Structure and site evolution of molybdenum carbide catalysts upon exposure to oxygen

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Abstract

Acid site densities could be reversibly tuned by a factor of ~30 using an O₂ co-feed, which reversibly creates Brønsted acid sites on the carbide surface without altering the bulk crystal structure of 2-5 nm Mo₂C crystallites. Unimolecular isopropanol (IPA) dehydration at 415 K, a probe reaction, occurred on Brønsted acid sites of these oxygen-modified carbides with an intrinsic activation energy of 93 ± 1.3 kJ mole⁻¹ via an E₂ elimination mechanism with a kinetically relevant step of β-hydrogen scission. Site densities were estimated via in situ 2,6-di-*tert*-butylpyridine (DTBP) titration and used to calculate a turnover frequency (TOF) of 0.1 s⁻¹, which was independent of site density. Oxygen co-processing allows for facile in situ tunability of acidic and metallic sites on highly oxophilic metal carbides.

Keywords: Brønsted acid, dehydration, molybdenum carbide, interstitial carbide, bifunctional catalyst, site density, oxophilic, transition metal

1. Introduction

Catalytically active interstitial carbides first rose to scientific prominence through the early work of Yates[1], Boudart[2], and Madey[3], demonstrating the catalytic variation of molybdenum and tungsten formulations as a function of both surface and bulk composition as evinced by development of metallic hydrogenolysis or acidic isomerization functionalities with concurrent carburization. Liu et al. [4] investigated the Mo_2C surface as a water gas shift (WGS) catalyst using periodic density functional theory (DFT), demonstrating the variation in catalyst activity based on surface termination as pure Mo, C, or O. Subsurface diffusion and development of an oxycarbide phase led to decreased WGS reactivity, and deposition of surface oxygen atoms (O^*) from reaction products was shown to suppress WGS reactions due to thermodynamically favorable binding and dissociation of product H_2O that did not allow for facile O^* removal.

Leary and coworkers[5] experimentally demonstrated the role of surface O^* on Mo_2C as a poison for ethylene hydrogenation at 298 K, a metallic functionality. Leary and coworkers used online GC and MS to observe the complication of bulk carbon removal concurrent with O^* removal as a function of varying activation techniques including temperature ramps under H_2 and He flow. Posada-Pérez et al. [6] used X-ray photoelectron spectroscopy (XPS) to monitor the O 1s region (528 – 533 eV) during sequential CO_2 dosing of the $\beta\text{-Mo}_2\text{C}$ surface at 300 K. Both O^* and adsorbed CO were observed with the relative ratio of CO/O^* increasing with CO_2 dosage, demonstrating the ability of O^* on the Mo_2C surface to inhibit cleavage of the second $\text{C}=\text{O}$ bond and sequential hydrogenation reactions to CH_3OH and CH_4 . Flaherty et al. [7] used reflection

absorption infrared spectroscopy under ultra-high vacuum (UHV) conditions (1×10^{-10} torr) to monitor formic acid decomposition via dehydrogenation to produce CO_2 or dehydration to produce CO. Clean Mo(110) performed predominantly dehydration; C-modification of the surface decreased the rate of dehydration without altering the activation energy for dehydration while formation of a carbidic layer on the Mo(110) surface decreased the activation energy of dehydrogenation from 34 to 13 kJ mole^{-1} . Activation energies were calculated using kinetic measurements of reactive molecular beam scattering.

Chen and coworkers[8, 9] used DFT calculations and temperature programmed desorption/high-resolution electron energy loss spectroscopy (TPD/HREELS) to demonstrate the tunability of the carbide surface with Ni and Cu adatoms to break C-C, C-O, or C-H bonds of oxygenates including ethanol, propanal, propanol, and furfural. The pure carbide surface under UHV conditions could dehydrate and dehydrogenate/hydrogenate oxygenates, but complete atomic decomposition of reactant oxygenates to surface adatoms typically accounted for nearly 50% of reactivity. Total reactant conversion was less than 0.2 molecules reacted per surface metal atom in the reported studies, implying that the Mo_2C reactivity reported might be stoichiometric. These results stress the variation in Mo_2C reactivity as a function of both surface adatoms and time-on-stream.

Ledoux and coworkers[10] synthesized a MoO_xH_y phase that formed an isostructural oxycarbohydride phase while simultaneously developing n-butane isomerization activity, demonstrating in situ catalytic modification via structure alteration. In situ temperature programmed oxidation (TPO) of the oxycarbohydride phase with intermittent ex situ X-

ray diffraction (XRD) showed the concurrent loss of lattice carbon as CO_2 and structural oxidation to MoO_2 and MoO_3 ; lattice carbon loss was separate from a higher temperature coke oxidation, nearly identical to CO_2 loss from an MoO_2 sample that showed minimal isomerization activity. Iglesia et al. [11] also manipulated catalytic isomerization activity via oxygen exposure of tungsten carbide catalysts, using transient and isotopic kinetic measurements to evince bifunctional isomerization via rapid dehydrogenation on WC_x sites and sequential WO_x Brønsted acid catalyzed methyl shifts in contrast with Pt/SiO_2 catalyzed sequential cyclization/hydrogenolysis. Matsuda[12] used both n-heptane isomerization and 2-propanol (IPA) dehydration as probe reactions to investigate high-surface area MoO_xH_y species and correlated acidic activity to both catalyst Brunauer-Emmett-Teller (BET) surface area and ex situ NH_3 TPD site density estimates. The reports outlined above demonstrate that reactive characteristics of metal carbide catalysts are strongly influenced by heteroatom adsorption on the catalyst surface and subsurface domains. In this study, we probe the identity and number of active centers created by heteroatom addition to molybdenum carbide formulations.

In this work, we use rigorous kinetic analysis of IPA dehydration over oxygen-treated Mo_2C formulations to investigate in situ catalytic site modification and report both the identity and number of sites generated by such treatments. As-synthesized Mo_2C with no exposure to oxygen exhibits strong alkaline and metallic functionalities, catalyzing carbon chain growth to C_6^+ products via carbonyl condensation pathways and IPA dehydrogenation to near equilibrium values under simple IPA/Ar flow. Catalysts were composed of 2-5 nm orthorhombic Mo_2C domains. Concurring XRD and transmission electron microscopy (TEM) analysis showed that bulk crystalline Mo oxides or

oxycarbides were not formed with passivation or reaction under O₂ flow. Oxygen modification of the surface over time via (i) O* deposition from IPA dehydration or H₂O co-feed, or (ii) O₂ co-feed, greatly suppresses carbon chain growth and dehydrogenation rates and concurrently bolsters acid reactivity, forming dehydration products propylene and di-isopropylether (DIPE) with ~90% carbon selectivity. Carbon chain growth pathways and substantial dehydrogenation activity are irreversibly eliminated after O₂ exposure, but acid-catalyzed product rates can be reversibly altered by a factor of ~30 via acid site density modification with an O₂ co-feed. Acid site densities were measured with in situ 2,6-di-*tert*-butylpyridine (DTBP) titration experiments, and turnover frequencies (normalized with acid site density by assuming a 1:1 stoichiometry of DTBP:acid site) are invariant with site density. Kinetic experiments, including partial pressure variation, activation energy measurements, and kinetic isotope experiments, lead to the conclusion that IPA dehydration occurs on oxygen-modified molybdenum carbide catalysts via E₂ β-hydrogen elimination on Brønsted acid sites. We propose that the oxygen-modification of highly oxophilic transition metal carbides can be used as a regenerable and tunable source of catalytic Brønsted acidity[13].

2. Experimental

2.1 Catalyst synthesis

Catalyst synthesis was carried out using a temperature programmed reaction method used in previous work[14-16]. Catalysts were prepared in a quartz tubular reactor (I.D. 10 mm). Batches of catalyst were synthesized using 0.025 - 1.5 g ammonium paramolybdate (sieved, 177-400 μm, (NH₄)₆Mo₇O₂₄·4H₂O, Sigma, 99.98%, trace metal

basis). The paramolybdate was heated in a three-zone split tube furnace (Applied Test Systems) at 0.06 K s^{-1} to 623 K and held at 623 K for 12 h under total flow of $3.0\text{ cm}^3\text{ s}^{-1}$ of 15 vol% CH_4 (Matheson, 99.97%) in H_2 (Minneapolis Oxygen, 99.999%). The temperature was then ramped at 0.046 K s^{-1} from 623 K to 873 K and held at 873 K for 2 h. The reactor was then cooled under the same gas flow to either reaction temperature or ambient temperature, to begin reaction or passivation, respectively.

For passivation, the product was then treated in flowing 1% O_2/He (Matheson, Certified Standard Purity) at $1.0\text{ cm}^3\text{ s}^{-1}$ for at least 1 h in an effort to passivate the carbide surface and avoid violent bulk oxidation with atmospheric O_2 [17, 18]. Passivated samples were used for ex situ characterization methods.

2.2 Catalyst characterization

Mo_2C samples were characterized using an ASAP Micrometrics 2020 analyzer to determine surface area, porosity, and CO chemisorption values. BET surface area and porosity measurements using N_2 were performed at liquid nitrogen boiling temperature. Prior to N_2 physisorption measurements, samples were degassed to $< 6\text{ }\mu\text{m Hg}$ and heated to 523 K at 0.17 K s^{-1} and held for 2-4 h.

CO chemisorption measurements were performed at 323 K. Before measurement, passivated samples were evacuated to $< 2\text{ }\mu\text{m Hg}$ at 383 K for 0.5 h, followed by treatment in flowing H_2 at 723 K for 2 h, degassing at 723 K for 2 h, followed by the first adsorption measurement at 323 K. Weakly adsorbed CO was removed with degassing at $2\text{ }\mu\text{m Hg}$, then the CO adsorption isotherm was repeated. The difference between the first and second isotherms was plotted, and this curve was extrapolated to zero pressure to calculate the amount of irreversibly adsorbed CO[18].

XRD was performed with a Bruker D8 Discover 2D X-ray diffractometer equipped with a 2-D VANTEC-500 detector and a 0.8 mm collimator. Cu K α_1 and K α_2 radiation was used in conjunction with a graphite monochromator. Scans were performed in three frames during 900 s centered at $2\theta = 35^\circ$, 60° and 85° , for a total range of $2\theta = 17.5^\circ$ to 102.5° . The three 2-D scans were converted to 1-D intensity vs. 2θ with a step size of $0.04^\circ 2\theta$ and merged for analysis. A zero background holder was used with a small amount of vacuum grease for sample support.

X-ray photoelectron spectroscopy (XPS) measurements were performed on an SSX-100 system (Surface Science Laboratories, Inc.) equipped with a monochromated Al K α X-ray source, a hemispherical sector analyzer (HSA) and a resistive anode detector. The base pressure was 1.0×10^{-9} Torr. During data collection, the pressure was $\sim 2.0 \times 10^{-8}$ Torr. An area of approximately 1 mm x 1 mm was illuminated with 200 W X-rays. The survey spectra were collected using 150 eV pass energy and 1 eV step $^{-1}$. The high-resolution spectra were collected using 50 eV pass energy and 0.1 eV step $^{-1}$.

The atomic percentages were calculated from the survey spectrum using the ESCA Hawk software provided with the XPS system. The adventitious carbon 1s peak was set at 285.0 eV and used as the reference for all of the other elements. A combination of Gaussian/Lorentzian functions was used for curve fitting with the Gaussian percentages being at 80% or higher. The Mo 3d $_{5/2}$ and 3d $_{3/2}$ peaks were fixed with a shift of 3.2 eV for Mo $^{6+}$ and 3.15 eV for both Mo $^{4+}$ and Mo $^{3+}$. Area ratios of the Mo 3d doublets were optimized so that $A_{5/2}/A_{3/2} \sim 1.5$.

Prior to TEM analysis, a representative sample of post-reaction Mo $_2$ C catalyst particles was crushed mechanically in an agate mortar with N,N-dimethylformamide

(ACS, 99.8%). The resulting suspension was then sonicated for 3 hours and drop cast on a holey/thin carbon film on a copper grid. The samples were examined in a FEI Titan G2 60-300 aberration-corrected scanning transmission electron microscope (STEM) equipped with a CEOS DCOR probe corrector and a Super-X energy-dispersive X-ray (EDX) spectrometer. High-angle annular dark-field (HAADF) images (2048 pixels x 2048 pixels) were acquired on the STEM operating at 200 kV using a dwell time of 6 μ s per pixel at a camera length of 100 mm. The beam convergence angle was measured to be $\alpha_{\text{obj}} = 25$ mrad and the inner and outer collection angles of the HAADF detector were 67 and 412 mrad respectively. Under these conditions, the probe size was ~ 1.0 Å.

2.3 Reaction and titration methods

IPA (ACS, 99.97%) was used as received. Reaction temperature was measured using a K-type thermocouple in a thermal well on the exterior of the quartz reactor (i.d. ~ 1 cm). Liquid feed was introduced via either a KD Scientific syringe pump (KDS120) or an M6 Vici Valco high pressure liquid chromatography (HPLC) pump into stainless steel reactor lines heated by resistive heating tape. Reactor effluent was vented to ambient pressure; system pressure varied from 101 kPa to 130 kPa as measured by a PX209-300G5V pressure transducer. Reactor temperature varied from 403 – 438 K with kinetic experiments and titrations performed isothermally at 415 K. Volumetric flow rate was kept constant at $2.0 \text{ cm}^3 \text{ s}^{-1}$ unless otherwise specified.

Reactor effluent was analyzed by an online Agilent 7890A gas chromatograph (GC) using a flame ionization detector (FID). Eluent separation was achieved using a 50.0 m x 320 μ m x 0.52 μ m dimethylpolysiloxane J&W HP-1 column. CH_4 was included with reactant flow as an internal standard for eluent quantification, typically at 0.067 cm^3

s⁻¹. Online mass spectrometry (MS) analysis was performed using a Cirrus 2 MKS quadrupole mass spectrometer. O₂ partial pressure was altered from 0.0 – 13.5 kPa by adding O₂ co-feed and removing an equal volumetric flow of carrier gas (He or Ar) to maintain a constant space velocity. Space velocity variations were achieved by proportional alteration of all reactant and diluent flows.

Titration experiments were performed with liquid mixtures of IPA and DTBP. Steady state dehydration rates were achieved, then reactant flow was switched from pure IPA flow to the IPA/DTBP mixture at the same volumetric flow rate. DTBP mole fractions in the IPA/DTBP mixture were typically 1x10⁻³ to 1x10⁻⁴. Propylene formation rate was monitored using online gas chromatography and was extrapolated to zero to calculate total titrant uptake as a measure of acid site density.

3. Results and Discussion

3.1 Catalyst synthesis and characterization

A typical carbide synthesis was performed as described in Section 2.1 with an additional temperature ramp up to 1053 K under flowing H₂/CH₄ with concurrent online MS effluent monitoring (Fig. S.1). H₂O was the primary oxygen-containing product; minimal CO and CO₂ were evolved, similar to previously reported Mo₂C syntheses[19]. H₂O evolved during the 190 K increase beyond typical synthesis conditions (T = 873 K) was less than 1% of total H₂O evolution during synthesis. The lack of further oxygen loss at high temperature under reductive conditions implies that all oxygen has essentially been eliminated from the paramolybdate at 863 K, typical synthesis conditions used in this study.

Nitrogen physisorption measurements were used to calculate BET surface areas typically on the order of $60 - 100 \text{ m}^2 \text{ g}_{\text{cat}}^{-1}$, and CO chemisorption measurements were typically on the order of $150 - 250 \mu\text{mol g}_{\text{cat}}^{-1}$; these values are characteristic of carbides synthesized via temperature programmed reaction methods[20, 21]. N_2 physisorption analysis exhibited classic type IV hysteresis of the isotherm, indicative of mesoporous morphology (Fig. S.2). Typical catalyst sample surface area was over 50% from internal, porous surfaces, and calculated pore volumes via the Barrett-Joyner-Halenda (BJH) method[22] estimate over half of the porous surface area arose from pores of $< 6 \text{ nm}$ diameter. This porous morphology is evident in transmission electron micrographs shown in Figures 1(a) and (b), exhibiting pores as small as 1 nm . EDX spectrum analysis of a representative particle confirms the presence of Mo, C, and O in a passivated sample.

Mo_2C phase analysis was performed with both TEM and XRD. Mo_2C phase identification literature has discrepancies between surface science and experimental nomenclature. Experimentally, Mo_2C is generally characterized by XRD as having a hexagonally close packed structure (hcp $\beta\text{-Mo}_2\text{C}$, JCPDS PDF # 00-035-0787) [23-27] or a metastable face-centered-cubic structure (fcc $\alpha\text{-Mo}_2\text{C}$, JCPDS PDF # 00-015-0457) [21, 25, 27]. Surface science[28] and DFT[4, 29] literature often refers to $\alpha\text{-Mo}_2\text{C}$ as the orthorhombic unit cell indexed by Parthé and Sadagopan[30](JCPDS PDF # 01-072-1683). This phase was originally believed to be hcp until Parthé and Sadagopan used neutron diffraction in conjunction with XRD analysis to deduce an orthorhombic structure, composed of slightly distorted hexagonally packed layers of Mo such that each Mo has three planar C neighbors. Differences between the hcp and the orthorhombic structures are difficult to observe in X-ray diffractograms because of the similarities of

their diffraction patterns as shown in Fig. S.3 in conjunction with small crystallite sizes resulting in broad peaks. For the sake of consistency with experimental literature, we refer to the metastable fcc Mo_2C as the α phase and the orthorhombic Mo_2C phase as β .

X-ray diffractograms of passivated catalyst samples before and after reaction are shown in Fig. 2. Samples both before and after reaction exhibit primarily orthorhombic β - Mo_2C with a small fraction of metastable fcc α - Mo_2C . The post reaction sample shows a smaller α component. This sample was used for kinetic analysis for over 96 h time-on-stream at 415 K; the metastable α component of the catalyst most likely reformulated into the thermodynamically stable β phase over the extended reaction time. Samples before and after reaction were passivated in O_2 flow and exposed to the atmosphere, and neither sample exhibits crystalline oxide domain formations as shown by the lack of any features in the region of the highest intensity peaks for the MoO_2 and MoO_3 phases. The primary peaks of the bulk MoO_xC_y phase at $2\theta = 43^\circ$ and 15° observed by Ledoux and coworkers[31] were also absent, indicating that both passivation and reaction under O_2 co-feed did not oxidize the bulk structure of Mo_2C crystallites.

Mo_2C structure can be seen in the micrographs shown in Figures 1(c) and (d). Fig. 1(c) is a view down the $[010]$ zone axis of orthorhombic β - Mo_2C as reported by Parthé and Sadagopan[30], clearly showing the distorted hexagonal lattice of Mo atoms. This theoretical structure was rotated, scaled, and overlaid on the atomic columns visible in the high resolution HAADF-STEM image of the representative particle, shown in Fig. 1(d). The excellent match in both size and symmetry confirms the presence of orthorhombic β - Mo_2C . No observed particles exhibited hcp symmetry.

XPS analysis of a similarly passivated sample (Fig. S.4) shows that the surface state of the passivated carbide comprises 51% Mo⁶⁺, 23% Mo⁴⁺, and 26% Mo³⁺, with Mo 3d_{5/2} peaks centered at 232.4, 229.9, and 228.9 eV, respectively. The more highly oxidized Mo 3d_{5/2} peaks we ascribe to the MoO₃ and MoO₂ phases, representing 51% and 23% of the surface, respectively. Djéga-Mariadassou and coworkers[32] synthesized carbides via similar TPR methods, and the X-ray diffractogram of the post-passivation carbide exhibited characteristic peaks at $2\theta = 39^\circ$, 52° , and 62° , similar to our results. XPS analysis of this carbide showed 3d_{5/2} peaks at 230 eV, characteristic of Mo⁴⁺ due to MoO₂ formation on the carbide surface with 1%O₂/Ar passivation at ambient temperature for 1 h. Thompson and coworkers[33] characterized pure MoO₃ in the Mo⁶⁺ state with a 3d_{5/2} binding energy (b.e.) of 232.5 eV, similar to the value we report above, indicative of MoO₃ surface formation with our protocols for carbide passivation. Excess oxidation to form MoO₃ in addition to MoO₂ would be the simple result of longer passivation times or aging times before analysis. Thompson and coworkers also analyzed H₂-reduced MoO₃, observing a 3d_{5/2} b.e. at 228.9 eV; this peak was attributed to a possible molybdenum bronze/suboxide that was believed to be responsible for catalytic heteroatom removal, having a Mo³⁺ oxidation state. Mo 3d_{5/2} b.e. of 228.2 and 227.9 eV, representative of Mo²⁺ in Mo₂C and metallic Mo, respectively, were reported by Ledoux and coworkers. Both peaks were absent in our carbide sample, implicating the lack of significant quantities of these species on the surface of our passivated catalyst[34].

3.2 Oxygen modification of Mo₂C: IPA dehydration kinetics, mechanism, and site requirements

3.2.1 Induction period during oxygen modification of Mo₂C

In situ synthesized molybdenum carbide samples with negligible oxygen content (as described in Section 3.1) were used for catalytic reactions of IPA. Rates were normalized by a stoichiometric conversion between the mass of paramolybdate loaded and Mo₂C, with g_{cat} referring to the calculated Mo₂C loading ($0.578 \text{ g}_{\text{cat}} \text{ g}_{\text{paramolybdate}}^{-1}$). At early times-on-stream, IPA is converted to predominantly acetone and C₆⁺ products (~95% selectivity) with these products dwarfing propylene production (<1% selectivity). Products were analyzed using an Agilent GC/MS and included hexenes, hexadienes, 4-methyl-2-pentanol, methyl-isobutyl-ketone, nonenes, nonadienes, acetone, and minimal propylene/propane. Acetone formation at early times-on-stream for catalyst loadings of $0.29 \text{ g}_{\text{cat}}$ approached near equilibrium conversion (Section S.2 of Supplementary Information). These products are the result of IPA dehydrogenation to acetone, acetone condensation pathways followed by concurrent hydrogenation/dehydration, IPA dehydration, and possible propylene oligomerization. The proposed IPA reaction network is summarized in Scheme 1.

O₂ co-feed induced simultaneous increases in the rate of formation of propylene and DIPE, both acid-catalyzed dehydration products[35-37]. The increase in acid-catalyzed product formation rates was concurrent with a decrease in C₆⁺ and acetone formation rates. This induction period could be transiently observed with slow O₂ co-feed (Fig. S.5; P_{O₂} ~ 0.1 kPa). O₂ co-feed was typically introduced to the freshly synthesized carbide at pressures of P_{O₂} = 1 – 13 kPa. These high oxygen co-feed pressures shortened the induction period to the order of minutes so as to usually be completed during the time of a typical GC injection used during this work (~20 min). This introduction of O₂ to the extremely oxophilic carbide was accompanied by a temperature exotherm on the order of

100 K with loadings of 0.29 g_{cat}. After the O₂ exposure induction period, dehydration products dominate the product carbon selectivity (~90% carbon selectivity). Acetone production rates were severely inhibited by O₂ introduction but still remained on the order of ~10% carbon selectivity after the majority of C₆⁺ products were eliminated. Propane formation also decreased to trace quantities with increasing oxygen exposure.

Acetone condensation over TPR-synthesized Mo₂C was observed by Thompson and coworkers, condensing acetone with <10% product selectivity at >35% conversion of ~10 kPa acetone/He at 483 K and ambient pressure with the remaining acetone conversion resulting in IPA and propylene formation[17]. Acetone condensation activity was attributed to the presence of basic sites exhibited by CO₂ TPD. An MgO sample was shown to adsorb CO₂ and not NH₃; the MgO sample was active for acetone condensation at 473 K and produced no IPA dehydration products. Mo₂C adsorbed CO₂ and NH₃ as evinced by TPD and was also active for acetone condensation, implicating basic sites on the carbide surface as the cause of this activity. Thompson and coworkers also demonstrated selective poisoning of IPA dehydrogenation via in situ CO₂ co-feed, which did not affect the rate of IPA dehydration at 433 K and atmospheric pressure, indicating that basic sites may be partly responsible for dehydrogenation activity and that they have no effect on acidic dehydration rates[38].

Iglesia et al. [11] observed a decrease in n-heptane hydrogenolysis areal rates with increasing oxygen treatment of tungsten carbide formulations; increasing oxygen treatment both decreased metallic (CO binding) site density and concurrently increased acidic (isomerization) areal rates, evincing that interstitial carbide oxygen exposure (i) suppresses metallic functionalities and (ii) generates acidic activity. Our results fall in

line with those of Thompson and Iglesia, showing the elimination of alkaline/metallic activity via O₂ introduction to Mo₂C. The systematic analysis of the metallic and basic activity of the oxygen-free carbide catalysts will be reserved for later work while this report focuses on the reactivity of oxygen treated samples.

3.2.2 Systematic IPA dehydration tunability with O₂ co-feed

After metallic and alkaline activity has been significantly suppressed via O₂ exposure, IPA was converted to primarily propylene, DIPE, and acetone, with acetone typically accounting for <10% carbon selectivity of reaction products. Fig. 4 shows the effects of adding and removing an O₂ co-feed. The addition of O₂ to the reactants increases the rate of formation of both propylene and DIPE, reaching an increased and stable steady-state production of these products. DIPE rates were smaller than propylene rates, yet the two scaled similarly as shown in Fig. 4, indicating the changes in rates originate from alteration of acid sites. Removal of the O₂ co-feed was observed to restore propylene and DIPE rates to their pre-O₂-introduction values. This drop in rate was typically on the timescale of ~8 hours for catalyst loadings of 0.013 g_{cat}, but the drop in rate could be expedited with an H₂ co-feed. Alkaline and metallic activity did not resume with O₂ co-feed removal.

This rate of propylene formation can be reversibly manipulated and quantified as a function of co-feed oxygen partial pressure as shown in Fig. 5. O₂ co-feed pressure was monotonically increased, sequentially awaiting the stabilization of the propylene production transient. O₂ co-feed was then removed, allowing propylene formation rates to drop and stabilize. This process was repeated to quantify propylene synthesis rate as a

function of O₂ pressure. Fig. 5 incorporates four independent experiments in conjunction with repeated experimental measurements, demonstrating the reproducibility of this effect. Propylene production rates with constant O₂ co-feed remained stable over the course of 16 hours (Fig. S.6).

3.2.3 IPA dehydration kinetics

Propylene formation rates were measured at differential conditions at 415 K as a function of IPA pressure (0.048 - 4.8 kPa). Calculations using Mears' criteria show the lack of any internal and external heat and mass transfer limitations (Section S.5 of Supplementary Information). Independent experiments showed a linear increase in IPA conversion as a function of contact time, implying no external mass transfer limitations and no product inhibition are present at the examined reaction conditions (Fig. S.7). Propylene formation rates decreased ~16% with a fourfold increase in contact time (Fig S.8); this could be accounted for by secondary reaction pathways as demonstrated through the linear dependence of conversion on contact time and the increase in C₆⁺ product formation at higher contact times, implicating secondary propylene oligomerization pathways as have been noted before over acid catalysts[39]. IPA dehydration was independently performed with 0.5 kPa IPA and a 0.7 kPa H₂O co-feed; no kinetic inhibition or deactivation was observed, demonstrating that H₂O does not inhibit or deactivate propylene synthesis.

IPA pressure dependence and activation energies of IPA dehydration to form propylene were measured with O₂ co-feeds of 0, 0.27, 1.34, and 5.38, and 13.45 kPa O₂, and the results are plotted in Figures 3(a) and (b). Activation energies for propylene

formation rates were measured by varying temperatures from 403 – 438 K. Propylene formation rate has a zero order dependence on the IPA pressure as shown in Fig. 3(a), indicative of an IPA-saturated surface. The IPA saturated surface implied by the zero order rate dependence upon IPA pressure designates calculated activation energies as intrinsic. Dehydration rates remained independent of IPA pressure, and activation energies remained constant at $\sim 93 \text{ kJ mole}^{-1}$, independent of O_2 pressure from $P_{\text{O}_2} = 0 - 13.5 \text{ kPa}$ (Figure 3(b)).

3.2.4 In situ acid site identification and quantification via 2,6-di-tert-butylpyridine titration

The acid site density of the oxygen-modified Mo_2C catalysts was measured using in situ DTBP titrations. The DTBP mole fraction of the titration mixture was such that the overall partial pressure of IPA varied negligibly ($3 \times 10^{-4} - 1.7 \times 10^{-3}$ mole fraction DTBP). The drop in the propylene production rate was monitored using an online GC. During the time when the propylene production rate dropped linearly, it was assumed that each DTBP was absorbed on an acid site in a 1:1 stoichiometry. This rate of titration was extrapolated to the time when the propylene production rate would reach zero. The flow rate of DTBP multiplied by this time to complete titration was used to calculate the number of acid sites in the catalyst, and the steady-state rate of propylene production was then normalized by this number of acid sites to calculate a turnover frequency (TOF), as shown in Fig. 6. Experiments with simultaneous online MS monitoring confirmed that DTBP breakthrough did not occur during the initial stages of titration, validating our extrapolation method. Titrations were performed at various O_2 co-feed partial pressures,

and the TOF is plotted with respect to propylene production rate per gram of catalyst in Fig. 7.

Fig. 7 shows that while the rate of propylene production per gram of catalyst varies over a factor of 80, the TOF per acid site remains invariant within a factor of ~ 2 . DTBP proved to be an irreversible titrant as shown in Fig. 6; after titration and subsequent return to pure IPA flow, propylene rates did not recover to their previous pre-titration values. Titrations would decrease propylene production rate significantly, but rates did not reach zero. This implies that either (i) a small fraction of active sites cannot be titrated either due to steric restrictions imposed by the porous nature of the catalyst and/or the bulky nature of DTBP, or (ii) there are additional dehydration sites that are chemically distinct from those titrated by DTBP.

The rate that remained un-titrated varied from 8-60% of the pre-titration rate, and the fraction of the rate that remained un-titrated was higher at lower site density conditions (Fig. S.9). Both TEM and BJH pore diameter estimation confirm the presence of pores 2 nm or smaller. Fig. 1(b) in particular shows pores on the order of 1 nm; the mass thickness contrast of the TEM specimen would be almost entirely due to the heavy Mo, so additional steric hindrance caused by any surface buildup during catalytic reaction would only serve to further hinder DTBP access to sites within these pores, but these hindered sites could still be accessible for IPA dehydration. This would explain the un-titrated rate as an effect of sterically inaccessible sites circumscribed within catalyst pores.

Hypothetically, if a small portion of omnipresent Lewis acid sites on the catalyst surface were responsible for this residual rate, and these sites were indeed chemically

distinct from those titrated by DTBP, then these sites would dehydrate IPA via a distinct mechanism with a distinct activation energy. These Lewis acid sites would cause a change in the measured activation energy of dehydration due to the large contribution of Lewis acid sites to the total dehydration activity at low site density. Fig. 3(b) clearly shows that the activation energy for unimolecular dehydration remains constant at $\sim 93 \text{ kJ mole}^{-1}$ at the lowest measured acid site density; this provides strong evidence against the existence of a discernibly large population of Lewis acid sites, which in turn strengthens the postulate that the un-titrated rate is simply due to a fraction of Brønsted acid sites being sterically inaccessible.

Work by Bond et al. [40] measured intrinsic activation energy of IPA dehydration over bulk and supported Keggin polyoxometalates (POM) $\text{PW}_{12}\text{O}_{40}$ at conditions where the reaction rate was independent of IPA pressure over temperature ranges of 328 – 408 K. Measured activation energies varied from 43 – 147 kJ mole^{-1} simply based on catalyst pre-treatment and the nature of the support, demonstrating that even slight alterations to the nature of the acidic active site can manifest in the apparent activation energy of dehydration. The constant activation energy of $\sim 93 \text{ kJ mole}^{-1}$ over a tunable range of propylene production rates (see Figure 3(b)) implies that the nature of the active site remains invariant with oxygen treatment.

The fact that dehydration rates were irreversibly titrated by the sterically hindered DTBP implies that this acidic activity is Brønsted in nature. Brown and coworkers[41] synthesized DTBP and noted that DTBP reacted with HCl but not BF_3 . Brown and coworkers also prepared three solutions of SO_3 in SO_2 at 263 K, to which they added equimolar amounts of pyridine, 2,6-lutidine, and DTBP. Pyridine and 2,6-lutidine

readily formed addition products with SO_3 , whereas DTBP did not form the addition product and formed sulfonic acid instead. This work demonstrates the selective binding of DTBP to Brønsted acids and its inability to bind to Lewis acids.

Iglesia and coworkers[42, 43] used DTBP as a selective in situ Brønsted acid titrant for n-hexane isomerization over Keggin POMs and 2-butanol dehydration over WO_x/ZrO_2 catalysts from 343-473 K at ambient pressure. DTBP titrations completely and irreversibly eliminated isomerization and dehydration activity over both of these Brønsted acid catalysts, however, DTBP did not inhibit dehydration of 2-butanol at 403 K over $\gamma\text{-Al}_2\text{O}_3$, known to possess only Lewis acidity. High surface area $\text{MoO}_x/\text{TiO}_2$ species synthesized via TPR methods similar to those used in this work were investigated by Al-Kandari, [44] and these catalysts exhibited Brønsted acidity as observed via characteristic pyridinium ion N-H stretching frequencies located at 1636 cm^{-1} and 1536 cm^{-1} [45]. Pan et al. [46] synthesized Lewis acidic Zr-incorporated zeolite catalysts as characterized by IPA dehydration activity and a lack of characteristic Brønsted FTIR signals at 1540 cm^{-1} and 1640 cm^{-1} .

3.2.5 IPA dehydration mechanism determination using the kinetic isotope effect

The kinetically relevant step of IPA dehydration was investigated with the use of the kinetic isotope effect (KIE). A flow of isotopically labeled IPA, either $\text{C}_3\text{H}_7\text{OD}$ or $\text{C}_3\text{D}_8\text{O}$, was switched with an equivalent volumetric flow rate of $\text{C}_3\text{H}_8\text{O}$ with the use of a four-way valve. Reactant flows were switched after at least 1 h of steady-state propylene production. Dehydration of $\text{C}_3\text{H}_8\text{O}$ was resumed after isotopically labeled IPA

dehydration; this reference condition was used to ensure that any drop in propylene production rate could be entirely attributed to the IPA isotopic content.

The $\text{C}_3\text{H}_7\text{OD}$ exhibited a KIE of 1.02, and the $\text{C}_3\text{D}_8\text{O}$ exhibited a KIE of 1.86. This implies that scission of the O-H bond is not kinetically relevant, but a C-H bond is involved in the rate-determining step (RDS). A KIE of 1.86 implies a primary kinetic isotope effect, meaning the direct scission of the isotopically labeled bond is the RDS. The measured KIE of 1.86 is smaller than the theoretically predicted KIE for C-H bond scission at 415 K (Section S.6 of Supplementary Information); this implies that the transition state involves incomplete severance of the C-H bond.

IPA contains 6 β -hydrogen atoms and one α hydrogen. Since the propylene formed still retains one α -hydrogen, it would be highly unlikely that this hydrogen would be removed in the RDS and then subsequently replaced. This implies that the kinetically relevant step for IPA dehydration over oxygen-modified Mo_2C is the rate of β -hydrogen abstraction in classic E_2 elimination fashion, similar to that seen in amine hydrodenitrogenation (HDN) over Mo_2C [47]. Schwartz et al. [47] concluded that HDN occurred via a β -elimination mechanism due to the decrease in HDN rates with increasing degree of substitution at the β -position (relative to the nitrogen atom) of reactant amines, an almost identical heteroatom removal mechanism to that observed in this work.

3.2.6 Proposed IPA dehydration mechanism over $\text{O}^*-\text{Mo}_2\text{C}$

The mechanism proposed for the dehydration of IPA over oxygen-modified Mo_2C is shown in Scheme 2, where $^*\text{A}^*\text{B}$ is the catalytically active acid-base pair, K_{IPA} is the equilibrium binding constant of IPA to the active site, k_1 is the intrinsic dehydration rate

constant, and K_w is the equilibrium dissociative binding constant of water to the active site. The mechanism is a simple dehydration mechanism over a single acid-base pair, requiring the adsorption of the reactant IPA onto the active site and a kinetically relevant RDS of β -hydrogen scission. We assume that empty sites and IPA are the only relevant surface species because of the lack of product inhibition observed from space velocity variation experiments (Fig. S.7) and independent studies that show the absence of product inhibition by H_2O as discussed in Section 3.2.3.

The reaction mechanism shown in Scheme 2 yields the following rate expression:

$$r = \frac{[L]k_1K_{IPA}P_{IPA}}{1 + K_{IPA}P_{IPA}} \quad (\text{Eq. 1})$$

where r is the rate of propylene formation in $\text{mol s}^{-1} \text{ g}_{\text{cat}}^{-1}$, $[L]$ is the acid site density in sites $\text{g}_{\text{cat}}^{-1}$, k_1 is the intrinsic IPA dehydration rate constant in $\text{mol s}^{-1} \text{ site}^{-1}$, K_{IPA} is the equilibrium binding constant of IPA to the oxygen modified Mo_2C surface, and P_{IPA} is the partial pressure of IPA in the feed. Fig. 3(a) shows that for all O_2 co-feed pressures, the rate of propylene formation is essentially independent of IPA pressure over two orders of magnitude, indicating a surface saturated with IPA; this yields a rate expression of the form $r = k_1[L]$. This model implies that the measured rate constant and activation energy are the intrinsic as opposed to apparent values. Scheme 2 was designed for an arbitrary acid-base pair on an active surface, but irreversible titration by DTBP implies the presence of Brønsted acidity. This would make the active acid site, $*_A$, a Brønsted acidic proton, and the conjugate base, $*_B$, would most likely be a nearby Mo-O species. Matsuda et al. [12] showed similar IPA dehydration activity over H_2 -reduced MoO_3 catalysts that showed no significant induction period, further implying the importance of the oxidized surface for dehydration activity in contrast to the nature of the bulk carbide.

We cannot ascertain the exact nature of the active phase on the surface as far as a carbide, oxide, or oxycarbide designation, but the active site for this acidic activity is an O₂-induced Brønsted acid site.

This active site is similar to that theorized by Chia et al. [48] involving a partially oxidized ReO_x/Rh or MoO_x/Rh, creating a strong Re-O or Mo-O bond and subsequently a weak O-H bond and high nucleophilicity of an adjacent O serving as a conjugate base. Chia and coworkers investigated the hydrogenolysis of cyclic ethers, observing hydrogenolysis of secondary C-O bonds over both Rh-ReO_x/C and Rh-MoO_x/C. This catalysis was hypothesized as the result of the bifunctionality of ReO_x or MoO_x Brønsted acidic ring-opening and subsequent metallic hydrogenation. Acidity was verified by both NH₃ TPD experiments and rate suppression via NaOH co-feed; catalytic activity was also noted to decrease under higher H₂ pretreatment temperatures, known to reduce ReO_x or MoO_x. These findings were supported by DFT reaction pathway energetic calculations using a ReO_x/Rh(111) postulated active site, evincing the development of acidic active sites via oxidation of oxophilic transition metals.

Brønsted acidic activity resulting from oxidation of the Mo formulation adequately explains the observed IPA dehydration, and pre-oxidation metallic and hydrogenation activity is rationalized by Mo₂C catalysis as previously observed by Thompson and coworkers[17]. O₂-induced elimination of metallic and alkaline activity is the result of the oxidation of these surface carbide sites, similar to the effects seen by Iglesia et al., [11] and the lack of reversibility of this catalytic stifling is because of the extreme oxophilicity of the surface and thermodynamic favorability of O* binding as previously observed by Leary[5] and Liu[4]. In an independent experiment, H₂O co-feed

was also shown to diminish metallic activity of the carbide, but the oxidation was not as severe or complete as with the use of an O₂ co-feed. A freshly synthesized carbide was treated with 10 kPa H₂O for 2.5 h; rates of propylene production increased nearly fourfold while rates of C₆⁺ formation dropped by nearly half when compared to a fresh in situ carbide with no H₂O or O₂ exposure. The similar effects of O₂ and H₂O implicate the oxidation of the catalyst surface as the underlying cause of the shift from a metallic/alkaline catalyst to an acidic catalyst.

This reaction pathway analysis may not be valid for all reaction conditions as the versatility of these oxycarbide formulations varies based on reaction conditions. Lee[14, 15] and Prasomsri[49] investigated catalytic HDO of furfural and anisole, molecules which cannot undergo simple dehydration due to the lack of a sp³-hybridized β-hydrogen. These molecules underwent deoxygenation over similar molybdenum oxycarbide formulations at 423 K, evincing deoxygenation mechanisms distinct from the dehydration observed in this work. Similarly, UHV studies of the Mo₂C surface by Chen and coworkers[8, 9] demonstrate C₂-C₃ alcohols and ketones undergoing primarily decomposition to surface adatoms; this reactivity under non-catalytic conditions differs from oxygenate dehydration exhibited in this study.

The culmination of these findings demonstrates the complex and tunable nature of molybdenum formulations as catalysts. Mo₂C catalytic activity can be manipulated from primarily metallic and alkaline to primarily acidic, and acidic dehydration rates can be controllably modified via simple O₂-induced site density alteration. This research demonstrates that catalytic Brønsted acidity of oxophilic transition metal carbide

formulations is the result of oxidation and that acid site density in these materials can be altered without affecting bulk crystal structure.

4. Conclusions

Catalytically multifunctional, porous, high-surface area Mo_2C was synthesized; this formulation converted IPA via metallic dehydrogenation, alkaline condensation, and acidic dehydration pathways. Catalyst structure comprised of 2-5 nm Mo_2C crystallites of orthorhombic $\beta\text{-Mo}_2\text{C}$ as inferred from X-ray diffractograms and observed in TEM. Prior to oxygen exposure, the carbide showed significant metallic and alkaline activity, specifically dehydrogenation and carbonyl condensation reactions. Increasing catalyst surface oxidation repressed metallic dehydrogenation and alkaline condensation rates irreversibly while concurrently amplifying acidic dehydration rates.

This acidic activity could be reversibly manipulated via O_2 co-feed to tune dehydration rates of IPA. Acidic tunability was a result of acid site density manipulation as demonstrated by (i) constant intrinsic activation energy for unimolecular IPA dehydration and (ii) constant IPA dehydration TOF of $\sim 0.1 \text{ s}^{-1}$ as measured by in situ DTBP titrations. Acidity was Brønsted in nature, and DTBP titrations demonstrated the porous nature of the catalyst, which evinced the existence of a fractional population of chemically indistinguishable yet sterically hindered active sites. Reversible manipulation of Brønsted acid site density via O_2 co-feed at 415 K was shown to not affect the structure of bulk Mo_2C crystals; X-ray diffractograms showed no evidence for crystalline molybdenum oxide or oxycarbide formation.

The oxophilic nature of the oxygen-modified carbide surface was made evident by a kinetically observable IPA saturated surface at IPA pressures as low as 0.048 kPa and O₂-induced exotherms. IPA dehydration was independent of IPA pressure and occurred with an intrinsic activation energy of 93 ± 1.3 kJ mole⁻¹, and the IPA dehydration was devoid of product inhibition at product partial pressures comparable to reactant feed pressures. IPA dehydration occurred via an E₂ elimination mechanism involving a rate-determining step of β -hydrogen scission as demonstrated by a primary KIE. The oxygen-modification of highly oxophilic transition metal carbides to reversibly generate Brønsted acidity is analogous to that noted for oxophilic metals such as Re and Mo.

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Figure 1(a). HAADF STEM image of a representative post-reaction Mo_2C catalyst particle exhibiting visible porosity in the range of 1-2 nm. **(b)** High magnification of boxed region of image (a) showing crystallinity, size of grains, and porous features. **(c)** View down the [010] zone axis of orthorhombic $\beta\text{-Mo}_2\text{C}$ as reported by Parthé and Sadagopan[30]. **(d)** Representative high resolution HAADF STEM image of [010] zone axis of the same sample. Two stacking faults on the (100) planes are marked with lines. Such defects were common throughout the specimen.

Figure 2. X-ray diffractograms of Mo₂C catalysts before and after reaction, including reference diffractograms for fcc α -Mo₂C (JCPDS PDF # 00-015-0457) and orthorhombic β -Mo₂C (JCPDS PDF # 01-072-1683). The highest intensity MoO₂ and MoO₃ peaks ((110) and (210), respectively) are also included.

Figure 3(a). Propylene synthesis rates as a function of IPA and O₂ partial pressures. T = 415 K, ~ 0.015 g_{cat}, P = 114 kPa, P_{CH₄} = 4 kPa (internal standard), balance He. Space velocity of 133 cm³ s⁻¹ g_{cat}⁻¹.

Figure 3(b). Logarithmic plot of propylene synthesis rate vs. reciprocal temperature at varying O_2 partial pressures. $T = 415 \text{ K}$, $\sim 0.015 \text{ g}_{\text{cat}}$, $P = 114 \text{ kPa}$, $P_{\text{CH}_4} = 4 \text{ kPa}$ (internal standard), balance He. Space velocity of $133 \text{ cm}^3 \text{ s}^{-1} \text{g}_{\text{cat}}^{-1}$.

Figure 4. Reversible alteration of steady-state propylene and DIPE synthesis rates via O_2 co-feed at $T = 415 \text{ K}$, $P = 124 \text{ kPa}$, space velocity of $152 \text{ cm}^3 \text{ s}^{-1} \text{ g}_{\text{cat}}^{-1}$, $0.0151 \text{ g}_{\text{cat}}$ loading, $P_{\text{IPA}} = 0.48 \text{ kPa}$, $P_{\text{H}_2} = 19 \text{ kPa}$, $P_{\text{CH}_4} = 4 \text{ kPa}$ (internal standard), balance He. IPA conversion $< 2\%$.

Figure 5. Propylene synthesis rate as a function of O_2 co-feed partial pressure at 415 K, $\sim 0.015 \text{ g}_{\text{cat}}$, $P = 114 \text{ kPa}$, $P_{\text{IPA}} = 0.48 \text{ kPa}$, $P_{\text{CH}_4} = 4 \text{ kPa}$ (internal standard), balance He. P_{O_2} varied from 0 – 13.5 kPa at a space velocity of $133 \text{ cm}^3 \text{ s}^{-1} \text{ g}_{\text{cat}}^{-1}$, $P_{O_2} = 25.3 \text{ kPa}$ at a space velocity of $66.7 \text{ cm}^3 \text{ s}^{-1} \text{ g}_{\text{cat}}^{-1}$.

Figure 6. Propylene synthesis rate as a function of time after introduction of the DTBP titrant. $T = 415\text{ K}$, $\sim 0.29\text{ g}_{cat}$, $P = 114\text{ kPa}$, $P_{IPA} = 1\text{ kPa}$, $P_{CH_4} = 4\text{ kPa}$ (internal standard), balance He, space velocity of $6.9\text{ cm}^3\text{ s}^{-1}\text{ g}_{cat}^{-1}$. Titrant flow is an equivalent volumetric flow of IPA/DTBP with $< 1 \times 10^{-3}$ DTBP mole fraction. Pure IPA flow resumed at ~ 180 min after titrant introduction. The diagonal dashed line shows the linear extrapolation used to calculate propylene turnover frequency (TOF).

Figure 7. Propylene turnover frequency (TOF) as a function of propylene synthesis rate normalized by catalyst loading. Propylene rate per gram was manipulated with O_2 co-feed variation from $P_{\text{O}_2} = 0 - 13.5 \text{ kPa}$, and TOF was calculated using Brønsted acid site density measured by in situ DTBP titrations. $T = 415 \text{ K}$, $\sim 0.29 \text{ g}_{\text{cat}}$, $P = 114 \text{ kPa}$, $P_{\text{IPA}} = 1 - 2 \text{ kPa}$, $P_{\text{CH}_4} = 4 \text{ kPa}$ (internal standard), balance He, space velocity of $6.9 \text{ cm}^3 \text{ s}^{-1} \text{g}_{\text{cat}}^{-1}$.

Scheme 1. Proposed reaction network for IPA over acidic, basic, and metallic Mo₂C catalytic sites.

Scheme 2. Proposed reaction mechanism for IPA dehydration over O^{*}-Mo₂C Brønsted acid sites.

O^{δ-}-Mo₂C

Low Brønsted Acid
Site Density

High Brønsted Acid
Site Density