

# Mo<sub>2</sub>C Modification by CO<sub>2</sub>, H<sub>2</sub>O, and O<sub>2</sub>: Effects of Oxygen Content and Oxygen Source on Rates and Selectivity of *m*-Cresol Hydrodeoxygenation

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Supporting Information

**ABSTRACT:** Vapor-phase *m*-cresol hydrodeoxygenation rates on oxygenate-modified Mo<sub>2</sub>C catalysts prepared by pretreating fresh Mo<sub>2</sub>C catalysts in 1 kPa of O<sub>2</sub>, H<sub>2</sub>O, and CO<sub>2</sub> at 333 K showed that (i) molecular oxygen has a higher propensity to deposit oxygen (O/Mo<sub>bulk</sub> before HDO = 0.23  $\pm$  0.02) on fresh Mo<sub>2</sub>C, compared to CO<sub>2</sub> and H<sub>2</sub>O (O/ Mo<sub>bulk</sub> before HDO  $\approx$  0.036), as assessed from temperatureprogrammed surface reaction with H<sub>2</sub>, and (ii) oxygen adsorbed in amounts exceeding ~0.06  $\pm$  0.01 of O/Mo<sub>bulk</sub> poisons the metal-like sites for toluene synthesis as inferred from a 10-fold decrease in toluene synthesis rate per gram on the O<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C compared to that on fresh



 $Mo_2C$ ,  $H_2O-1$  kPa (333 K)- $Mo_2C$ , and  $CO_2-1$  kPa (333 K)- $Mo_2C$  catalysts. Invariant turnover frequencies of toluene synthesis measured from *in situ* CO titration among the  $O_2$ -,  $H_2O$ -, and  $CO_2$ -modified samples demonstrate that the effect of adsorbed oxygen is independent of the oxygen source.

**KEYWORDS:** *m*-cresol, hydrodeoxygenation, lignin, biofuels, oxygenate-modification

# 1. INTRODUCTION

Transition-metal carbides have been shown to catalyze hydrodeoxygenation (HDO) reactions to convert biomassderived compounds to fuels and chemicals.<sup>1-8</sup> These catalysts are selective in cleaving C–O and C=O bonds at ambient  $H_2$ pressure and low temperatures (423-623 K),<sup>1,2,7,9,10</sup> such that the aromaticity of furan and benzene rings can be retained during HDO.<sup>10,11</sup> Molybdenum carbides exhibit stable surfaces that vary with surface coverage of O and C, as a result of reaction environments or synthesis protocols,<sup>12</sup> and display heterogeneity in both bulk<sup>13</sup> and surface<sup>14,15</sup> compositions, and in surface structures, including distinct binding sites<sup>16-19</sup> and nonstoichiometric surface compositions.<sup>13,20</sup> This complexity in bulk and surface structure of molybdenum carbides is accentuated in the presence of oxygenates during HDO of bio-oil or pyrolysis vapor on the oxophilic transition-metal carbides,<sup>21–24</sup> which can deposit oxygen on the catalyst. Surface oxygen species can poison the metal-like sites required for HDO<sup>25</sup> and/or generate Brønsted acid sites.<sup>26</sup>

Oxygen (~4.7 × 10<sup>-4</sup> mol  $g_{cat}^{-1}$ ) and carbon (equivalent of ~1.4 × 10<sup>-3</sup> mol  $g_{cat}^{-1}$  C<sub>6</sub> species) deposition was observed during an initial transient observed during anisole HDO on bulk  $\beta$ -Mo<sub>2</sub>C that had been passivated in 1% O<sub>2</sub>/He and pretreated in H<sub>2</sub> for 1 h at 723 K prior to reaction at 423 K.<sup>25</sup> Cyclohexane was observed in the effluent during this initial transient, as observed from online mass spectrometric analysis.

Oxygen deposition occurred during this transient; concurrently, cyclohexane rates dropped to almost zero and benzene was observed, suggesting that hydrogenation of benzene to cyclohexane was inhibited by oxygen deposition (see Figure 4a in ref 25). A similar effect of oxygen deposition was reported in our recent studies, noting that the hydrogenation rates of benzene and toluene on  $Mo_2C$  were irreversibly inhibited when water or methanol was co-fed (see Figure 5 in ref 10). These results demonstrate that oxygen deposition under reaction environments alters catalyst composition and function; the effect of the source of oxygen on HDO catalysis is yet unclear.

Metal-like sites were found to be involved in selective benzene synthesis (>90%  $C_6^+$  selectivity) from vapor-phase hydrodeoxygenation of anisole on Mo<sub>2</sub>C and W<sub>2</sub>C catalysts, as co-feeds of carbon monoxide were noted to inhibit HDO rates under reaction conditions and turnover frequencies of benzene synthesis at 423 K (~10<sup>-3</sup> mol mol<sub>CO</sub><sup>-1</sup> s<sup>-1</sup> for Mo<sub>2</sub>C and ~10<sup>-4</sup> mol mol<sub>CO</sub><sup>-1</sup> s<sup>-1</sup> for W<sub>2</sub>C) were noted to be invariant with different CO co-feed pressures.<sup>25,27</sup> The turnover frequency of benzene synthesis from anisole HDO on a fresh Mo<sub>2</sub>C formulation (~1.7 × 10<sup>-3</sup> mol mol<sub>CO</sub><sup>-1</sup> s<sup>-1</sup>) was found to be almost the same as that on an O<sub>2</sub>-modified Mo<sub>2</sub>C catalyst

Received: September 27, 2016 Revised: December 17, 2016 (~1.5 × 10<sup>-3</sup> mol mol<sub>CO</sub><sup>-1</sup> s<sup>-1</sup>; O/Mo<sub>bulk</sub> (molar ratio) = 0.075), while the benzene synthesis rate normalized per gram catalyst was three times higher on the fresh Mo<sub>2</sub>C, indicating that the number of sites responsible for anisole HDO on Mo<sub>2</sub>C decreases with O<sub>2</sub> treatment.<sup>25</sup>

Oxygen-modified tungsten carbide materials prepared by exposing freshly synthesized tungsten carbides to O<sub>2</sub> at various temperatures have been reported to exhibit bifunctionality.<sup>28–</sup> Alkane (n-hexane and n-heptane) hydrogenolysis rates on bifunctional tungsten carbides decreased concurrently with an increase of alkane isomerization rates as the extent of oxygen modification, quantified by temperature-programmed reduction (TPR) and ex situ CO chemisorption, increased.<sup>28,29</sup> Sullivan et al.<sup>26</sup> reported that a  $\sim$ 30-fold increase in propylene synthesis rates per gram Mo<sub>2</sub>C catalyst from isopropyl alcohol dehydration at 415 K was observed when O<sub>2</sub> co-feed was varied from 0 to 13.5 kPa. Brønsted acid sites were found to be responsible for isopropyl alcohol dehydration to propylene on Mo<sub>2</sub>C formulations with oxygen co-feed (0-13.5 kPa), as evidenced by the invariance of propylene rates normalized to acid sites titrated in situ by 2,6-di-tert-butylpyridine.<sup>26</sup> The O 1s peak at 532.5 eV assigned to surface hydroxyl species observed from X-ray photoelectron spectroscopy (XPS) on a Mo<sub>2</sub>C catalyst after H<sub>2</sub> pretreatment was correlated with the surface acidity of Mo<sub>2</sub>C measured from temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD).<sup>1</sup> These surface hydroxyl groups (O 1s peak at 532.5 eV) were also observed on spent Mo<sub>2</sub>C catalysts from the hydrodeoxygenation of acetic acid at 623 K without exposure to air.<sup>1</sup> These results show that a change in site densities of metal and acid functions on tungsten carbide formulations can result from changing O<sub>2</sub> pretreatment conditions and the functionality of Mo<sub>2</sub>C can be adjusted to primarily acidic by varying the O<sub>2</sub> co-feed pressure during the reaction.

The propensity for  $O_{2}$ ,  $CO_{2}$ , and  $H_{2}O$  as oxidants to oxidize pure  $\beta$ -Mo<sub>2</sub>C surface was evaluated using density functional theory (DFT) calculations on  $\beta$ -Mo<sub>2</sub>C (011) and (101) surfaces with mixed Mo/C terminations.<sup>31</sup> The reaction energies for surface oxidation by O2, CO2, and H2O to deposit 0.125 monolayer (ML) to 1 ML of oxygen on these surfaces showed that O<sub>2</sub>-Mo<sub>2</sub>C reactions have a much larger enthalpy (-13 eV to -2 eV) than those of H<sub>2</sub>O-Mo<sub>2</sub>C and  $CO_2$ -Mo<sub>2</sub>C (approximately -2 eV to 0 eV or >0 eV) reactions at 0 K.<sup>31</sup> However, it is still unclear (i) how the differences in the oxidation propensity of O2, CO2, and H2O translate to the amount of oxygen adsorbed on bulk Mo<sub>2</sub>C, which may contain residual oxygen in the structure after catalyst synthesis,<sup>32</sup> and (ii) what are the resulting consequences of oxygen loadings from different oxygen sources on HDO rates and selectivity catalyzed by Mo<sub>2</sub>C.

We report the effects of oxygenate modification on Mo<sub>2</sub>C for *m*-cresol HDO on Mo<sub>2</sub>C catalysts treated in 1 kPa of O<sub>2</sub>, CO<sub>2</sub>, or H<sub>2</sub>O at 333 K. Independent kinetic and *in situ* chemical titration studies showed that two distinct sites—one of which has metal-like characteristics—are involved in *m*-cresol HDO. Temperature-programmed surface reaction with H<sub>2</sub> (TPSR with H<sub>2</sub>) was used to quantify the amount of oxygen incorporated in the catalyst from oxygenate treatment (O/Mo<sub>bulk</sub> before HDO) and/or from *m*-cresol HDO (O/Mo<sub>bulk</sub> after HDO). Molecular oxygen has a higher propensity to deposit oxygen on Mo<sub>2</sub>C (O/Mo<sub>bulk</sub> before HDO = 0.23 ± 0.02), compared to CO<sub>2</sub> and H<sub>2</sub>O (O/Mo<sub>bulk</sub> before HDO ≈ 0.036), as inferred from TPSR with H<sub>2</sub> before HDO. In situ

chemical titration and m-cresol HDO studies on fresh and oxygenate-modified  $Mo_2C$  catalysts showed that adsorbed oxygen poisons the metal-like sites responsible for *m*-cresol HDO and that the effect of adsorbed oxygen is independent of the source of oxygen.

# 2. MATERIALS AND METHODS

2.1. Kinetics and In Situ Chemical Titration Studies for m-Cresol HDO. 2.1.1. Catalyst Synthesis and Characterization. Molybdenum carbide catalysts were synthesized based on protocols reported in a prior report.<sup>10</sup> Ammonium molybdate tetrahydrate (~1.2 g, Sigma, 99.98%, trace metal basis; sieved, 177-400 µm, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O) was loaded to a tubular quartz reactor (inner diameter (ID) of 10 mm) placed in a tube furnace (Applied Test System, Series 3210) controlled by a Watlow Temperature Controller (96 series) and was treated in a gas mixture (total flow rate of  $\sim 2.75$  cm<sup>3</sup>  $s^{-1}$ ) of 15 vol %/85 vol % of CH<sub>4</sub> (Matheson, 99.97%) and H<sub>2</sub> (Minneapolis Oxygen, 99.999%) at ~623 K for 5 h at a ramping rate of  $\sim 0.06$  K s<sup>-1</sup> from room temperature (RT), then treated at ~863 K for 3 h at a ramping rate of ~0.047 K s<sup>-1</sup>. Passivation of the resulting material was done at RT using 1% O<sub>2</sub>/He (Matheson, Certified Standard Purity; total flow  $\approx$ 1.67 cm<sup>3</sup> s<sup>-1</sup>) for ~2 h.

 $N_2$  adsorption/desorption (Micromeritics ASAP 2020) measurements at  $\sim$ 77 K were used to determine the Brunauer-Emmett-Teller (BET) surface area of Mo<sub>2</sub>C catalysts; the sample was degassed (<10  $\mu$ m Hg) at 523 K for at least 4 h before  $N_2$  adsorption. X-ray diffraction (XRD) (using a Bruker, Model D8 Discover, 2D X-ray diffractometer with a two-dimensional VÅNTEC-500 detector) was used to determine the bulk structure of molybdenum carbide after mcresol HDO. Two-dimensional images were collected using Cu  $K\alpha$  X-ray radiation with a graphite monochromator and a 0.8 mm point collimator measured in three measurement frames at  $2\theta = 25^{\circ}$ ,  $55^{\circ}$ , and  $85^{\circ}$  with a 900 s frame/dwell, which were then converted to one-dimensional (1D) intensity vs  $2\theta$  for analysis. Ex situ CO chemisorption (Matheson, 99.5%) uptake at 323 K for Mo<sub>2</sub>C samples was measured using a Micromeritics ASAP 2020 instrument, in which ~0.14 g passivated  $Mo_2C$  was treated in  $H_2$  at 723 K for 1 h, followed by degassing  $(\sim 2 \ \mu m Hg)$  at 723 K for 2 h, after being evacuated at 383 K  $(\sim 2 \,\mu m \text{ Hg})$  for 0.5 h. The uptake of irreversibly adsorbed CO was then obtained from the difference between two adsorption isotherms (from 100 mm Hg to 450 mm Hg at 323 K) extrapolated to zero pressure; the second isotherm was taken after the cell was degassed at  $\sim 2 \mu m$  Hg to remove weakly adsorbed species. Ex situ CO chemisorption measurements were conducted within a seven-day period prior to the kinetic studies for vapor-phase *m*-cresol HDO.

X-ray photoelectron spectroscopy (XPS) measurements were performed using an SSX-100 spectrometer (Surface Science Laboratories, Inc.) with an Al K $\alpha$  X-ray source operating at 200 W on 1 mm × 1 mm area samples. High-resolution spectra were collected using 50 eV pass energy and 0.1 eV step<sup>-1</sup>. The atomic percentages were calculated from the survey spectrum (150 eV pass energy and 1 eV step<sup>-1</sup>) using the ESCA Hawk software. The lowest energy Mo 3d<sub>5/2</sub> peak was used as the reference (228.0 eV for Mo<sub>2</sub>C).<sup>33,34</sup> A combination of Gaussian/Lorentzian functions with the Gaussian percentages being at 80% or higher was used for curve fitting.

2.1.2. Kinetic Studies for Vapor-Phase Hydrodeoxygenation (HDO) of m-Cresol. Steady-state vapor-phase HDO Scheme 1. Experimental Procedures Used in This Study to Investigate the Effect of Oxygenate Pretreatment on  $Mo_2C$  for Hydrodeoxygenation (HDO)



reactions of m-cresol on Mo<sub>2</sub>C catalyst were carried out in a tubular quartz reactor (ID = 10 mm) placed in a tube furnace (Applied Test System, Series 3210), controlled by a Watlow Temperature Controller (96 series). The reaction temperature was monitored by a thermocouple inserted in the outer thermowell of the reactor. The reactant gas mixture was comprised of *m*-cresol  $(0.03\%)/H_2$  (84%)/He (balance) (mol%) at a total flow rate of ~3.33 cm<sup>3</sup> s<sup>-1</sup> and a total pressure of ~112 kPa. *m*-Cresol (Sigma, FG,  $\geq$ 98%) was added to the flow line, using a syringe pump (KD Scientific, Model 100). Reactor effluents were analyzed with a flame ionization detection (FID) device, using an online gas chromatography (GC) system (Agilent, Model 7890) with a methyl-siloxane capillary column (HP-1, 50 m  $\times$  320  $\mu$ m  $\times$  0.52  $\mu$ m). All passivated molybdenum carbide samples were treated in H<sub>2</sub> (Minneapolis Oxygen, 99.999%;  $\sim 1.67$  cm<sup>3</sup> s<sup>-1</sup>) at 773 K ( $\sim 0.1$ K  $s^{-1}$ ) for 1 h prior to reaction. All flow lines were heated to at least 398 K via resistive heating to prevent condensation of the compounds. *m*-Cresol conversion and  $C_6^+$  product selectivity were calculated as follows:

$$m\text{-cresol conversion (\%)} = \frac{(\text{sum of moles of C in products})_{\text{out}}}{(\text{moles of C in }m\text{-cresol})_{\text{in}}} \times 100$$
(1)

$$C_6^+ \text{ product selectivity } (\%) = \frac{\text{moles of } C_6^+ \text{ product } i}{\text{moles of } C_6^+ \text{ products}} \times 100$$
(2)

2.1.3. In Situ CO Titration for Vapor-Phase Hydrodeoxygenation (HDO) of m-Cresol. In situ CO titration studies were conducted to probe the identity and density of the operational catalytic sites for m-cresol HDO on  $Mo_2C$ formulations. A co-feed of CO with Ar or He as an internal tracer (0.0125, 0.025, or 0.0375 cm<sup>3</sup> s<sup>-1</sup> CO in 0.033 cm<sup>3</sup> s<sup>-1</sup> Ar) was introduced to the reactant mixture after steady-state mcresol synthesis rates were observed. The transient responses of CO and Ar/He were monitored by an online mass spectrometer (MKS, Model Cirrus 200 Quadrupole mass spectrometer system). Toluene synthesis rates before and after CO co-feed were quantified by online GC.

**2.2.** Oxygenate Treatment Studies. 2.2.1. Oxygenate Treatment on Fresh  $Mo_2C$ . Fresh  $Mo_2C$  (~1  $g_{cat}$ ) was

synthesized following the procedures described in Section 2.1.1, and was subsequently cooled to the oxygenate treatment temperature (333, 363, or 423 K) in the same  $CH_4/H_2$  flow. The freshly synthesized Mo<sub>2</sub>C was then exposed to a gas stream containing the oxygenate (0.05-6 kPa)-O<sub>2</sub>, CO<sub>2</sub>, or  $H_2O$ — and an inert (Ar or He) at a total gas flow rate of 1.67  $cm^3$  s<sup>-1</sup> at ambient pressure for 2 h; the corresponding oxygenate treatment pressures are summarized in Scheme 1. Water was added to the flow lines by a syringe pump (KD Scientific, Model 100). The catalyst was then heated to 423 K in 0.5 h and held at 423 K for 1.5 h in a flow of helium (10%)/H<sub>2</sub> (balance) (mol %) at ambient pressure and at a total flow rate of  $\sim 1.83$  cm<sup>3</sup> s<sup>-1</sup> to remove any loosely bound species from the catalyst. The nomenclature for the oxygenatemodified Mo<sub>2</sub>C catalysts reported in this work is of the form, oxygenate-treatment pressure (temperature)-Mo<sub>2</sub>C. A freshly synthesized molybdenum carbide catalyst that was treated with 1 kPa  $O_2$  at 333 K, for example, is denoted as  $O_2-1$  kPa (333) K)-Mo<sub>2</sub>C. All oxygenate-modified Mo<sub>2</sub>C catalysts studied in this work are listed in Scheme 1.

2.2.2. m-Cresol HDO on Fresh/Oxygenate-Treated Mo<sub>2</sub>C. Vapor-phase HDO was used as a probe reaction to study the effect of oxygenate modification on Mo<sub>2</sub>C catalysts. The reactor setup is the same as that described in section 2.1.2. The reactant flow in all oxygenate treatment studies was comprised of *m*-cresol (1%)/He (10%)/H<sub>2</sub> (balance) (mol %), the total flow rate was 1.83 cm<sup>3</sup> s<sup>-1</sup> at a total pressure of ~107 kPa and a temperature of 423 K.

2.2.3. Temperature-Programmed Surface Reaction (TPSR) with  $H_2$ . Temperature-programmed surface reaction (TPSR) with  $H_2$  was performed to quantify the amount of oxygen deposited on a fresh Mo<sub>2</sub>C catalyst from oxygenate modification and on a fresh and an oxygenate-modified Mo<sub>2</sub>C catalyst from *m*-cresol HDO at 423 K. The catalyst was heated from 423 K to 773 K in 1 h and held at 773 K for 0.5 h in a flow of helium  $(10\%)/H_2$  (balance) (mol %) at a total flow rate of ~1.83 cm<sup>3</sup> s<sup>-1</sup> at ambient pressure. The oxygen uptake on the catalyst (i) after oxygenate treatment, denoted as O/Mo<sub>bulk</sub> after HDO, and (ii) after *m*-cresol HDO, denoted as O/Mo<sub>bulk</sub> after HDO, was estimated by the H<sub>2</sub>O signal monitored by an online mass spectrometer (MKS, Model Cirrus 200 Quadrupole mass spectrometer system) during the TPSR process (Figure S1 in the Supporting



Figure 1. (a) Toluene selectivity and (b) *m*-cresol conversion for *m*-cresol hydrodeoxygenation (HDO) on Mo<sub>2</sub>C. Feed = *m*-cresol (0.04%)/H<sub>2</sub> (balance) (mol %) at a total pressure of ~108 kPa and at a temperature of 423 K; total flow rate  $\approx 2.17$  cm<sup>3</sup> s<sup>-1</sup>; 0.14 g<sub>cat</sub> of Mo<sub>2</sub>C catalyst; *ex situ* CO uptake  $\approx 94 \ \mu$ mol g<sub>cat</sub><sup>-1</sup>.



**Figure 2.** (a) Effect of ( $\blacksquare$ ) H<sub>2</sub> pressure and ( $\bullet$ ) *m*-cresol pressure on turnover frequencies (TOFs) of toluene synthesis determined by *ex situ* CO chemisorption (184–240  $\mu$ mol g<sub>cat</sub><sup>-1</sup>) on Mo<sub>2</sub>C catalysts at a total pressure of ~110 kPa and a temperature of 423 K. H<sub>2</sub> pressure was varied from 10 kPa to 110 kPa (balance being helium) at a *m*-cresol pressure of 0.03 kPa; the *m*-cresol pressure was varied from 0.03–1.5 at a H<sub>2</sub> pressure of 50 kPa (balance being helium); total flow rate  $\approx 3.33$  cm<sup>3</sup> s<sup>-1</sup>; ~0.02–0.06 g<sub>cat</sub> of Mo<sub>2</sub>C. (b) Temperature dependencies for TOF of toluene synthesis determined by *ex situ* CO chemisorption (236  $\mu$ mol g<sub>cat</sub><sup>-1</sup>) from *m*-cresol HDO at a total pressure of ~112 kPa and a temperature of 400–450 K. *m*-Cresol pressure  $\approx 0.028$  kPa; total flow rate  $\approx 3.33$  cm<sup>3</sup> s<sup>-1</sup>; ~0.016 g<sub>cat</sub> of catalyst.

Information). Water was found to be the major oxygencontaining compound eluted during TPSR, as also noted by Lee et al.<sup>25</sup> and Choi et al.<sup>32</sup> for TPSR with H<sub>2</sub> on Mo<sub>2</sub>C after anisole HDO at 423 K and TPSR with H<sub>2</sub> for the as-prepared Mo<sub>2</sub>C catalysts, respectively. Scheme 1 illustrates the experimental procedures for the oxygenate treatment studies. An O/Mo<sub>bulk</sub> value was obtained from eq 3.

$$O/Mo_{bulk} = \frac{\text{moles of oxygen uptake measured from TPSR}}{\text{moles of Mo in Mo}_2C \text{ sample}}$$
(3)

Independent H<sub>2</sub> TPSR experiments were conducted on the fresh Mo<sub>2</sub>C, O<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C, H<sub>2</sub>O-1 kPa (333 K)-Mo<sub>2</sub>C, and CO<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C catalysts, in which, after the oxygenate treatment, the catalyst was heated to 773 K in 1 h and held at 773 K for 0.5 h, then subsequently heated to 973 K in 0.5 h and held at 973 K for 2 h in a flow of helium (10%)/H<sub>2</sub> (balance) (mol %) at a total flow rate of ~1.83 cm<sup>3</sup> s<sup>-1</sup> and at ambient pressure (Figure S1).

#### 3. RESULTS AND DISCUSSION

**3.1. Kinetics and In Situ Chemical Titration Studies for** *m*-Cresol HDO. 3.1.1. Kinetic Studies for Vapor-Phase *Hydrodeoxygenation (HDO) of m*-Cresol. Molybdenum carbide catalysts have been shown to selectively catalyze vapor-phase anisole HDO at 423 K and ambient H<sub>2</sub> pressure  $(>90\% C_6^+$  selectivity for benzene and cyclohexane).<sup>27,35</sup> Similar to anisole HDO on Mo<sub>2</sub>C, high selectivity for toluene (>90%  $C_6^+$  selectivity) was observed from *m*-cresol HDO on Mo<sub>2</sub>C at ambient pressure and at temperatures between 423 K and 483 K for ~240 ks time-on-stream (TOS) (Figure 1a). A decrease of <5% in *m*-cresol conversion at 423 K was observed after two temperature cycles (423-483 K) were employed during the  $\sim$ 240 ks TOS (Figure 1b), demonstrating that the catalyst was stable for *m*-cresol HDO. High selectivity (>75%) to toluene from vapor-phase m-cresol HDO has also been reported under ambient pressure on Pd/Fe<sub>2</sub>O<sub>3</sub> catalysts at 573 K,<sup>36</sup> Pt/H-BEA at 623 and 673 K,<sup>37,38</sup> Pt/SiO<sub>2</sub> at 553 K,<sup>39</sup> and 10 wt %  $MoO_3/ZrO_2$  (>99% toluene selectivity)<sup>40</sup> at 593 K, and at ~5 atm on Pt/TiO<sub>2</sub> at 623 K.<sup>41</sup> m-Cresol conversion on these catalysts, however, decreases with TOS.<sup>38</sup>

The turnover frequencies (TOFs) of toluene synthesis determined by *ex situ* CO chemisorption on  $Mo_2C$  are zero-order-dependent on *m*-cresol pressure (0.03–1.5 kPa) and are almost-half-order-dependent on H<sub>2</sub> pressure (10–110 kPa) (Figure 2a). The concurrent zero-order dependence on the *m*-cresol pressure and the almost-half-order dependence on H<sub>2</sub> pressure for toluene synthesis suggests that two distinct sites, which catalyze (i) hydrogen dissociation and (ii) *m*-cresol



**Figure 3.** (a) Toluene synthesis rates versus time-on-stream (TOS) and (b) normalized transient mass spectrometer signals of toluene (m/z = 91), Ar (m/z = 40), and CO (m/z = 28), as a function of time during the course of *in situ* CO titration for *m*-cresol HDO over ~4 g<sub>cat</sub> of Mo<sub>2</sub>C catalyst (75  $\mu$ mol g<sub>cat</sub><sup>-1</sup> *ex situ* CO uptake) at a total pressure of ~120 kPa and a temperature of 423 K. *m*-Cresol (0.3%)/H<sub>2</sub> (balance) (mol %), total flow rate  $\approx$  3.33 cm<sup>3</sup> s<sup>-1</sup>, 28% conversion. Co-feed flow rates: 0.0125, 0.025, or 0.0375 cm<sup>3</sup> s<sup>-1</sup> CO in 0.033 cm<sup>3</sup> s<sup>-1</sup> Ar.

Table 1. O/Mo <sub>bulk</sub> Ratio before and after <i>m</i> -Cresc	I HDO"
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	O <sub>2</sub> -0.05 kPa (333 K)-Mo <sub>2</sub> C <sup>b</sup>	O <sub>2</sub> -1 kPa (333 K)-Mo <sub>2</sub> C	H <sub>2</sub> O-1 kPa (333 K)-Mo <sub>2</sub> C	CO <sub>2</sub> -1 kPa (333 K)-Mo <sub>2</sub> C	fresh Mo <sub>2</sub> C
O/Mo <sub>bulk</sub> before HDO	$0.030 \pm 0.005$	$0.23 \pm 0.02$	$0.038 \pm 0.010$	$0.035 \pm 0.010$	0
O/Mo <sub>bulk</sub> after HDO	$0.054 \pm 0.005$	$0.23 \pm 0.02$	$0.07 \pm 0.01$	$0.06 \pm 0.01$	$0.05 \pm 0.01$
conversion (%)	~18	~1.5	~18	~18	~21
toluene synthesis rate (× $10^{-8}$ mol $g_{cat}^{-1}$ s <sup>-1</sup> )	7.9	0.61	8.3	8.7	9.6
toluene TOF ( $\times 10^{-3} \text{ mol mol}_{CO}^{-1} \text{ s}^{-1}$ )	$3.8 \pm 0.8$	$2.1 \pm 0.4$	$3.4 \pm 0.5$	$4.5 \pm 0.8$	$4.5 \pm 0.7$
metal-like site density $(\mu \text{mol } g_{\text{cat}}^{-1})$	21	3	25	19	21
BET surface area $(m^2 g_{cat}^{-1})$	83	76	n/a	81	96
toluene selectivity (%)	95	91	96	96	95
methylcyclohexanes <sup>c</sup> selectivity (%)	3	5	2	2	3
selectivity of others $^{d}(\%)$	2	4	2	2	2

<sup>*a*</sup>*m*-Cresol conversion, toluene synthesis rates, turnover frequencies of toluene synthesis, toluene selectivity, methylcyclohexane selectivity, and the selectivity of others from *m*-cresol HDO on fresh Mo<sub>2</sub>C, O<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C, H<sub>2</sub>O-1 kPa (333 K)-Mo<sub>2</sub>C, CO<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C, and O<sub>2</sub>-0.05 kPa (333 K)-Mo<sub>2</sub>C catalysts and their corresponding BET surface area after *m*-cresol HDO. Feed = *m*-cresol (1%)/He (10%)/H<sub>2</sub> (balance) (mol %) at ~107 kPa total pressure and at 423 K; total flow rate = 1.83 cm<sup>3</sup> s<sup>-1</sup>; 1 g<sub>cat</sub> of catalyst. <sup>*b*</sup>O<sub>2</sub>-0.05 kPa (333 K)-Mo<sub>2</sub>C treatment conditions: 0.083 cm<sup>3</sup> s<sup>-1</sup> 1% O<sub>2</sub>/He with 1.58 cm<sup>3</sup> s<sup>-1</sup> Ar. <sup>*c*</sup>Methylcyclohexanes is the sum of methylcyclohexane and methylcyclohexenes. <sup>*d*</sup>Others is the sum of unidentified C<sub>6</sub><sup>+</sup> hydrocarbons having boiling points higher than 500 K, as inferred from the retention time of the species in the GC chromatogram, which were quantified using m-cresol to give upper bounds of selectivity and rate.

activation, are required for *m*-cresol HDO on molybdenum carbide catalysts in a Langmuir–Hinshelwood-type surface reaction mechanism. These results are consistent with the previously reported reaction mechanism for anisole HDO on bulk Mo<sub>2</sub>C and W<sub>2</sub>C catalysts.<sup>27,35</sup> The apparent activation energy for toluene synthesis estimated from the Arrhenius plot (Figure 2b) between 400 K and 450 K is ~94 ± 2 kJ mol<sup>-1</sup> for *m*-cresol HDO on Mo<sub>2</sub>C.

3.1.2. In Situ CO Titration for Vapor-Phase Hydrodeoxygenation of m-Cresol. The number of operational sites during vapor-phase m-cresol HDO was determined by *in situ* CO titration and was subsequently used to assess the TOF of toluene synthesis. A co-feed of pure CO (0.4-1.1 kPa) with Ar as an internal tracer was introduced (the shaded areas in Figure 3a) after steady-state toluene synthesis rates were observed. Toluene synthesis rates from m-cresol HDO on Mo<sub>2</sub>C catalyst were inhibited in the presence of a CO co-feed and were recovered when the co-feed was removed, suggesting that CO is a reversible titrant for m-cresol HDO, similar to anisole HDO on Mo<sub>2</sub>C and W<sub>2</sub>C catalysts.<sup>25,27</sup> These results suggest that metal-like sites<sup>42,43</sup> are involved in Ar–OH bond cleavage.

The amount of CO adsorbed during the course of in situ titration for *m*-cresol HDO was obtained by integrating the area circumscribed by the Ar and CO signals in the mass spectrometric measurement  $( au_{CO})$  (see Figure 3b) and multiplying it by the corresponding CO flow rate. No CO<sub>2</sub> signal was observed in the presence of a CO co-feed, suggesting that the water-gas-shift reaction occurs at negligible rates under the reaction conditions investigated. Less than 1% of the adsorbed CO undergoes hydrogenation reaction to form CH<sub>4</sub>, as estimated by multiplying  $\tau_{\rm CO}$  by the observed methane synthesis rates (0.7–1.2  $\times$  10<sup>-9</sup> mol  ${\rm g_{cat}}^{-1}$  s<sup>-1</sup>) in the presence of a CO co-feed. The TOF of toluene synthesis was estimated by dividing the difference in toluene synthesis rates without and with a CO co-feed by the amount of CO adsorbed. The TOF of toluene synthesis from *m*-cresol HDO on Mo<sub>2</sub>C is  $\sim$ (3.6 ± 0.7)  $\times$  10<sup>-3</sup> mol mol<sub>CO</sub><sup>-1</sup> s<sup>-1</sup> at 423 K, which is of the same order of magnitude as the TOF of benzene synthesis from anisole HDO on Mo<sub>2</sub>C formulations at 423 K ( $\sim 1 \times 10^{-3}$  mol  $mol_{CO}^{-1} s^{-1}$ ,<sup>25,27</sup> suggesting that the same catalytic sites cleave Ar–OH and Ar-OCH<sub>3</sub> bonds.

**3.2.** Oxygenate Treatment Studies. 3.2.1.  $Mo_2C$  Modification by  $CO_2$ ,  $H_2O$ , and  $O_2$ . Edamoto et al.<sup>44</sup> showed from surface science studies that  $O_2$  can adsorb dissociatively on a Cor Mo-terminated  $Mo_2C(0001)$  surface at room temperature, as evidenced by XPS analysis in which the peaks on the C 1s and Mo 3d spectra of an  $O_2$ -treated  $Mo_2C(0001)$  surface broadened and shifted to higher binding energies, compared to those measured on a  $Mo_2C(0001)$  surface without exposure to  $O_2$ . DFT calculations from Shi et al.<sup>45</sup> also showed that  $O_2$ adsorbs dissociatively and exothermically on low-index surfaces, including pure or oxygen-covered  $\beta$ -Mo<sub>2</sub>C(100) and  $\beta$ -Mo<sub>2</sub>C(011) surfaces with negative adsorption energies (approximately -3 eV at 0 K). Lee et al.<sup>25</sup> previously prepared an  $O_2$ -modified bulk  $\beta$ -Mo<sub>2</sub>C, using an approach similar to that reported by Ribeiro et al.<sup>46,47</sup> TPSR with H<sub>2</sub> on the  $O_2$ modified bulk  $\beta$ -Mo<sub>2</sub>C catalyst monitored by an online mass spectrometer showed that oxygen was left behind on the surface and was removed as H<sub>2</sub>O by H<sub>2</sub>.

Density functional theory (DFT) calculations in studying the mechanism for water–gas-shift on Mo- or C-terminated  $\beta$ -Mo<sub>2</sub>C(001) surfaces<sup>48</sup> and on a  $\beta$ -Mo<sub>2</sub>C(001) slab<sup>49</sup> suggest that H<sub>2</sub>O and CO<sub>2</sub> can dissociate on these surfaces. The reaction energies for O\* formation from  $H_2O_{(g)}$  ( $H_2O_{(g)} \rightarrow O^*$ +  $H_{2(\sigma)}$ ) on Mo- and C-terminated  $\beta$ -Mo<sub>2</sub>C(001) surfaces with 0.2-1.2 monolayers of oxygen coverage were found to be -1.5eV to -5.5 eV and -0.5 eV to -1.5 eV, respectively.<sup>48</sup> Porosoff et al.<sup>50</sup> have probed and established  $\overline{\text{CO}_2}$  dissociation on a model Mo<sub>2</sub>C surface prepared by carburizing an Mo(110) substrate, using ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and TPSR experiments monitored by mass spectrometry. A C 1s peak at 283.6 eV assigned to an oxycarbide (O-Mo-C) and an O 1s peak at 531.7 eV assigned to an oxygen bonded to carbon were observed on the model Mo<sub>2</sub>C surface both when exposed to 150 mTorr CO<sub>2</sub> and under CO<sub>2</sub> hydrogenation reaction conditions (150 mTorr CO<sub>2</sub> and 553 mTorr H<sub>2</sub> at 523 K),<sup>50</sup> suggesting that CO<sub>2</sub> is dissociated to O and CO on a  $Mo_2C/Mo(110)$  surface.

The amounts of oxygen deposited from oxygenate treatment (O/Mo<sub>bulk</sub> before HDO) on Mo<sub>2</sub>C samples at 333 K with 1 kPa of O<sub>2</sub>, H<sub>2</sub>O, and CO<sub>2</sub> were quantified using TPSR with H<sub>2</sub> at 773 K and are summarized in Table 1. The value of O/  $Mo_{bulk}$  before HDO is ~6 times higher on  $O_2\text{-modified}\ Mo_2C$  $(O/Mo_{bulk} = 0.23 \pm 0.02)$  than that on H<sub>2</sub>O  $(O/Mo_{bulk} = 0.038)$  $\pm$  0.010) and CO\_2-modified (O/Mo\_{bulk} = 0.035  $\pm$  0.010) samples, demonstrating that O2 has a stronger propensity to leave behind adsorbed oxygen on a fresh Mo<sub>2</sub>C. A temperature exotherm ( $\Delta T \approx 20$  K) was observed when 1 kPa of O<sub>2</sub> was introduced to the fresh Mo<sub>2</sub>C at 333 K; however, the temperature exotherm observed when introducing 1 kPa of  $H_2O$  or  $CO_2$  to the fresh  $Mo_2C$  at 333 K was only ~2 K. These experimental observations mirror the DFT studies reported by Liu and Rodriguez,<sup>48</sup> in which O<sub>2</sub> adsorption energies on Moterminated and C-terminated pure  $Mo_2C(001)$  surfaces (-8.15) eV and -5.4 eV) were found to be larger than those for H<sub>2</sub>O adsorption (-1.52 eV and -1.33 eV) and CO<sub>2</sub> adsorption (-0.88 eV and -0.27 eV) on the same surfaces. Thermodynamic calculations also show that the oxidation propensity of  $O_{2(g)}$  is stronger than that of  $H_2O_{(g)}$  for the formation of  $MoO_{2(s)}$  ( $\Delta G_{rxn, 600 \text{ K}} = -1301 \text{ kJ mol}^{-1}$  vs  $\Delta G_{rxn, 600 \text{ K}} = -17 \text{ kJ}$  mol<sup>-1</sup>) or  $MoO_{3(s)}$  ( $\Delta G_{rxn, 600 \text{ K}} = -1530 \text{ kJ mol}^{-1}$  vs  $\Delta G_{rxn, 600 \text{ K}} = 183 \text{ kJ mol}^{-1}$ ) from  $Mo_2C_{(s)}^{51,52}$ .

We confirmed that the majority of the oxygen added to the fresh Mo<sub>2</sub>C catalyst from the oxygenate treatment is accounted for from TPSR with H<sub>2</sub> at 773 K based on the observations that (i) an amount of residual oxygen (O/Mo<sub>bulk</sub>  $\approx$  0.07; Figure S1a

in the Supporting Information) is observed on a freshly synthesized Mo<sub>2</sub>C catalyst and it can only be removed at a temperature higher than 823 K (Figure S1a), and (ii) the values of O/Mo<sub>bulk</sub> before HDO quantified from TPSR with H<sub>2</sub> at 773 K are comparable to those quantified via TPSR with H<sub>2</sub> at 973 K (±10%) after subtracting the amount of residual oxygen (O/Mo<sub>bulk</sub>  $\approx$  0.07) in a freshly synthesized Mo<sub>2</sub>C catalyst (Table S1 in the Supporting Information). Therefore, TPSR with H<sub>2</sub> at 773 K is used to quantify the oxygen loadings from oxygenate modification or HDO reaction on Mo<sub>2</sub>C in this work.

3.2.2. m-Cresol HDO on  $CO_2$ -,  $H_2O$ -, or  $O_2$ -Modified  $Mo_2C$ . Vapor-phase *m*-cresol HDO at 423 K was performed on fresh  $Mo_2C$  and on  $Mo_2C$  samples treated with 1 kPa of  $O_2$ ,  $H_2O$ , and  $CO_2$  at 333 K to investigate the effects of oxygenate modification on the metal-like properties of  $Mo_2C$ . Toluene synthesis rates from *m*-cresol HDO at 423 K reported in this work (Table 1) are average values taken between 7.2–14.4 ks TOS, since the decrease in toluene synthesis rates observed in this regime is <5% on all the samples (Figure 4). Toluene



**Figure 4.** Toluene synthesis rates from *m*-cresol HDO over (•) fresh  $Mo_2C$ , ( $\triangle$ )  $H_2O-1$  kPa (333 K) $-Mo_2C$ , ( $\diamondsuit$ )  $CO_2-1$  kPa (333 K) $-Mo_2C$ , and ( $\Box$ )  $O_2-1$  kPa (333 K) $-Mo_2C$  catalysts. Feed = *m*-cresol (1%)/He (10%)/H<sub>2</sub> (balance) (mol %) at a total pressure of ~107 kPa and a temperature of 423 K; total flow rate = 1.83 cm<sup>3</sup> s<sup>-1</sup>; 1 g<sub>cat</sub> of catalyst.

synthesis rates from *m*-cresol HDO are similar on fresh Mo<sub>2</sub>C, and H<sub>2</sub>O and CO<sub>2</sub>-modified Mo<sub>2</sub>C catalysts ((8.3–9.6) × 10<sup>-8</sup> mol g<sub>cat</sub><sup>-1</sup> s<sup>-1</sup>, Table 1), suggesting that the surface environment of these catalysts is similar. However, the toluene synthesis rate on O<sub>2</sub>-modified Mo<sub>2</sub>C is an order of magnitude smaller ( $6.1 \times 10^{-9}$  mol g<sub>cat</sub><sup>-1</sup> s<sup>-1</sup>) than rates measured on fresh Mo<sub>2</sub>C, and H<sub>2</sub>O and CO<sub>2</sub>-modified Mo<sub>2</sub>C. The lower toluene synthesis rate on O<sub>2</sub>-modified Mo<sub>2</sub>C, compared to that on the fresh samples and H<sub>2</sub>O- and CO<sub>2</sub>-modified samples could possibly result from (i) a decrease in the surface area due to the large temperature exotherm ( $\Delta T \approx 20$  K) during 1 kPa O<sub>2</sub> treatment and/or (ii) a change in the number and/or the identity of the active sites as discussed below and in section 3.2.3.

Brunauer–Emmett–Teller (BET) surface area measurements were performed on the spent fresh Mo<sub>2</sub>C, O<sub>2</sub>–1 kPa (333 K)–Mo<sub>2</sub>C, and CO<sub>2</sub>–1 kPa (333 K)–Mo<sub>2</sub>C catalysts after *m*-cresol HDO, which were subsequently treated in 1% O<sub>2</sub>/He at ~5.8 cm<sup>3</sup> s<sup>-1</sup> for ~1 ks at RT to passivate Mo<sub>2</sub>C, which is pyrophoric. The BET surface area (Table 1) for the spent O<sub>2</sub>–1 kPa (333 K)–Mo<sub>2</sub>C catalyst (76 m<sup>2</sup> g<sub>cat</sub><sup>-1</sup>) is only ~20% lower than that for the spent fresh Mo<sub>2</sub>C catalyst (96 m<sup>2</sup>



**Figure 5.** Toluene synthesis rates vs time-on-stream (TOS) for *m*-cresol HDO on (a) fresh Mo<sub>2</sub>C, (b) O<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C, (c) H<sub>2</sub>O-1 kPa (333 K)-Mo<sub>2</sub>C, and (d) CO<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C catalysts. Feed = *m*-cresol (1%)/Ar (10%)/H<sub>2</sub> (balance) (mol %) at a total pressure of ~107 kPa and a temperature of 423 K; total flow rate = 1.83 cm<sup>3</sup> s<sup>-1</sup>; 1 g<sub>cat</sub> of catalyst. CO co-feed: CO (0.5%-0.93%)/*m*-cresol (1%)/He (10%)/H<sub>2</sub> (balance) (mol %) at a total pressure of ~107 kPa and a temperature of 423 K; total flow rate = 1.83 cm<sup>3</sup> s<sup>-1</sup> (CO pressure for panel (b) is 0.05-0.07 kPa).

 $g_{cat}^{-1}$ ), which cannot account for the observed 10-fold decrease in toluene synthesis rate on O<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C, compared to that on the fresh Mo<sub>2</sub>C catalyst. Therefore, the change in surface area is not the major cause for the decrease in toluene synthesis rates on the O<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C catalyst.

Oxygen uptake on the catalyst after m-cresol HDO was quantified subsequently by TPSR with  $H_{2}$ , and the values of O/ Mo<sub>bulk</sub> after HDO are reported in Table 1. Oxygen accumulation was observed on the fresh  $Mo_2C$  (O/Mo<sub>bulk</sub>  $\approx$  $0.05 \pm 0.01$ ) from *m*-cresol HDO at 423 K. A similar amount of oxygen accumulation (O/Mo<sub>bulk</sub>  $\approx$  0.045) from anisole HDO on a passivated Mo<sub>2</sub>C that was treated in H<sub>2</sub> at 723 K for 1 h prior to the reaction study at ambient pressure and 423 K was reported by Lee et al.,<sup>25</sup> using TPSR with  $H_2$ . The values of O/ Mo<sub>bulk</sub> after HDO on H<sub>2</sub>O-1 kPa (333 K)-Mo<sub>2</sub>C and CO<sub>2</sub>-1 kPa (333 K)–Mo<sub>2</sub>C catalysts are similar (Table 1, O/Mo<sub>bulk</sub>  $\approx$  $0.06 \pm 0.01$ ) but higher than the values of O/Mo<sub>bulk</sub> before HDO on the same catalysts (Table 1, O/Mo<sub>bulk</sub>  $\approx$  0.038 and 0.035), demonstrating that additional oxygen was deposited on these catalysts from *m*-cresol HDO at 423 K. The values of O/ Mo<sub>bulk</sub> after HDO and before HDO on O<sub>2</sub>-1 kPa (333 K)- $Mo_2C$  were found to be similar (O/Mo<sub>bulk</sub>  $\approx 0.23 \pm 0.02$ ), suggesting that the oxygen left behind from the treatment in 1 kPa of  $O_2$ , which is in excess of that deposited with 1 kPa of  $H_2O$  or  $CO_2$  at 333 K, or from HDO conditions with 1 kPa of m-cresol at 423 K, is not removed during HDO. These results also show that the value of O/Mo<sub>bulk</sub> after HDO correlates with m-cresol HDO rates on oxygenate-modified Mo<sub>2</sub>C catalysts as (i) toluene synthesis rates are the same on the fresh  $Mo_2C$ ,  $H_2O-1$  kPa (333 K)-Mo<sub>2</sub>C, and CO<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C catalysts-samples with comparable values of O/Mo<sub>bulk</sub> after

HDO (Table 1, O/Mo<sub>bulk</sub>  $\approx 0.06 \pm 0.01$ )—and (ii) toluene synthesis rate is ~10-fold lower on O<sub>2</sub>-1 kPa (333 K)–Mo<sub>2</sub>C (Table 1), and the value of O/Mo<sub>bulk</sub> after HDO (~0.23 ± 0.02) on this sample is four times higher than that on the other three samples.

3.2.3. The Roles of Adsorbed Oxygen on CO<sub>2</sub>-, H<sub>2</sub>O-, or O<sub>2</sub>-Modified Mo<sub>2</sub>C for m-Cresol HDO. In situ CO titration experiments were conducted to probe the identity and the density of active sites responsible for *m*-cresol HDO on fresh Mo<sub>2</sub>C and on Mo<sub>2</sub>C samples treated with 1 kPa of O<sub>2</sub>, H<sub>2</sub>O, and CO2 at 333 K. TOFs of toluene synthesis on fresh and H<sub>2</sub>O and CO<sub>2</sub>-modified Mo<sub>2</sub>C catalysts are  $\sim$ (3.4–4.5) × 10<sup>-3</sup> mol mol<sub>CO</sub><sup>-1</sup> s<sup>-1</sup> at 423 K (see Table 1, Figure 5, and Figure S3 in the Supporting Information) and are comparable to the TOF of toluene synthesis measured on a Mo<sub>2</sub>C formulation that had been passivated by 1% O<sub>2</sub>/He but pretreated in H<sub>2</sub> prior to reaction studies ( $\sim$ (3.6 ± 0.7) × 10<sup>-3</sup> mol mol<sub>CO</sub><sup>-1</sup> s<sup>-1</sup> at 423 K), as discussed in Section 3.1.2. The TOF of toluene synthesis on the O<sub>2</sub>-modified Mo<sub>2</sub>C ( $2.1 \times 10^{-3}$  mol mol<sub>CO</sub><sup>-1</sup> s<sup>-1</sup>) is ~2fold lower, compared to that on H2O- and CO2-modified samples, which results from (i) the lower toluene synthesis rate on  $O_2$ -1 kPa (333 K)-Mo<sub>2</sub>C (Table 1, 6.1 × 10<sup>-9</sup> mol g<sub>cat</sub><sup>-1</sup>  $s^{-1}$ ) and (ii) the narrow operating window for CO co-feed pressure (0.05-0.07 kPa) required to concurrently achieve an observable CO signal and a measurable CO residence time during in situ CO titration on the mass spectrometer (Figure S3b in the Supporting Information). Therefore, we conclude that, within our ability to measure experimentally, TOFs of toluene synthesis are similar across the fresh Mo<sub>2</sub>C, and O<sub>2</sub>-, H<sub>2</sub>O-, and CO<sub>2</sub>-modified Mo<sub>2</sub>C catalysts, demonstrating that the incorporation of oxygen in  $Mo_2C$  does not alter the identity of the metal-like sites for *m*-cresol HDO, similar to the

	$O_2 - 0.1 \text{ kPa} (333 \text{ K}) - \text{Mo}_2 \text{C}^b$	$O_2$ -0.25 kPa (333 K)- $Mo_2C^c$	$O_2 - 0.4 \text{ kPa} (333 \text{ K}) - \text{Mo}_2 \text{C}^d$	O <sub>2</sub> -1 kPa (333 K)-Mo <sub>2</sub> C
O/Mo <sub>bulk</sub> before HDO	$0.060 \pm 0.003$	$0.11 \pm 0.01$	$0.14 \pm 0.02$	$0.23 \pm 0.02$
O/Mo <sub>bulk</sub> after HDO	$0.061 \pm 0.010$	$0.10 \pm 0.01$	$0.13 \pm 0.02$	$0.23 \pm 0.02$
toluene synthesis rate $(\times 10^{-8} \text{ mol } g_{cat}^{-1} \text{ s}^{-1})$	6.7	3.0	0.8	0.6

Table 2.	O/Mo <sub>bulk</sub>	Ratio	before a	and aft	er <i>m</i> -Cre	sol HDC	and	Toluene	Synthesis	Rate	from	m-Creso	l HDO o	on $O_2$	Modified
Mo <sub>2</sub> C C	atalysts <sup>a</sup>														

<sup>*a*</sup>*m*-Cresol HDO conditions: Feed = *m*-cresol (1%)/Ar (10%)/H<sub>2</sub> (balance) (mol %) at a total pressure of ~107 kPa and a temperature of 423 K; total flow rate = 1.83 cm<sup>3</sup> s<sup>-1</sup>; 1 g<sub>cat</sub> of catalyst. <sup>*b*</sup>O<sub>2</sub>-0.1 kPa (333 K)-Mo<sub>2</sub>C: 0.167 cm<sup>3</sup> s<sup>-1</sup> 1% O<sub>2</sub>/He in 1.5 cm<sup>3</sup> s<sup>-1</sup> Ar. <sup>*c*</sup>O<sub>2</sub>-0.25 kPa (333 K)-Mo<sub>2</sub>C: 0.416 cm<sup>3</sup> s<sup>-1</sup> 1% O<sub>2</sub>/He in 1.25 cm<sup>3</sup> s<sup>-1</sup> Ar. <sup>*d*</sup>O<sub>2</sub>-0.4 kPa (333 K)-Mo<sub>2</sub>C: 0.67 cm<sup>3</sup> s<sup>-1</sup> 1% O<sub>2</sub>/He in 1 cm<sup>3</sup> s<sup>-1</sup> Ar.

observation reported for anisole HDO on an  $\mathrm{O_2}\text{-treated}\ \mathrm{Mo_2C}$  catalyst.  $^{25}$ 

The density of the metal-like sites responsible for *m*-cresol HDO was estimated by dividing the toluene synthesis rate by the TOF of toluene synthesis (Table 1). The metal-like site densities obtained from *in situ* CO titration for *m*-cresol HDO are similar on fresh Mo<sub>2</sub>C, and H<sub>2</sub>O- and CO<sub>2</sub>-modified Mo<sub>2</sub>C catalysts (~19–25  $\mu$ mol g<sub>cat</sub><sup>-1</sup>), and are ~7-fold lower on O<sub>2</sub>-modified Mo<sub>2</sub>C (~3  $\mu$ mol g<sub>cat</sub><sup>-1</sup>), which presumably results from the metal-like sites being poisoned by the additional amount of oxygen adsorbed (>0.06 ± 0.01 O/Mo<sub>bulk</sub> after HDO) on the O<sub>2</sub>–1 kPa (333 K)–Mo<sub>2</sub>C catalyst (Table 1), compared to that on fresh and CO<sub>2</sub>- and H<sub>2</sub>O-modified Mo<sub>2</sub>C.

Oxygen adsorbed in amounts exceeding  $O/Mo_{bulk} \approx 0.06 \pm$ 0.01 on  $O_2$ -1 kPa (333 K)-Mo<sub>2</sub>C was found to inhibit HDO rate by poisoning the metal-like sites as discussed above. The bulk structure of the spent and passivated fresh Mo<sub>2</sub>C and O<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C catalysts remained as  $\beta$ -Mo<sub>2</sub>C and no MoO<sub>2</sub> or MoO<sub>3</sub> peaks were observed in the XRD patterns of spent catalysts (Figure S2 in the Supporting Information), indicating that the decrease in HDO rate did not result from bulk oxidation of Mo<sub>2</sub>C. The percentage of surface Mo in Mo<sup>5+</sup> and/or Mo<sup>6+</sup> (231.5 eV) states measured from XPS on the spent and passivated O<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C (26.7%) was found to be higher than that on the spent and passivated fresh  $Mo_2C$  (15.5%) (Table S2 in the Supporting Information), suggesting that (i) the decrease in the number of metal-like sites on O<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C, compared to that on fresh Mo<sub>2</sub>C (Table 1), could result from the surface Mo being oxidized to higher oxidation states, and (ii) the higher amount of oxygen deposited from 1 kPa of O<sub>2</sub> correlates with a higher fraction of surface Mo being in the Mo<sup>5+</sup> and Mo<sup>6+</sup> oxidation states.

An O<sub>2</sub>-0.05 kPa (333 K)-Mo<sub>2</sub>C catalyst (O/Mo<sub>bulk</sub> before HDO  $\approx 0.03$ ) was prepared to investigate the effect of oxygen source on adsorbed oxygen as H<sub>2</sub>O-1 kPa (333 K)-Mo<sub>2</sub>C and CO<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C catalysts have similar values of O/ Mo<sub>bulk</sub> before HDO (~0.038 and ~0.035, respectively; see Table 1) and exhibit similar toluene synthesis rates, TOF of toluene synthesis, and O/Mo<sub>bulk</sub> after HDO (Table 1). Toluene synthesis rates  $(7.9 \times 10^{-8} \text{ mol } g_{cat}^{-1} \text{ s}^{-1})$  and TOF of toluene synthesis (3.8  $\pm$  0.8  $\times$  10<sup>-3</sup> mol mol<sub>CO</sub><sup>-1</sup> s<sup>-1</sup>) from *m*-cresol HDO at 423 K and the value of O/Mo<sub>bulk</sub> after HDO (0.054  $\pm$ 0.005) on  $O_2$ -0.05 kPa (333 K)-Mo<sub>2</sub>C catalyst were found to be similar to that measured on  $H_2O-1$  kPa (333 K)-Mo<sub>2</sub>C, CO<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C, and fresh Mo<sub>2</sub>C catalysts (Table 1), clearly demonstrating that the effect of adsorbed oxygen on Mo<sub>2</sub>C is independent of the oxygen source under the reaction conditions investigated.53

Schaidle et al.<sup>1</sup> reported the existence of surface acidity on a  $Mo_2C$  pretreated in  $H_2$  from XPS and  $NH_3$ -TPD studies.

Ribeiro et al.,<sup>28</sup> Iglesia et al.,<sup>29</sup> and Boudart and co-workers<sup>30</sup> showed that the bifunctionality of tungsten carbide formulations can be adjusted by varying the oxygen loadings on O2modified catalysts prior to reaction studies, and Sullivan et al.<sup>26</sup> reported that the catalytic function of Mo<sub>2</sub>C can be adjusted to be primarily Brønsted acidic when O<sub>2</sub> is co-fed to the system during IPA dehydration in the absence of H<sub>2</sub>. Approximately 2% selectivity for unidentified  $C_6^+$  hydrocarbons (denoted as "others" in Table 1 and Table S3 in the Supporting Information), which have boiling points of >500 K, as inferred from the retention time of the species in the GC chromatogram, was observed on the fresh Mo<sub>2</sub>C, H<sub>2</sub>O-1 kPa (333 K)-Mo<sub>2</sub>C, CO<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C, and O<sub>2</sub>-0.05 kPa (333 K)–Mo<sub>2</sub>C catalysts. The formation of unidentified  $C_6^+$ hydrocarbons during m-cresol HDO mirrors the observation by Lee et al.<sup>11</sup> for the formation of  $C_{10}^{+}$  products (~30% selectivity) in furfural HDO on Mo<sub>2</sub>C formulations at 423 K, presumably because of the presence of acid sites on molybdenum carbides.<sup>1</sup> A higher selectivity for the unidentified  $C_6^+$  hydrocarbons (4%, Table 1) and a lower toluene selectivity (~91%, Table 1) are observed on the 1 kPa  $O_2$ -modified Mo<sub>2</sub>C, compared to the other four samples. However, the synthesis rates per gram of catalyst of both the unidentified C<sub>6</sub><sup>+</sup> hydrocarbons and toluene on  $O_2-1$  kPa (333 K)-Mo<sub>2</sub>C are ~6-fold and ~10-fold lower, compared to that on the other four catalysts, respectively (Table S3 and Table 1). These results suggest that the formation of the unidentified  $C_6^+$ hydrocarbons in m-cresol HDO cannot be selectively adjusted by the oxygen loading on Mo<sub>2</sub>C and suggest that bifunctionality, metal and acid, is likely required for the formation of the unidentified  $C_6^+$  hydrocarbons.

3.2.4. Changing O/Mo<sub>bulk</sub> Ratios and HDO Rates by Varying Oxygenate Treatment Conditions. Oxygen treatment pressures varied between 0.1 and 1 kPa were used to investigate the consequences of oxygen loadings between  $O/Mo_{bulk} = 0.06$ and  $O/Mo_{hulk} = 0.23$  on toluene synthesis rates from *m*-cresol HDO on molybdenum carbides. A 2-fold increase in the value of O/Mo<sub>bulk</sub> after HDO (from ~0.06 to 0.13) results in an 8fold decrease in the toluene rate (from ~6.7 × 10<sup>-8</sup> mol  $g_{cat}^{-1}$  s<sup>-1</sup> to 8.2 × 10<sup>-9</sup> mol  $g_{cat}^{-1}$  s<sup>-1</sup>) (Table 2). The drop in toluene rate decreases as the value of O/Mo<sub>bulk</sub> after HDO increased from  $\sim 0.13$  to  $\sim 0.23$ , in which the toluene synthesis rate on  $O_2$ -1 kPa (333 K)-Mo<sub>2</sub>C (O/Mo<sub>bulk</sub> after HDO  $\approx$  0.23) is ~70% of that on  $O_2$ -0.4 kPa (333 K)-Mo<sub>2</sub>C (O/Mo<sub>bulk</sub> after HDO  $\approx$  0.13) (Table 2). These results suggest that (i) the adsorbed oxygen does not poison the metal-like sites selectively—similar to what has been reported by Shi et al.,<sup>31</sup> using computational calculations that O2 adsorption can occur preferentially on pure Mo<sub>2</sub>C surfaces, as inferred from the reaction energy of surface oxidation by  $O_2$  at 0 K on  $Mo_2C(101)$  being ~2 eV more negative than that on

 $Mo_2C(011)$ —and/or (ii) adsorbed oxygen from  $O_2$  can be incorporated into the bulk structure of  $Mo_2C$  at higher values of the O/Mo<sub>bulk</sub> ratio.<sup>13,54</sup>

We showed that  $O_2$  can deposit ~0.03 O/Mo<sub>bulk</sub> (Table 1) of oxygen on a fresh Mo<sub>2</sub>C at a treatment pressure of 0.05 kPa, whereas 1 kPa of H<sub>2</sub>O, CO<sub>2</sub>, and *m*-cresol is required to achieve the same value (Table 1). We increased H<sub>2</sub>O and CO<sub>2</sub> treatment pressures (5–6 kPa) and temperatures (333, 363, and 423 K) to investigate the amount of oxygen H<sub>2</sub>O and CO<sub>2</sub> can deposit under ambient pressure. The values of O/Mo<sub>bulk</sub> before HDO on H<sub>2</sub>O–5 kPa (423 K)–Mo<sub>2</sub>C, CO<sub>2</sub>–5 kPa (423 K)–Mo<sub>2</sub>C, CO<sub>2</sub>–6 kPa (363 K)–Mo<sub>2</sub>C, and CO<sub>2</sub>–6 kPa (333 K)–Mo<sub>2</sub>C catalysts were found to be similar (Table 3, O/

Table 3. O/Mo<sub>bulk</sub> before *m*-Cresol HDO on H<sub>2</sub>O-Modified and CO<sub>2</sub>-Modified Mo<sub>2</sub>C Catalysts

	$O/Mo_{bulk}$ before HDO
H <sub>2</sub> O-5 kPa (423 K)-Mo <sub>2</sub> C	$0.050 \pm 0.004$
CO <sub>2</sub> -5 kPa (423 K)-Mo <sub>2</sub> C	$0.046 \pm 0.005$
CO <sub>2</sub> -6 kPa (363 K)-Mo <sub>2</sub> C	$0.050 \pm 0.002$
CO <sub>2</sub> -6 kPa (333 K)-Mo <sub>2</sub> C	$0.053 \pm 0.003$
CO <sub>2</sub> -1 kPa (333 K)-Mo <sub>2</sub> C	$0.035 \pm 0.010$

 $Mo_{bulk} \approx 0.046-0.053$ ) and comparable to the amount of oxygen deposited from *m*-cresol HDO at 423 K (Table 1, ~0.05 ± 0.01 O/Mo<sub>bulk</sub>). These results demonstrate that oxygen adsorbed in amounts exceeding O/Mo<sub>bulk</sub>  $\approx 0.05 \pm 0.01$  can be achieved by varying the O<sub>2</sub> treatment pressure at a treatment temperature of 333 K; however, oxygenates such as CO<sub>2</sub>, H<sub>2</sub>O, and *m*-cresol can only deposit O/Mo<sub>bulk</sub>  $\approx 0.05 \pm 0.01$ , even at a higher treatment pressure and temperature (~6 kPa and 423 K, respectively).

## 4. CONCLUSIONS

Kinetic and in situ chemical titration studies on vapor-phase mcresol hydrodeoxygenation (HDO) showed that two distinct sites-one of them having metal-like site characteristics-are involved in toluene synthesis. m-Cresol HDO was used as a probe reaction to study the effect of oxygenate modification on the metal-like function of Mo<sub>2</sub>C. The amount of adsorbed oxygen (O/Mo<sub>bulk</sub>) on O<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C, H<sub>2</sub>O-1 kPa (333 K)-Mo<sub>2</sub>C, and CO<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C catalysts, prepared by pretreating fresh Mo<sub>2</sub>C catalysts in 1 kPa of O<sub>2</sub>, CO2, and H2O at 333 K, was quantified using temperatureprogrammed surface reaction with  $H_2$  (TPSR). The value of O/  $Mo_{bulk}$  before HDO on  $O_2-1$  kPa (333 K)- $Mo_2C$  (0.23 ± 0.02) is ~6 times higher than that on  $H_2O-1$  kPa (333 K)-Mo<sub>2</sub>C and CO<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C (O/Mo<sub>bulk</sub> before HDO  $\approx$  0.036), demonstrating that molecular oxygen has a higher propensity to deposit oxygen on a fresh Mo<sub>2</sub>C sample. The value of O/Mo<sub>bulk</sub> after HDO was found to correlate with toluene synthesis rates, suggesting that the relevant surface environment for catalysis is that measured under reaction conditions. A 10-fold decrease in toluene synthesis rates was observed on O<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C, compared to that on fresh Mo<sub>2</sub>C,  $H_2O-1$  kPa (333 K)-Mo<sub>2</sub>C, and CO<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C catalysts; however, turnover frequencies (TOFs) of toluene synthesis measured from in situ CO titration on these samples are similar (~(2.1-4.5) ×  $10^{-3}$  mol  $mol_{CO}^{-1}$  s<sup>-1</sup>), indicating that adsorbed oxygen poisons the metal-like sites responsible for m-cresol. The effect of adsorbed oxygen on toluene synthesis is independent of the source of oxygen, as inferred from *in situ* CO titration and *m*-cresol HDO reactions on  $O_2$ -0.05 kPa (333 K)-Mo<sub>2</sub>C, H<sub>2</sub>O-1 kPa (333 K)-Mo<sub>2</sub>C, and CO<sub>2</sub>-1 kPa (333 K)-Mo<sub>2</sub>C catalysts.

## ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b02762.

Additional results for TPR, *in situ* CO titration, and *m*cresol HDO studies; XRD patterns and XPS data for Mo<sub>2</sub>C formulations (PDF)

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#### Notes

The authors declare no competing financial interest.

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