motifs, suggesting a preponderance of isolated oxide monomers in samples prepared in this way. This is consistent with what we would expect for a low metal loading prepared via IWI, where we reason that the impregnation method lends to better dispersion of metal oxide species over PM, where the mechanism for impregnation is diffusion of external material into the zeolite pore at elevated temperatures. Notably, we also expect to see MoO_2^{2+} monomeric species in samples prepared in this way because the higher acidity of zeolite and low loading is expected to lead to availability of the requisite double Al sites for this motif. However, from the set of structures from DFT that we used to fit the EXAFS spectra, no MoO_2^{2+} species were identified among the best fits. In 3-Mo/Z-IWI (15), MoO_2^{2+} monomers were among the best fits along

with the MoO_2OH^+ monomers that also fit 1-Mo/Z-IWI (15). We additionally identify dimeric $\text{Mo}_2\text{O}_5^{2+}$ among the best fits for 3-Mo/Z-IWI (15). This is consistent with our expectations for a sample with increased Mo loading, where it is more probable for two anchored MoO_2OH^+ monomers to exist anchored in proximity to one another such that they may condense to form the Mo dimeric species. We show an

example of a predicted EXAFS spectrum and the DFT-predicted structure from which it arises in 2 comparison to the experimentally measured EXAFS spectrum for which it is identified as a good fit in

Figure 11. The MoO_2OH^+ structure identified as a good fit for the spectrum of 3-Mo/Z-IWI is MoO_2OH^+ -

5, Al 8, which is not among the most stable structures for Al at T-site 8. Because all DFT-predicted

structures are ground state ($T = 0$ K) calculations, it is likely that thermal motion and variation in local

structure may be contributing to the experimental observations and that off-minimum features not captured

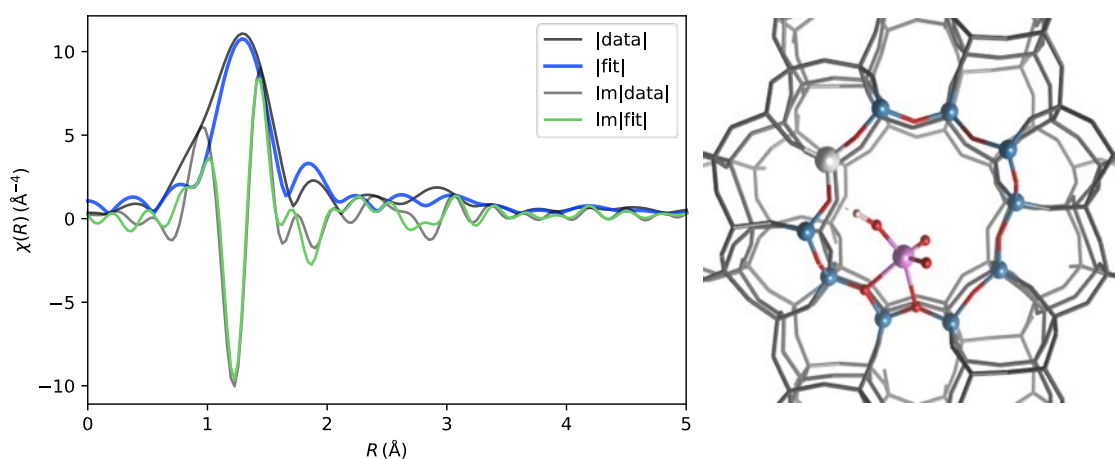


Figure 11. Experimentally measured EXAFS spectra, predicted spectra from the DFT structure, and the DFT-predicted structure (MoO_2OH^+ -5, Al 8), for sample 1-Mo/Z-IWI (15) (k -range 3.0–11.5 $\text{\AA}^{-1}$ and R -range 1.0–5.0 $\text{\AA}$).

in the DFT structures contribute to spectra observed. It is reasonable also that at elevated temperatures

structures that are not the most probable will be dynamically explored by the system, although the stability

of the identified structure, MoO_2OH^+ -5, Al 8, is ~ 100 kJ mol^{-1} less stable than the most stable comparable

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10 monomer with Al at T-site 8, and it is unlikely that this specific structure is to be observed. Nonetheless,

the slight differences among DFT-predicted structures for each motif allow for consideration of the ways
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12 these motifs may manifest in H-ZSM-5 and for identification of spectral signatures that may indicate their

presences.

Considering the samples prepared via physical mixing, 1-Mo/Z-PM (15) shows good fits of EXAFS

spectra to both isolated MoO_2OH^+ monomer motifs as well as $\text{Mo}_2\text{O}_5^{2+}$ dimer motifs, even at low metal 50
16 loadings. We attribute this to the likelihood of poor dispersion and spatial clustering of anchored oxides 17
due to the temperature and mechanism of metal oxide impregnation in PM-prepared samples. We note 18 that
the two dimeric $\text{Mo}_2\text{O}_5^{2+}$ species identified as best fits are one each of NNN- and NNNN-type siting

19 of Al, supporting that these species may form on either Al siting arrangement. Notably we do not identify

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3 1 any best-fit candidates among dimer motifs with coordinative separation of Al sites greater than NNNN.

2 The same observations for 1-Mo/Z-PM (15) apply for 3-Mo/Z-PM (15), where monomeric MoO_2OH^+ and

3 dimeric $\text{Mo}_2\text{O}_5^{2+}$ provide the best fits. For monomeric species, we identify a comparable but not identical

4 set as in the case of 1-Mo/Z-PM (15). For dimeric species, we again identify both NNN- and NNNN-type

Al sitings among the best fits. The absence of MoO_2^{2+} monomeric species among best fits is both notable and consistent with our expectations. We attribute this to the likely spatial clustering of the impregnated $^{2+}$ species requires an 7 Mo-oxide in the zeolite pore, regardless of metal loading. Formation of the MoO_2 $^+$ species to exist in proximity to a vacant BAS such that disproportionation of a water 8 anchored MoO_2OH molecule may occur. Because of the likely spatial clustering of Mo-oxides in PM preparations, these sites are less likely to arise, even at low metal loadings in relatively acidic zeolites. A complete accounting of our stable structures that give reasonable EXAFS fits for IWI- and PM-prepared samples are reported in the Supporting Information in **Figures S9-12** and **Table S11**. The respective QuantEXAFS fitting parameters including the $\sigma\sigma^2$, bond distances, and ΔE_0 are presented in **Table S12**. The identified stable structures that give reasonable EXAFS fits (those that have an R-factor value of <0.2 and have realistic EXAFS fit parameters) and are consistent with our other experimental results are summarized in **Figure 12** and presented as a function of synthesis technique and metal loading.

When performing preliminary catalytic activity measurements contrasting the activity of the catalysts

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prepared by IWI and PM with 4 wt.% Mo loading in MDA we found that that possible subtle differences in structures of the Mo-oxide species due to different synthesis methods did not lead to significant differences in the catalytic performance (**Figure S13**). This is not entirely surprising as catalyst activation for MDA is achieved by reducing the Mo-oxide species under high temperature reducing conditions and the effect of the Mo-oxide structure on the reduced Mo sites is not yet known. Furthermore, this result aligns with previous work in which researchers employing these different synthesis techniques still achieve very similar benzene yields when employing similar Mo loadings. However, we also note that the reactor employed for our measurements only provides global average kinetic data and may not allow for a distinction in the intrinsic kinetics resulting from the different Mo-oxide speciation. Rigorous evaluation of the microkinetic details and the intrinsic kinetics of the catalysts prepared by the different synthesis techniques would require performing transient kinetic experiments, for instance in a temporal analysis of products (TAP) reactor, which are not within the scope of the work we are presenting here.

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4. Conclusions

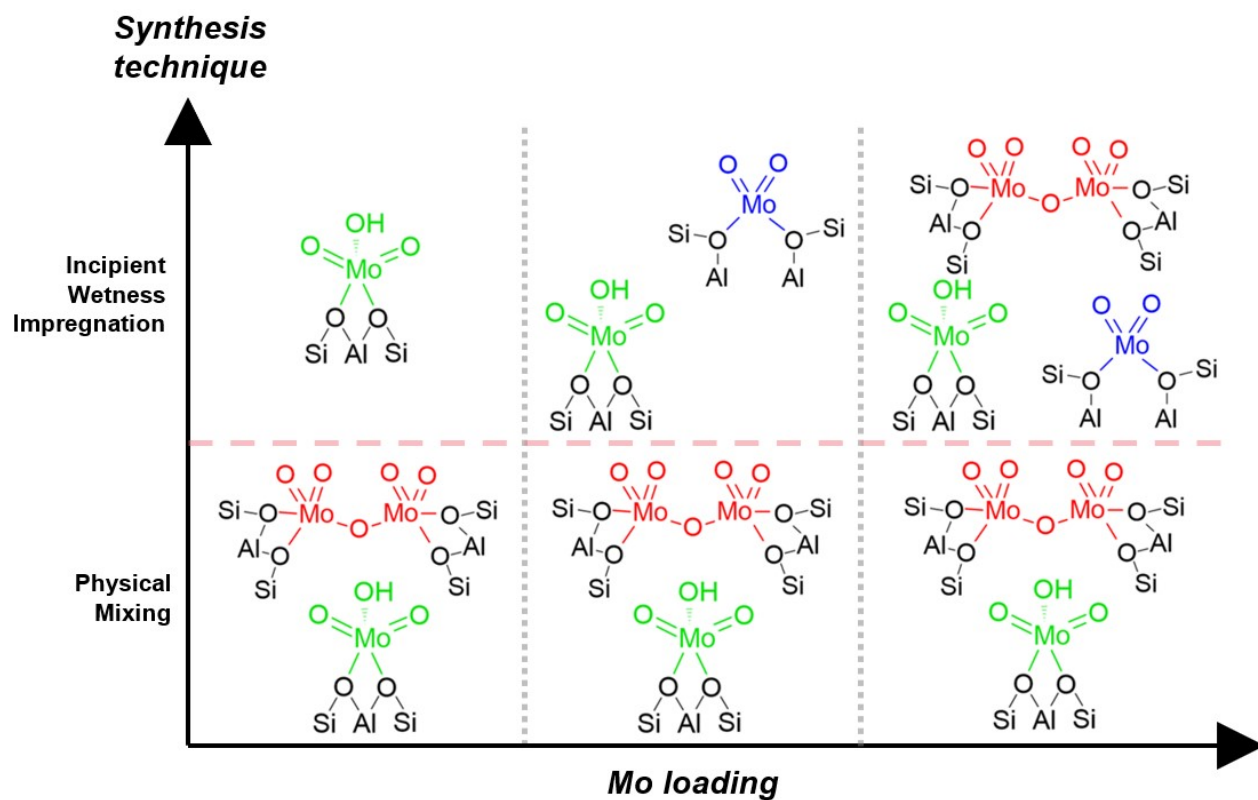


Figure 12. Summary of most probable Mo-oxide species in Mo/H-ZSM-5 as affected by synthesis technique and Mo loading.

In the preceding work, we have presented fundamental and synergistic experimental and computational investigations of H-ZSM-5 impregnated with Mo-oxides as a platform system for building broader understanding of the effects of metal loading and impregnation method on the resultant metal oxide speciation in acidic zeolites. We have selected this system for its relevance as a prominent catalyst with yet-unsettled fundamental questions about its nature in the literature around MDA, but we note that metal oxides impregnated in zeolites are of interest for a variety of applications in catalysis. We have used

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11 a combination of TPO experiments, XANES and EXAFS experiments, DFT calculations, and
12 QuantEXAFS analysis to investigate the speciation of Mo-oxides in H-ZSM-5, establishing that the metal
13 oxide catalyst precursors are likely to exist in multiple qualitatively distinct motifs, and that the
14 distribution of motifs observed may be controlled to a limited extent through amount of metal oxide added
15 to the zeolite as well as through the method in which the metal oxide is impregnated into the zeolite. In
16 our analysis, we have considered the three most proposed motifs for Mo-oxides in H-ZSM-5. Because
17 these motifs, MoO_2OH^+ , MoO_2^{2+} , and $\text{Mo}_2\text{O}_5^{2+}$, each are understood to anchor differently within the H-

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3 1 ZSM-5 channels at Brønsted acidic sites, quantified evolution of H_2O during TPO provides evidence for
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5 2 differences in the distributions of these anchored species in terms of the H/Mo ratio observed. Our TPO
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7 3 experiments demonstrate that IWI preparations result in more water evolution per metal anchored relative
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9 4 to PM preparations, indicating different distributions of Mo-oxide species between these preparations.
10 5 TPO further provides evidence that anchoring occurs at different temperatures via monitoring
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12 6 temperature-dependent evolution of H_2O , with IWI-prepared metal oxides anchoring at 200 – 500 °C and
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14 7 PM-prepared oxides anchoring at 350 – 700 °C. These results are corroborated and further supported by
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16 8 complementary operando XANES experiments showing temperature-dependent evolution of the Mo K-

edge consistent with changes in local Mo coordination consistent with our TPO results. Our measured EXAFS spectra also serve as inputs complementary to our suite of DFT-predicted structures in our QuantEXAFS analysis. To establish a database of structures for QuantEXAFS analysis and to understand the ways in which these various Mo-oxide motifs may manifest in H-ZSM-5, we performed DFT calculations on 42 MoO_2OH^+ monomeric oxides, eight MoO_2^{2+} monomeric oxides, and 12 $\text{Mo}_2\text{O}_5^{2+}$ dimeric oxides to form a database of 62 unique candidate structures. Our DFT calculations characterize these oxide structures and demonstrate that Mo-oxides may viably anchor in a variety of ways in H-ZSM-5. Notably, our DFT calculations demonstrate that, while not energetically favored, it is feasible for Mo oxides to anchor in the vicinity of BAS without direct coordination to the BAS and that dimeric Mo-oxides may form from condensation of monomers anchored near Al-substituted T-sites of greater separation than the Al siting restrictions necessary for formation of MoO_2^{2+} monomeric species. We combine our EXAFS spectra with our DFT-predicted structures in QuantEXAFS analysis to identify from among our candidate structures which provide best-fit agreement with measured spectra. Through this analysis we find that both metal loading (1 – 3 wt.% Mo) and impregnation method (IWI vs. PM) lead to different EXAFS spectra, which are best-fit by qualitatively different Mo-oxide motifs. Samples prepared with IWI showed spectra consistent with a greater prevalence of monomeric Mo-oxides, with increased metal loading resulting in spectra suggesting formation of more dimeric species. This is consistent with the understanding of IWI leading to better dispersion of smaller Mo-oxides within H-ZSM-5 prior to anchoring at higher temperatures. Complementarily, PM-prepared samples indicated a presence of dimeric oxide species even at the lowest loading of 1 wt.%, consistent with the understanding of the anchoring mechanism of larger oxide particles breaking up and diffusing as smaller agglomerates only at

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30 temperatures already capable of facilitating anchoring of these oxides at BAS of H-ZSM-5, resulting in 31 overall lower metal oxide dispersion.

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Overall, we have brought complementary experimental and theoretical techniques together to build an improved understanding of Mo-oxides in H-ZSM-5, a catalytically relevant system for MDA catalysis.

Our work suggests and supports the existence of a distribution of Mo-oxides in H-ZSM-5 comprised of a combination of various qualitatively distinct motifs reported in previous literature. We additionally provide evidence that the catalyst precursor synthesis approach leads to different abundances of the various oxide species, an observation that can reconcile some of the long-standing lack of consensus surrounding these systems. We rationalize our observations through consideration of the impregnation methods and the likely processes underlying the anchoring of these catalyst precursors. This work thus provides for the first time a rational understanding and basis for engineering speciation of oxides through choice of preparation method and metal loading. While it is yet unsettled what implications these various anchored oxide motifs may have on the structure, stoichiometry, and performance of the activated (carburized) Mo sites, understanding the precursors is a necessary first step toward rational design of next generation MDA catalysts. Additionally, we envision that the conclusions drawn and the techniques employed may naturally extend to other comparable metal-oxide/zeolite composite materials.

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24 Computing Center.

25 6. Supporting Information

26 The Supporting Information is available free of charge at [URL]. Experimental and computational

27 methods, nomenclature, TPO results, TPO-XAS results, reactivity data, DFT-predicted structures and

28 properties, and QuantEXAFS data (.docx). Electronic supporting information (*.zip) contains VASP

29 structure files for 62 DFT-predicted structures and Excel sheet containing descriptive names of each

30 structure file.

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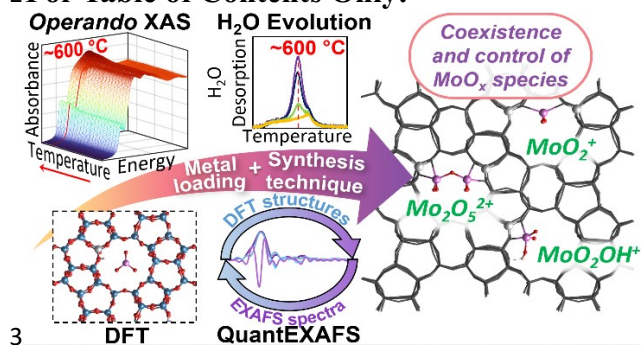
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