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Reactivity of a Carbon-Supported Single-Site Dioxo-Molybdenum Catalyst for Biodiesel Synthesis

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Supporting Information Placeholder

ABSTRACT. A single-site dioxo-molybdenum catalyst, $(O_c)_Mo(=O)_2@C$, was prepared via direct grafting of $MoO_2Cl_2(dme)$ (dme = 1,2-dimethoxyethane) on highsurface-area activated carbon. The physicochemical and chemical properties of this catalyst were fully characterized by N₂ physisorption, ICP-AES/OES, PXRD, STEM, XPS, XAS, Temperature-Programmed Reduction with H₂ (TPR-H₂), and Temperature-Programmed NH₃ Desorption (TPD-NH₃). The single-site nature of the Mo species is corroborated by XPS and TPR-H₂ data, and it exhibits the lowest reported MoO_x T_{max} of reduction reported to date, suggesting a highly reactive Mo center. (O_c)₂Mo(=O)₂@C catalyzes the transesterification of a variety of esters and triglycerides with ethanol, exhibiting high activity at moderate temperatures (60 - 90 °C) and with negligible deactivation. $(O_c)_2Mo(=O)_2@C$ is resistant to water and can be recycled at least 3x with no loss of activity. The transesterification reaction is determined experimentally to be first-order in [ethanol] and first-order in [Mo] with $\Delta H^{\ddagger} = 10.5$ (8) kcalmol⁻¹ and $\Delta S^{\ddagger} = -32$ (2) e.u. The low energy of activation is consistent with the moderate conditions needed to achieve rapid turnover. This highly active carbon-supported single-site dioxo-molybdenum species is thus an efficient, robust, and low-cost catalyst with significant potential for transesterification processes.

Keywords: heterogeneous catalysis, molybdenum, supported catalysts, biodiesel, transesterification.

Introduction

Lower alcohols – particularly methanol and ethanol – have attracted recent attention due to their utility in energy processes and fine chemical production. Methanol and ethanol are both bioavailable,^{1,2} making them attractive renewable feedstocks for upgrading potential fuels. Consequently, methanol and ethanol have both found use in commercially important transesterification processes, most notably fatty acid methyl and ethyl ester synthesis, for converting bioavailable triglycerides into biodiesel fuel.³ The transesterification of vegetable oils has proven a viable alternative to environmentally undesirable transformations requiring strong homogeneous bases such as KOH.⁴ However, the presence of impurities in the feedstock remains a challenge to developing practical catalytic transesterification processes.⁵ Here porous solid bases have made significant contributions.⁶⁻⁹

Among the transesterification catalysts reported to date, the most common classes are: 1) homogeneous strong Brønsted acids,¹⁰ which generate strongly acidic waste and cannot be recycled, and 2) Lewis acid catalysts, most notably, tin-based systems." Note that the toxicity of tin has driven the search for cheap, earth-abundant alternatives. Molybdenum-based catalysts are viable alternatives for transesterification, but typically suffer from poor recyclability¹² or require hightemperatures to achieve useful activity.13 This Laboratory and others have detailed the attractions of grafted single-site heterogeneous catalysts,14-24 an approach which permits rational design of active sites tailored to the reaction of interest. In designing an active site, note that recent catalytic studies in ethanol implicate in-situ generated molybdenumoxo moieties as the catalytically active species.²⁵ Further supporting this, early work by Iwasawa et al.,26 later corroborated by Kikutani,^{27,28} implicates dioxo-molybdenum as the active species in the oxidation of ethanol by MoO_x/SiO₂ catalysts. In homogeneous catalysis, dioxo-molybdenum complexes have demonstrated redox-active catalytic activity in olefin epoxidation^{29,30} and sulfide oxidation.³¹ Very recently, an MoO₂(acac), catalyst was found to be competent for transesterification in the cross-linking of polymers with tetraethylorthosilicate (TEOS),³² and supported MoO₃ was found to promote transesterification between diethyl oxalate and phenol.^{33,34} In the past, dioxo-molybdenum complexes have been successfully heterogenized on polymers³⁵ and mesoporous silicas.³⁶ We therefore envisioned that a welldefined dioxo-molybdenum transesterification catalyst with superior catalytic performance might be prepared by grafting a molecular dioxo-molybdenum precursor to an appropriate support.

Recently, activated carbon has emerged as an attractive alternative to conventional refractory oxide supports because of its high surface area, porous structure, and low cost.³⁷ Carbon materials exhibit tunable surface functionalities and enhanced hydrothermal stability arising from their hydrophobicity.^{38,39} Furthermore, Katz has shown that the aromatic character of activated charcoal results in favorable energetic contributions in the absorption of glucans having large hydrophobic backbones.⁴⁰ Such interactions should be of considerable value in biodiesel transformation due to the hydrophobic character of oil and triglyceride feedstocks.

This contribution reports the grafting of isolated welldefined dioxo-molybdenum sites on a high surface area carbon support with known physicochemical properties and acidity, to create the catalyst $(O_c)_2Mo(=O)_2@C$ (Scheme 1). This product is extensively



Scheme 1. Direct grafting of $MoO_2Cl_2(dme)$ onto activated carbon to make $(O_c)_2Mo(=O)_2@C$.

characterized by ICP-AES/OES, N₂ physisorption, PXRD, TEM, and X-ray Absorption Spectroscopy (XAS). In addition, the unique chemical character of the isolated Mo site is probed by XPS, Temperature-Programmed Reduction with H₂ (TPR-H₂), and Temperature-Programmed Desorption of NH₃ (TPD-NH₃). It is further demonstrated that this catalyst is competent for liquid-phase transesterification of triglycerides, as well as primary, secondary, and tertiary esters with lower alcohols under mild conditions (60 - 90 °C), displaying high activity and broad scope. The catalyst operates efficiently in organic solvents and shows no inhibition in the presence of water. Lastly, the catalyst exhibits no deactivation and minimal leaching under reaction conditions, as determined by recyclability studies, XPS, PXRD, and H₂ TPR. The results show $(O_c)_2 Mo(=O)_2 @C$ to be an economical, efficient, and robust catalyst for transesterification processes.

Results

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59 60 Support and catalyst characterization. The carbon-supported dioxo-molybdenum catalyst was prepared via direct grafting of $MoO_2Cl_2(dme)^{41}$ (dme = 1,2-dimethoxyethane) onto an activated carbon support in CH₂Cl₂ at room temperature, vielding the single-site well-defined (O_c)₂Mo(=O)₂@C structure (Scheme 1; see experimental details in the Supporting Information). With no post-thermal treatments such as calcination, the four-coordinate tetrahedral dioxo-molybdenum surface structure (Scheme 1) is proposed. The absence of Cl atoms in $(O_c)_2Mo(=O)_2@C$ is confirmed via ICP-OES (Table S1) and XPS (Figure S3). There have been previous reports of Cl⁻ substitution at Mo(O)₂Cl₂L₂ complexes indicating that Cl⁻ loss in this system is feasible.⁴²⁻⁴⁴ The carbon support shows XPS evidence of hydroxylated groups (and carboxylic, carbonyl, ether, and anhydride functionalities, SI Table S2) where the Mo can bind with release of HCl. This geometry

has been observed in previous MoO_x catalysts, and is suggested to be of high catalytic relevance.45-50 XPS analysis reveals no species other than C, O, and Mo on the catalyst, although ICP-AES indicates the presence of S, N, and P impurities in the starting support (and < 100 ppm Cl). These impurities in the carbon support were determined to be catalytically insignificant in control experiments (vide infra). A typical catalyst contains 2.1 wt% Mo. The maximum weight loading of Mo obtained is 5.0 wt%. The carbon support and $(O_c)_Mo(=O)_mC$ catalyst were fully characterized by PXRD, XPS, XAS, N₂ physisorption, Z-contrast STEM, and ICP-AES (SI, Figures S2-S4 and Table S2). Grafting of the Mo species results only in a minor change in surface area (from 1378 m^2/g to 1322 m^2/g) and no change in pore diameter or crystallinity in the catalyst (by BET and BJH). STEM confirms the amorphous character of the carbon (Figure S₂). Furthermore, images taken in Z-contrast mode reveal no significant Mo aggregate domains, in support of a catalyst formulation having primarily isolated dioxo-molybdenum active sites. As further confirmation, no crystalline MoO₂ phase is detected by XPS (Figure 1A), STEM (Figure S₂), or PXRD (Figure S₄) before or after catalytic reactions, suggesting the highly dispersed dioxo-molybdenum species remains stable under catalytic conditions.

The activated carbon was determined to be mildly acidic, possessing 150 ± 15 µmol/g acid sites with pKa between 6.5 and 10.3, according to Boehm titration.⁵¹ The corresponding acidity of $(O_c)_2Mo(=O)_2@C$ could not be determined due to Mo leaching under alkaline conditions. To determine whether strong acid sites are generated in grafting of the dioxomolybdenum species, Temperature-Programmed Desorption of NH₃ (TPD-NH₃) was measured as shown in Figure 1A. The lack of a significant shift in the T_{max} for ammonia desorption from the $(O_c)_2Mo(=O)_2@C$ indicates that no strong acid sites are present.⁵²⁻⁵⁴

Due to the highly absorptive optical nature of activated carbon at most spectral wavelengths, and the low loading of Mo, FTIR, Raman, and UV-vis spectroscopies could not observe the catalytically-active $(O_c)_2 Mo(=O)_2$ site. However, the catalyst can be characterized with Mo XAS, Mo(3d) XPS and TPR (Figure 1). Mo K-edge XANES exhibits pre-edge and edge peaks at 20.0067 and 20.0160 keV respectively, which are indicative of Mo^{VI} (SI, Figures S10-12 and Table S11 for Mo^{IV} and Mo^{VI} standards comparisons). EXAFS fitting shows 2 Mo=O bonds at a distance of 1.68 Å, 1 Mo-O bond at 1.98 Å and 1 Mo-O bond at 2.29 Å (Table S11 and Figure S13). XAS indicates that $(O_c)_2Mo(=O)_2@C$ is closely related to MoO_3 , and corroborates the 4-coordinate proposed structure in Scheme 1. As shown in Figure 1B, the binding energy of Mo^{VI} in MoO₂, measured as a reference in the same spectrophotometer, is found to be 233.3 eV. The binding energy of the Mo^{VI} in $(O_c)_2Mo(=O)_2@C$ catalyst is found to be 232.8 eV, slightly shifted from the bulk MoO3 environment but consistent with literature assignments of hexavalent Mo species and with enhanced hole-screening by the carbon support.55,56 No variation in the Mo binding energy is observed with loading, nor after the catalyst is recovered from catalytic reactions. No MoO₃, molybdenum carbide, or oxycarbide phase is detected by XPS, arguing that the active site remains as a highly dispersed dioxo-molybdenum species. The XPS C(1s)

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58 59 60 peak (Figure S₃B) contains three contributions. Bulk graphitic carbon is referenced to 285.0 eV. Additional features appear at 286.6 eV and 289.6 eV. These species are assignable to carbon species in -C=O and -COOH environments, as has been previously reported in the literature.^{57,58} The XPS O(1s) peak of the support (Figure 1C, Figure S₃C) can be deconvoluted into three components at 531.2 eV, 533.3 eV, and 536.1 eV. These ionizations can be assigned to carbonyl oxygen species, alcohol or etheric oxygen species, and adventitious water respectively,^{57,58} consistent with the species observed in the C(1s) spectrum.

Temperature-programmed reduction scans with H₂ (TPR-H₂) of $(O_c)_2Mo(=O)_2@C$ and related materials are shown in Figure 1D. Both the carbon support and reference MoO₃ exhibit no reduction events below 400 °C, although MoO₃ is observed to undergo reduction at > 550 °C. The carbon support

begins to consume H₂ independently above 450 °C, thus the analysis was limited to the region below 400 °C. The fresh 2.1wt% $(O_c)_2MO(=O)_2@C$ catalyst shows a single reduction event at 218 °C, suggesting that grafted dioxo-molybdenum sites are highly reducible in comparison to the Mo sites on MoO₃. The same catalyst was investigated after catalytic turnover (*vide infra*) and negligible changes are observed in the TPR profile, indicating that the active site remains intact/unchanged throughout catalysis, in support of the high activity and recyclability found for these $(O_c)_2MO(=O)_2@C$ catalysts (*vide infra*). H₂ consumption by 2.1 % $(O_c)_2MO(=O)_2@C$ during TPR-H₂ was quantified by calibrating the apparatus with CuO. From this analysis, it was determined that 50% of the Mo sites in $(O_c)_2MO(=O)_2@C$ consume H₂ during TPR, and thus it is reasonable to infer



Figure 1. (A) TPD-NH₃ traces comparing carbon (i, red) and 2.1 wt% (O_c)₂ $Mo(=O)_2@C$ (ii, orange). (B) XPS spectra of Mo(3d) peaks. (O_c)₂ $Mo(=O)_2@C$ is 2.1 wt% Mo. Black traces are from MoO₃ used as a reference. (C) XPS spectrum of O(1s) peaks. (O_c)₂ $Mo(=O)_2@C$ is 2.1 wt% Mo. (D) TPR-H₂ traces of reference MoO₃ (i, black), carbon (ii, red), fresh 2.1wt% Mo (iii, green), and used 2.1wt% Mo (iv, orange).

that >50% of the dioxo-Mo sites are catalytically significant. This number is in good agreement with previous reports of single-site heterogeneous catalysts, which typically have between 10 and 70% active sites.^{15,59-63,17,20,64,65-70} Mo K-edge XANES of the catalyst at 218 °C under H₂ flow indicates that the Mo remains in the VI oxidation state (Figure S1 and Table S11). EXAFS shows partial reduction to ~ 1.4 M=O bonds from 2 (M=O: 1.63 Å) which plausibly results from H₂ addition across a Mo=O bond at ~ 50% of the sites (Table S1 and Figure S13). At 218°C there is additionally 1 Mo-O bond at 1.98 Å. Reduction by H₂ at 218°C leads to a loss of 0.4 Mo=O bonds at 1.7 Å and 1 Mo-O at 2.29 Å. A XANES combination fit of Mo^{V1} and Mo^{IV} (MoO₂) is not viable, indicating that the species at 218 °C is most likely (O_c)₂Mo^{V1}(=O)(OH)(H).

Transesterification of lower alcohols and esters. A variety of esters were screened over $(O_c)_Mo(=O)_mC$ at 90 °C under 200 psi Ar_(g) for catalytic transesterification activity (Table 1).^{71,72} The weakly acidic activated carbon support alone is found to be inactive under these conditions, indicating that stronger acids are required for this transformation.⁵ Primary, secondary, and tertiary alkyl esters (1) undergo transesterification to produce the corresponding alcohols (2) and ethyl esters (3). Using *n*-octyl acetate as a model substrate, the conversion versus time yields a linear relationship, indicating a rate law that is zero-order in substrate concentration (Figure S5 and Table S6, see SI pages S4-S7 for kinetic analysis procedures). The conversion of *n*-octyl acetate with varying amounts of the same Mo catalyst (0.0 - 3.0 mol % Mo) yields a linear relationship (Figure S7 and Table S8) indicating that the rate law is first-order in Mo content. The conversion of *n*- octyl acetate also exhibits a linear relationship in EtOH concentration from monitoring the reaction with 0.0 – 4.0 equiv. of EtOH (Figure S6 and Table S7). Therefore, the overall rate equation under the present conditions is:

$$v \sim [Mo]^{1}[EtOH]^{1}[Ester]^{o}$$
 (1)

The conversion of *n*-octyl acetate was also monitored over a temperature range (60 to 90 °C) to generate an Eyring plot (Figure 2 and Table S₃), yielding activation parameters of $\Delta H^{\ddagger} = 10.5$ (8) kcalmol⁻¹ and $\Delta S^{\ddagger} = -32$ (2) e.u. (Table S4). The activation energy was determined to be 11.1 (7) kcalmol⁻¹ (Table S5), in accord with previous activation energies for alkaline transesterification of 6.2 to 14.7 kcal mol^{-1.73} The very low ΔH^{\ddagger} is in line with the low reaction temperatures (60 °C) and the high activity of the supported Mo-oxo catalyst. This is corroborated by the unprecedented low temperature (218 °C) of catalyst reduction. The large negative value of ΔS^{\ddagger} likely reflects the requirement for the incoming substrate to coordinate and react at the supported Mo surface. Conducting the transesterification in the presence of H_2O (o to 100 equiv, see Table S10) did not diminish the catalytic activity at 90 °C, indicating the (O_c)₂Mo(=O)₂@C catalyst is not poisoned under these conditions. No reaction occurs in the absence of catalyst or with the activated carbon support alone (Table 1, entries 1 and 2). In a control study with *n*-octyl acetate at 90 °C in dry EtOH, MoO₃ is found to exhibit some activity (Table S6); however, under identical reaction conditions, the yield (mmol product/mol Mo h^{-1}) is 5.8x higher with

(O_c)₂Mo(=O)₂@C, confirming the high activity of the carbon-supported dioxo-Mo species.



Figure 2. Eyring plot for the conversion of *n*-octyl acetate to *n*-octanol. Conditions: 1 mmol *n*-octyl acetate, 1.0 mol % Mo, 2 mL of anhydrous EtOH, under 200 psi $Ar_{(g)}$ and stirring at 500 rpm.

Transesterification of triglycerides. On a preparative scale, tristearin, a long chain (4, $R = n-C_{17}H_{35}$) triglyceride, was subjected to transesterification conditions in EtOH at 90 °C with 1 mol % Mo metal loading (Scheme 2). After 6 hours, the reaction mixture was diluted with water and ethyl ester 5 was extracted with CH₂Cl₂. Ester 5 was recovered as a white solid in 97 % isolated yield after removal of solvent in vacuo.

Catalyst recyclability. A recyclability test was performed for transesterification of *n*-octyl acetate in neat ethanol at a loading of 1 mol% Mo under the harshest conditions (90 °C, 200 psi Ar, 500 rpm, 1 - 3 hours). After reaction, the catalyst was collected by filtration, dried, and added directly to a second reaction mixture. This procedure was repeated an

 Table 1. Acetate Transesterification Substrate Scope^a

R	₹ R '	(O _c)₂Mo(=O)₂@C 90 °C	R-OH + Et	.0R'	
	1	EtOH	2	3	
	Subst	rate, 1	Product, 2/3	Time (h)	Conv. (Yield) %
1 ^b	n−C ₈ H	I ₁₇ OAc	n-C ₈ H ₁₇ OH	2	0
2 ^c	<i>n</i> -C ₈ H	I ₁₇ OAc	<i>n</i> -С ₈ Н ₁₇ ОН	2	0
3 ^d	<i>n</i> -C ₈ H	I ₁₇ OAc	n-C ₈ H ₁₇ OH	2	66 (-)
4	n C I			1	17 (20)
	$n - C_8 \Pi_{17} OAC$	<i>и-</i> С ₈ п ₁₇ Оп	16	99 (96)	
5	n−C ₈ H	I ₁₇ OC(O)C ₇ H ₁₅	<i>п</i> -С ₈ Н ₁₇ ОН	16	43 (2 , 43) (3 , 40)
6				16	47 (44)

7	16	54 (49)
8	16	76 (2 , 25) (3 , 30)
9	16	25 (25)
10	16	44 (2 , 14) (C=O,8)
11	16	99 (77)
12	16	97 (97)

^{a.}Conditions: 1.0 mmol substrate, 1.0 mol% Mo (0.046 g of 2.1 wt% (O_c)₂ $Mo(=O)_2@C$, 2.0 mL dry EtOH, 200 psi $Ar_{(g)}$, 500 rpm, conversion and yields determined by reference to mesitylene internal standard by ¹H NMR; products also confirmed by GC-MS analysis but not quantified by this method. Acetaldehyde diethyl acetal observed for reactions with an OAc group by ¹H NMR but were not quantified no catalyst. ^b no catalyst. ^c 0.0475 g of activated charcoal as catalyst. ^d 10 mol% MoO₃ as catalyst.

additional time, for a total of three sequential reactions (Table S9). Although a slight decrease in activity is observed (TOF = 1930 h⁻¹ to TOF = 1800 h⁻¹, reactions run up to 55 % conversion are consistent), the catalyst remains highly active even after a second recycle. After all three reactions, the 2.1 wt% (O_c)₂ $MO(=O)_2@C$ catalyst was analyzed for Mo content (by ICP-AES) and found to contain 1.7wt% molybdenum, suggesting that some leaching occurs under the present conditions; nevertheless it does not substantially impact the



Scheme 2. Preparative scale triglyceride transesterification.

catalytic activity. The additional Mo is present in the solution (SI, Table S9) This is consistent with the TPR-H₂ data, indicating that not all Mo species are catalytically active. Presumably, the non-active species are the only species susceptible to leaching under these conditions.

The leached species were determined to be catalytically inactive via a hot filtration experiment under identical conditions. A sample of catalyst was refluxed in ethanol under N_2 in a Schlenk flask and the colorless supernatant was cannulafiltered from the catalyst while still hot. After cooling, the

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58 59 60 supernatant was transferred to a standard reaction apparatus and found to be inactive for transesterification of *n*-octyl acetate at 90 °C. Further experimental details are available in the Supporting Information (SI, S7).

Discussion

Catalyst characteristics and nature of the active site. In contrast to traditional preparative methods such as incipient wetness impregnation with ammonium hepta-molybdate^{,25,74} which yields supported Mo catalysts with up to 30 wt% Mo in previous studies,^{25,74} the preparation of the present $(O_c)_2Mo(=O)_2@C$ catalysts by grafting reaches a maximum loading of 5 wt% Mo. The maximum surface density of Mosites is thus 0.22 Mo/nm², although most reactions reported here were carried out at 0.10 Mo/nm². No significant difference in activity per Mo was observed at either loading, suggesting the sites remain uniformly dispersed up to the maximum loading investigated of 0.22 Mo/nm². Dispersions of conventional MoO_x catalysts supported on refractory metal oxides are typically in the range of 0.15 - 5.0 Mo/nm² (e.g., the preparations in reference ⁷⁵⁻⁷⁷), but maximum activity is usually obtained at loadings closer to a monolayer75,78-80, suggesting substantial chemical differences between traditional MoO_x preparations and the present $(O_c)_2Mo(=O)_2@C$ catalyst. From these results, it can be inferred that the use of a discrete, monomeric Mo precursor in a controlled grafting reaction enables superior activity of the resulting single-site species and a greater profusion of active sites (in this case, ca. 50%).

BJH N, physisorption analysis of the $(O_c)_Mo(=O)_Mo(=O)_MO(=O)$ lysts indicates both meso- and microporosity.³⁷ Since the porosity does not change with Mo grafting, it is inferred that the Mo sites do not locally block carbon micropores. XPS is capable of detecting Mo species in the catalyst (Figure 1B) with a sampling depth of 10's of nms. The high chemical surface area of the carbon results from its mesoporous nature. It is therefore most likely that the $(O_c)_Mo(=O)_2@C$ species is well-dispersed throughout the meso- and micropores of the carbon, rather than localized on the carbon surface. This interpretation is consistent with a lack of pore blockage by Mo species and supported by the lack of change in BET and BJH N₂ physisorption after the grafting reaction. Thus, the $(O_c)_2Mo(=O)_2$ species must then be well-dispersed throughout the bulk of the carbon support, an interpretation consistent with the lack of change in BET and BJH N₂ physisorption after the grafting reaction. In contrast, while ICP-AES indicates the presence of sulfur, nitrogen, and phosphorous impurities (SI, Table S1), XPS does not detect these heteroatoms, suggesting that they are localized deep within the support and are not uniformly dispersed throughout. Therefore, it is proposed that the $(O_c)_2Mo(=O)_2@C$ sites are grafted onto carbon through the C-O functionalities detected by XPS (Figure 1B). The relatively low saturation point for surface Mo (0.22 Mo/nm²) suggests that the grafting reaction is surface-controlled and appropriate reactive surface sites are in low density.

Previous studies of supported MoO_x catalysts indicate that at high dispersions, the dominant Mo surface structure is a tetrahedral dioxo species.^{45-47,49,50,81} In the present

 $(O_c)_2$ Mo(=O)_2@C catalysts, Mo K-edge XAS and Mo(3d) XPS provides further evidence for the monomeric character of $(O_c)_2Mo(=O)_2@C$ sites. Mo^{IV} species exhibit no pre-edge XANES peak,⁸² and edge energies are significantly lower than for Mo^{VI} (see Table S11 for Mo^{IV} and Mo^{IV} XAS standards). It is known from the literature that Mo clusters exhibit sizedependent binding energy shifts due to final state effects.⁸³ Mo species in small oligomeric or polymeric clusters shift the $Mo^{VI}(3d)$ binding peak to higher energies than observed for Mo^{VI} in $MoO_3^{.84,85}$ In contrast, for Mo species constrained from polymerizing (e.g., when stabilized in Y zeolite⁸⁶) this shift is not observed. The carbon support employed for $(O_c)_2Mo(=O)_2@C$ is more polarizable than MoO_3 , so that final state effects would be expected to shift isolated Mospecies binding energies to lower values than for MoO₂. Comparison to reference MoO₃ in our spectrometer, as well as literature values, indicates that the predominant (O_c)₂Mo(=O)₂@C species is indeed hexavalent with no detectable Mo^V or Mo^{IV} species^{87,88}, and that the shift of the $Mo(3d_{5/2})$ peak to the low binding energy of 232.8 eV is indicative of monomeric Mo^{VI} species.

Temperature-programmed reduction (TPR-H₂) of the (O_c)₂Mo(=O)₂@C species confirms the XPS analysis (Figure 1D). (O_c)₂Mo(=O)₂@C reveals a single low-temperature reduction event at 218 °C, suggesting the Mo active site to be both highly uniform and highly reducible. Indeed, at least 50% of the Mo sites present in $(O_c)_2Mo(=O)_2@C$ consume H_2 in this experiment. To the best of our knowledge, 218 °C is the lowest reported reduction temperature of a supported MoO_x species. For example, Wang reported reductions of MoO_x/SBA-15 at surface densities from 0.25 - 10.24 Mo/nm² and reported no reduction events below 400 °C.89 In addition, reduction temperatures were found to decrease with increasing MoO_x oligomerization, suggesting monomeric species are the least reducible under the reported conditions, in direct contrast to the present $(O_c)_2Mo(=O)_2@C$ catalyst. Miranda studied MoO_x supported on a variety of silicaaluminas and observed no reduction below 350 °C.90 Feng supported ammonium heptamolybdate on activated carbon and found multiple reducible species with reduction temperatures decreasing with increasing loading. For example, Mo/C with 0.86 Mo/nm² showed a reduction event at 341 °C. At 2.3 Mo/nm², however, a lower-temperature reduction peak near 300 °C was also observed. Chary reported on MoO_x supported on Nb₂O₅-TiO₂ and showed that at the lowest MoO_x loading, the lowest-temperature reduction was at 414 °C.²⁴⁰

Previous studies indicated that highly dispersed MoO_x species generate Brønsted-acidic sites,⁷⁵ however, the relationship between Mo loading, acid site density, and the strength of the acid sites remains ill-defined.⁵² Typically, assignment of Brønsted acid strength can be established by the T_{max} peak position in NH₃ TPD; temperature ranges are designated as weak acid (150 – 300 °C), moderate acid (300 – 500 °C), and strong acid (> 500 °C).⁵³ Commonly, dispersing MoO_x species increases the density of weak and moderate acid sites while consuming strong acid sites.⁵² While (O_c)₂**Mo**(=O)₂**@C** is not stable above 450 °C, based on literature precedent, dispersed MoO_x species do not produce strong Brønsted-acid sites,^{13,52-54,75} so signals > 500 °C are not expected. Note that no new acid sites appear in $(O_c)_2Mo(=O)_2@C$ relative to the carbon support, and the T_{max} of the largest ammonia peak shifts down from 280 °C (carbon) to 250 °C (2.1wt% $(O_c)_2Mo(=O)_2@C)$. No new peaks corresponding to moderate acid sites are observed for $(O_c)_2Mo(=O)_2@C$ although desorption peaks from 2.1wt% $(O_c)_2Mo(=O)_2@C$ are considerably sharper than for the parent carbon; this is consistent with previous reports.⁷⁵ From these data, it appears that the present $(O_c)_2Mo(=O)_2$ sites do not operate as classic Brønsted-acidic catalysts, suggesting an alternative catalytic mechanism proposed in this work (*vide infra*) and others.³²

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59 60 The stability of highly-dispersed dioxo-molybdenum sites in $(O_c)_2Mo(=O)_2@C$ is confirmed via recyclability studies and further supported by spectroscopy and H₂-TPR measurements on expended catalysts. Mo(3d) XPS indicates no binding energy shift in the Mo species after catalysis. Similarly, H₂-TPR indicates that the Mo species remains uniform and highly reducible. Lastly, the activity of the $(O_c)_2Mo(=O)_2@C$ catalyst does not diminish significantly even after repeated use.

Catalytic scope and mechanism. Primary esters such as noctyl acetate (Table 1, entry 4) and *n*-octyl octanoate (Table 1, entry 5) react to form *n*-octanol, ethyl acetate, and ethyl octanoate respectively. N-octyl octanoate reacts at roughly half the rate (43 % conversion at 16 h) as *n*-octyl acetate (99%)conversion at 16 h), due most likely to increased steric hindrance.91 In n-octyl octanoate the fall in rate is more pronounced than in the case of the very sterically challenged and electronically different 1-methylcyclohexyl acetate (Table 1, entry 12), which reacts at a rate comparable to *n*-octyl acetate (97% conversion in 16 h). The secondary esters 2-octyl acetate and cyclohexyl acetate (Table 1, entries 6 and 7) react more slowly than the primary *n*-octyl acetate, excluding substitution at the alkyl position as a factor in rate. The lack of a distinct trend in degree of substitution implies that the mechanism does not proceed through a carbocation intermediate, excluding C-O cleavage or deacylation^{92,93} as a reaction pathway and suggesting instead the scenario presented in Scheme 3. Note that replacing the acyl group with an aryl moiety increases the rate (Table 1, entry 8). In the case of entry 8, although overall conversion is high (76%), the yield of recovered product is reduced (25% for the alcohol, 30% for the ethyl ester). This is likely a result of adsorption to the catalyst surface, although whether it is of the substrate or an aldehyde reaction intermediate is unclear.⁹⁴⁻⁹⁶ Subjecting γ valerolactone (Table 1, entry 9) to transesterification conditions in EtOH results in 25 % conversion to ethyl butyrate. Benzylic 1-phenethyl acetate undergoes 44 % conversion in 16 hours producing the corresponding alcohol as well as the ketone in 8 % yield (Table 1, entry 10). Again, the final yield of the aromatic product is low. The ketone presumably forms from the dehydrogenation of the alcohol.⁹⁷ In contrast to other aromatic substrates, entry 11 (Table 1) is recovered in good yield (77%), suggesting that adsorption of the substrate to the catalyst surface does not occur with all substrates and may require an α , β -unsaturated carbonyl functionality.

The transesterification of the long chain $(n-C_{17}H_{35})$ triglyceride tristearin with ethanol to produce the corresponding ethanoate and glycerol is performed on a large scale (Scheme 2). After aqueous workup followed by extraction with CH_2Cl_2 , the ethanoate product (5) is isolated as a white solid in 97 % yield, indicating that this catalyst and methodology is a viable alternative to harsh alkaline and/or Brønsted acidic process for the production of biodiesel.

A proposed catalytic cycle for the transesterification of esters with ethanol is shown in Scheme 3. The catalytic cycle follows those previously suggested in the literature³² and bears similarities to that of the well-studied mechanism for transesterification by oxo-tin compounds such as di-*n*-butyltin oxide (DBTO).⁹⁸ Activation of ethanol occurs via H^+ abstraction by the Mo=O fragment (Scheme 3, species a) and concomitant formation of a Mo-ethoxide species (Scheme 3, species **b**). Molybdenum oxo-hydroxo-alkoxides are known in the literature⁹⁹ and the resulting structures exhibit catalytic activity¹⁰⁰ and/or have been implicated in catalytic mechanisms.¹⁰¹⁻¹⁰⁴ Since the present kinetic studies show the reaction to be first-order in EtOH concentration, it is reasonable to propose addition of one equiv. EtOH to the pre-catalytic molybdenum-dioxo site to form the active species (Scheme 3, **b**). When the activated Mo-ethoxide species coordinates an ester (as in Scheme 3, i), the activated ester carbonyl (Scheme 3, c) undergoes nucleophilic attack by the ethoxide to yield the ethyl ester product (Scheme 3, ii) and a new



Scheme 3. Proposed catalytic cycle for the transesterification of esters with ethanol by $(O_c)_2Mo(=O)_2@C$.

Mo-OR fragment (Scheme 3, d). Further exchange of the Mo-OR fragment with EtOH (Scheme 3, iii) regenerates the activated Mo-OEt fragment (Scheme 3, c) and enables catalytic turnover. Since both stability and recyclability of the catalyst has been established, it is proposed that the $(O_c)_2Mo(=O)_2@C$ fragment (Scheme 3, a) can be recovered

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58 59 60 via elimination of an equivalent of EtOH to retain its chemical identity.

Conclusions

The synthesis of a stable, earth-abundant catalyst via chemical grafting of a dioxo-molybdenum species directly onto activated carbon is reported. $(O_c)_2Mo(=O)_2@C$ is extensively characterized by a battery of physicochemical techniques and shown to have unique chemical characteristics among known supported MoO_x materials. Under mild conditions, this catalyst is competent for the transesterification of alcohols and esters, including biomass relevant triglycerides. $(O_c)_2Mo(=O)_2@C$ shows high activity, selectivity, and recyclability, as well as water tolerance, yielding a robust and efficient catalytic system.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Physical and analytical measurements, catalyst preparation, physicochemical catalyst characteristics, STEM of $(O_c)_2Mo(=O)_2@C$ catalyst PXRD, Boehm titration procedure, XPS measurements, TPR-H₂ measurements, calibration of TPR-H₂ procedure, TPD-NH₃ measurements, general transesterification procedure, preparative scale triglyceride transesterification, *n*-octyl acetate conversion, *n*-octyl acetate conversion with varying [EtOH], n-octyl acetate conversion with varying [Mo], ¹H NMR of tristearin (triglyceride), ¹H NMR of tristearin transesterification product, recyclability study procedure, hot filtration study procedure, H₂O poisoning study data, kinetic analysis, activation parameters from Eyring plot, and error analysis procedure.

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Notes

The authors declare no competing financial interest.

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Table of Content Graphic:



"Single site" (O_c)₂Mo(=O)₂@C



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