

Effects of Nonstoichiometry on the Ambient Oxidation of Cubic Mo_2C and Impact on CO Hydrogenation

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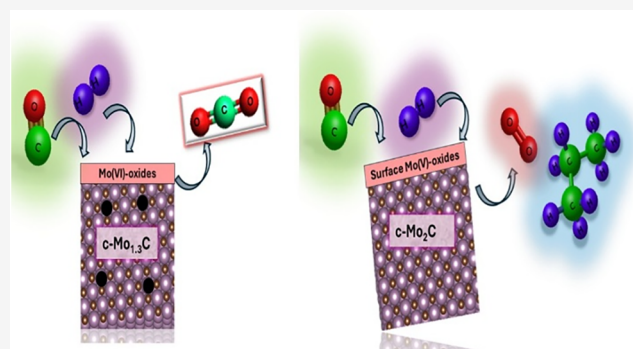


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Supporting Information

ABSTRACT: Hydrogenation of CO – Fischer–Tropsch synthesis (FTS), is of great interest for economic and environmental reasons to the synthetic fuel industry. A major challenge of prospective transition metal carbide catalysts, however, is the role that metal/carbon stoichiometry plays in catalyst surface oxidation and how this impacts catalyst activity and selectivity, which are hard to study with practical powdered catalysts. In this work, *in situ* X-ray Photoelectron Spectroscopy (XPS) and Constant Temperature Mass Spectrometry (CTMS) are used to investigate the response to oxidation of two cubic molybdenum carbide thin films synthesized by DC magnetron sputter deposition at two different temperatures: 300 and 700 K, giving rise to $\text{c-Mo}_{1.3}\text{C}$ and $\text{c-Mo}_2\text{C}$, respectively. For $\text{c-Mo}_2\text{C}$, a Mo(V) surface oxide is formed after ambient exposure and under reaction conditions (250 °C, $P_{\text{CO}+\text{H}_2} = 8 \times 10^{-4}$ Torr, $P_{\text{CO}}/P_{\text{H}_2} \sim 2$). $\text{c-Mo}_2\text{C}$ remains catalytically active yielding O_2 and C_3H_8 . In contrast, $\text{c-Mo}_{1.3}\text{C}$ forms a thicker surface oxide, including Mo(VI), upon ambient exposure, yielding CO_2 without a trace of either O_2 or C_3H_8 under the same reaction conditions. After surface Mo(VI) oxides were removed from $\text{c-Mo}_{1.3}\text{C}$, O_2 and C_3H_8 are formed under reaction conditions in the presence of Mo(V) oxide. Thus, Mo vacancies in $\text{c-Mo}_{1.3}\text{C}$ are specifically implicated in the formation of Mo(VI)—a d^0 oxidation state—and thus the loss of FTS activity. In contrast, stoichiometric $\text{c-Mo}_2\text{C}$ is stabilized against oxidation to Mo(VI) both in ambient conditions and under the reaction conditions employed and is therefore a promising Earth-abundant FTS catalyst.



INTRODUCTION

Transition metal carbides (TMCs), while of long-standing interest for catalysis due to electronic structure characteristics resembling those of Pt group metals,^{1,2} are known to be subject to varying degrees of oxidation due to ambient exposure and/or reaction conditions.^{3,4} Additionally, the nonstoichiometry of TMCs, and the corresponding impact on reactivities in various catalytic processes, has been the subject of both theoretical and experimental studies.^{5–8} What is not well understood, however, is (a) the degree to which metal/carbon nonstoichiometry can impact surface oxidation and (b) the degree to which different oxidation states impact reactions of practical and/or fundamental interest.

Herein, we focus on molybdenum carbide (Mo_2C), of long-standing interest for reactions involving selective CO bond breaking,^{1,2,7} including CO hydrogenation.^{1,2,7–9} The latter, of course, is of considerable importance for the formation of alkanes as N-free and S-free synfuels—the Fischer–Tropsch synthesis (FTS). In this respect, Mo_2C may afford some advantages over current commercial Fe- or Co-based carbide

catalysts, where *operando* oxidation, carburization, and resulting deactivation are important issues.¹⁰

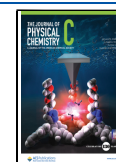
The possible effects of metal/carbide nonstoichiometry on TMC catalysts are of substantial practical importance. Industrial catalysts, of course, are typically powdered nanoparticles, for which metal/carbon nonstoichiometries are inherent, highly dependent on synthesis conditions, and are difficult to characterize in detail by traditional material-characterization methods.^{6–8} In particular, the use of *in situ* surface characterization methods, such as XPS, to accurately determine the surface structure and composition of nanoparticle carbide catalysts without extraneous contamination, is relatively rare in the literature, though of course, not unknown.⁷ This severely challenges the understanding of

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structure–function relationships in these materials known for their complex, dynamic surface structure.

Herein, *in situ* XPS and mass spectroscopy studies of catalytic reactions at constant temperature (constant temperature mass spectroscopy—CTMS) are employed to examine the oxidation of two different cubic molybdenum carbide (c-molybdenum carbide) thin films produced by magnetron sputter deposition—c-Mo₂C and c-Mo_{1.3}C. The stoichiometric film, c-Mo₂C, exhibits Mo(V) formation both upon ambient exposure and under a mild model condition for the FTS (S23 K, $P_{\text{CO+H}_2} = 8 \times 10^{-4}$ Torr) when starting from an Ar ion sputter-cleaned surface, which does not significantly impact FTS products detected by CTMS, including C₃H₈. In contrast, c-Mo_{1.3}C exhibits Mo(VI) formation upon ambient exposure, severely inhibiting alkane formation via FTS and significantly increasing the selectivity toward CO₂ formation. While these results were obtained on thin films under highly controlled model reaction conditions, the results corroborate previous studies of practical nanoparticle catalysts under industrially relevant FTS conditions^{8,11} and indicate, in this case, a bridging of the well-known “materials gap” in catalysis research.

METHODS

Thin Film Sputter Deposition

Molybdenum carbide films were sputter-deposited from a commercial Mo₂C sputter target (99.5% purity, 1.3 in. diameter, from Plasmaterials) and characterized by *in situ* Auger electron spectroscopy (AES) in an ultrahigh vacuum (UHV) system that permitted sample transport between deposition and analysis chambers under rigorously controlled vacuum conditions. This system has been described previously.¹² This is, to the best of our knowledge, the first time this method of the deposition of Mo₂C has been reported. Briefly, DC magnetron sputter deposition was carried out with a Meviac Minimak DC magnetron source with a source-to-substrate distance of 3 in. Base pressure in the sputter deposition chamber was 2.5×10^{-9} Torr. Sputter deposition was carried out at either 300 or 700 K, with the sample substrate heated by a ceramic-coated heater (Thermionics NW) designed for heating in reactive environments, and with temperature monitored by a type K thermocouple spotwelded in the vicinity of the sample. At both temperatures, sputter deposition was carried out in an atmosphere of 7.5 mTorr of Ar gas (Scott Specialty Gases, 99.9999% purity, CAS No. 7440-37-1) and at 25 W power. Samples were deposited on commercially available 1 × 1 cm fluorinated tin oxide (FTO) substrates. Before deposition, the substrates were sonicated in a sequence of soapy water, 0.1 M HCl, ethanol, acetone, and isopropyl alcohol baths and then air-dried.

In situ sample transfer between the deposition and AES analysis chambers (base pressure, 2.0×10^{-9} Torr) was carried out using a linear feedthrough. AES spectra were acquired with a single-pass cylindrical mirror analyzer with a concentric electron gun (EAS100, Staib, Inc.) and an electron beam energy of 3 keV. Intermittent sample transfer between deposition and analysis chambers after short deposition times permitted an estimate of the average film deposition rate via measured attenuation of the substrate Sn signal. These sputter deposition rates were extrapolated to longer sputtering times to obtain an estimate of the final film thickness. Estimated average deposition rates of 4 Å/min for both samples resulted in final estimated average film thicknesses of 240 and 220 Å for samples deposited at room temperature and at 700 K, respectively.

GIXRD, SEM/EDX, and AFM Studies

Grazing incidence X-ray Diffraction (GIXRD) studies were carried out using a Rigaku SmartLab SE Instrument employing Cu-K α radiation ($\lambda = 1.54059$ Å), with a scan speed of 2° per minute, step size of 0.01°, and scan range 20 to 80°. Information on film

morphology and bulk composition was obtained by SEM/EDX measurements (JEOL JSM-IT200 electron microscope) at a landing voltage of 15.0 kV and a working distance of 9.9 mm. AFM measurements (Q-Scope 250/400 Nomad) to determine surface roughness were carried out using a scan area of 40×40 μm with a scan rate of 1 Hz. The tapping mode cantilever tip was made of silicon with a spring constant of 48 N/m.

XPS

XPS and CTMS measurements were carried out in a system described previously in the literature,¹³ which is detailed briefly below and has been modified to carry out mass spectrometry measurements of species desorbed from the sample surface at constant temperature (CTMS), as shown schematically in Figure S1 (Supporting Information). Sample transfer between the XPS and CTMS chambers was accomplished *in situ* with a magnetically coupled feedthrough.

The UHV XPS chamber (base pressure 1×10^{-9} Torr) was equipped with a commercial dual anode (Mg K α /Al K α) non-monochromatic X-ray source (Physical Electronics), a 100 mm mean radius hemispherical analyzer (VSW) with a multichanneltron detector (PSP Vacuum), and an ion sputter gun (PHI Ion Gun 04-191) for sample cleaning. The XPS spectra were acquired with the analyzer in constant pass energy mode with a pass energy of 50 eV using Al-K α radiation. Measurements were carried out with the sample normal aligned with the analyzer axis (normal emission). XPS spectra were analyzed using commercial software, CASAXPS, version 2.3.24, and standard methods.¹⁴ Binding energy scales were calibrated by setting the C 1s binding energy of the adventitious carbon feature at 284.8 eV.¹⁵ Sample temperatures in the UHV chamber could be varied between room temperature and 1000 K via resistive heating. Sample temperatures were monitored by a Type K thermocouple spotwelded in proximity to the sample. Vacuum pressures in the chamber were monitored by a nude ion gauge calibrated to N₂.

C 1s, O 1s, and Mo 3d core-level spectra were deconvoluted into separate components using Gaussian–Lorentzian functions with a fwhm of 2.0 eV.⁴ Spin–orbit coupling was observed for the Mo 3d spectrum, and the doublet (3d_{5/2} and 3d_{3/2}) was separated by 3.2 eV.^{16,17} Spectral deconvolution was carried out with a constraint of 3:2 on the 5/2:3/2 peak intensities,^{16,17} and binding energies of the various oxidation states of Mo 3d were assigned as in the literature^{16–23}

CTMS Measurements

CTMS measurements were performed using a quadrupole mass spectrometer (Stanford Research Systems RGA300), which consists of an ionizer, a quadrupole mass filter, and a combined channeltron/Faraday cup detector that allows partial pressure measurements from 10^{-3} to 10^{-11} Torr. This was mounted in a UHV chamber with a base pressure of 1.8×10^{-9} Torr and a ceramic-coated heating stage (Thermionics NW) permitting heating in reactive environments. Each mass spectrum was acquired at a constant sample temperature. The mass spectrometer was covered by an insertion shroud (Figure S2, Supporting Information) to permit line-of-site analysis from the sample. CO and H₂ were introduced into the chamber through separate doser tubes, each controlled with separate manual leak valves. Both shrouded quadrupole mass analyzer and doser tubes were in proximity to the sample (~ 2 in., Figure S2, Supporting Information) to minimize gas–wall interactions.²⁴

The CTMS chamber (base pressure, 1×10^{-9} Torr, turbomolecularly pumped) was separated from the UHV XPS chamber by a manual gate valve, with sample transport between the two chambers accomplished with a linear magnetically coupled feedthrough, without exposure to non-UHV conditions (Figure S1, Supporting Information). Pressures in the CTMS chamber were monitored by a nude ion gauge calibrated for N₂ and by a millitorr gauge. The CO and H₂ gases employed were of electronic grade.

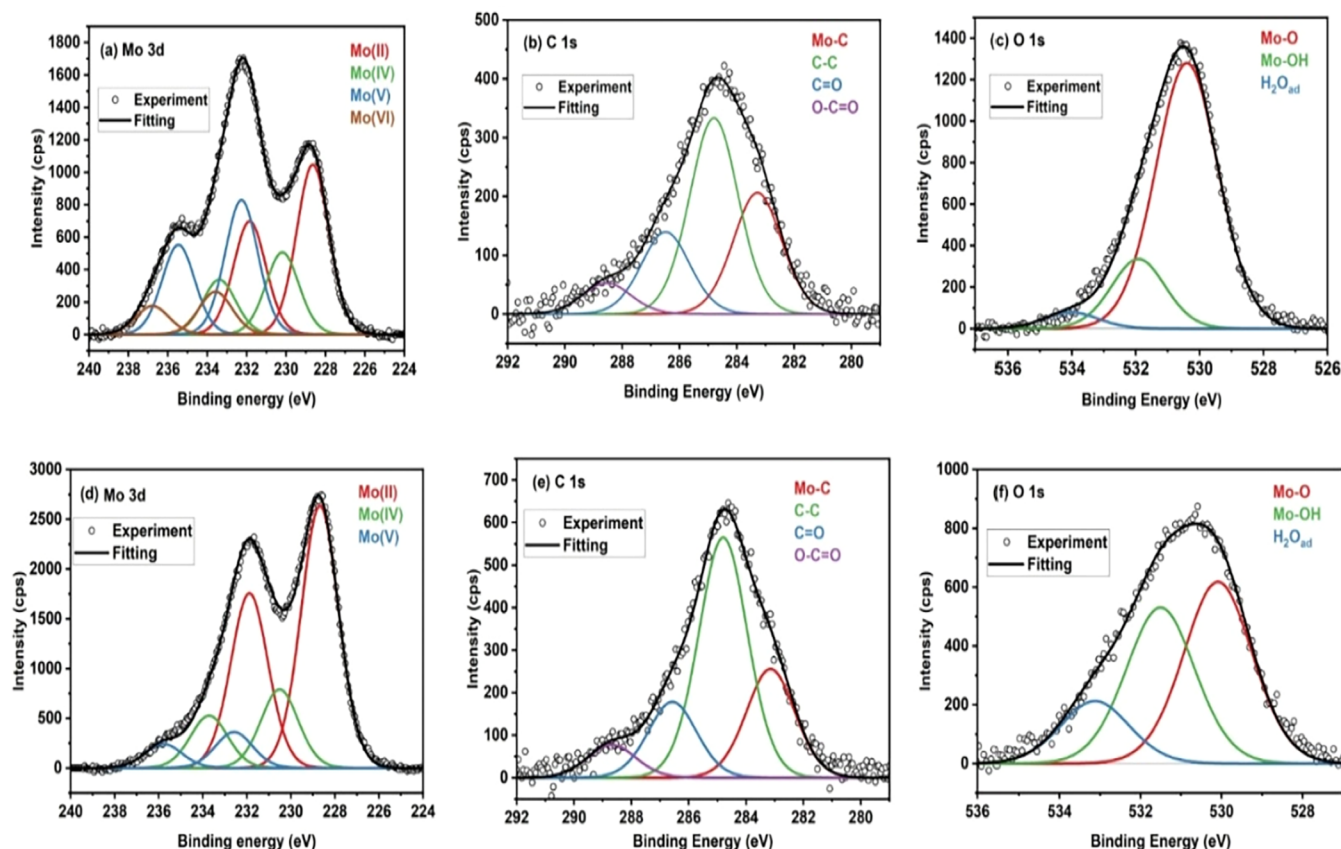


Figure 1. XPS spectra for (a–c) ambient-exposed c-Mo_{1.3}C, deposited at 300 K; (a) Mo 3d, (b) C 1s, and (c) O 1s; (d–f) corresponding spectra for ambient-exposed c-Mo₂C, deposited at 700 K.

RESULTS AND DISCUSSION

Characterization of Deposited Catalyst Films

In this section, we present detailed structural characterization of molybdenum carbide catalyst films deposited at 300 and 700 K with *in situ* AES, *ex situ* GIXRD, SEM/EDX, AFM, and *ex situ* XPS.

AES spectra acquired without exposure to ambient immediately after deposition for films deposited at 300 and 700 K are displayed in derivative mode in Figure S3a,b (Supporting Information), respectively. Mo/C atomic ratios were determined by standard methods¹⁴ as follows:

$$N_{\text{Mo}}/N_{\text{C}} = (I_{\text{Mo}}/I_{\text{C}})(\text{ASF}_{\text{C}}/\text{ASF}_{\text{Mo}}) \quad (1)$$

In (1), N_{Mo} and N_{C} refer, respectively, to the atomic concentrations of Mo and C, I_{Mo} and I_{C} are the respective peak-to-peak Auger intensities (in derivative mode), and ASF_{C} and ASF_{Mo} are the atomic sensitivity factors (Auger emission cross sections) at an excitation energy of 3 keV.²⁵ This method is validated by the fact that the C(KLL) spectra (Figure S3a,b, Supporting Information) exhibit the broad derivative line shape characteristic of metal carbides.²⁶ The Mo/C atomic ratios determined by eq 1 are 1.3 for the film deposited at room temperature and 1.9 for the film deposited at 700 K. The estimated uncertainties in the above ratios are 0.1 in each case, based on reported uncertainties in atomic sensitivity factors.^{14,25,27} These findings, as will be shown below, agree closely with Mo/carbide carbon ratios derived from a detailed analysis of the *ex situ* XPS spectra.

Corresponding GIXRD spectra are displayed in Figure S4a,b (Supporting Information). The X-ray diffraction patterns show that both samples have a face-centered cubic (fcc) crystal structure, with the lattice constant decreasing from 4.25 Å for the Mo-deficient film deposited at 300 K (Figure S4a, Supporting Information) to 4.18 Å for the stoichiometric film deposited at 700 K (Figure S4b, Supporting Information). This indicates that both films are of the fcc phase. Indexing of the patterns and matching to the JCPDS database are listed in Supporting Information (Tables S1 and S2) for c-Mo_{1.3}C (matches JCPDS 04-005-4902) and c-Mo_{1.9}C (matches JCPDS 00-015-0457), respectively. Other researchers have produced the same fcc phase for Mo carbides by various synthesis routes with similar lattice parameters.^{28–31} It should be noted, furthermore, that samples with XRD patterns as displayed in Figure S4a,b (Supporting Information) are frequently, but not always, referred to as the α phase.⁸ We therefore refer to the two samples as “cubic” or c-Mo_{1.3}C (deposited at 300 K) and stoichiometric c-Mo₂C to avoid confusion with denotations, e.g., α and β phases that are prevalent but inconsistently used in catalysis literature.^{16,32,33}

Thus, the data in Figure S4a,b (Supporting Information) indicate that both Mo carbide samples are of the same structure—c-Mo_{2-x}C, with $x \sim 0.7$ for the sample sputter-deposited at 300 K and $x \sim 0$ (stoichiometric) for deposition at 700 K. Of interest is the fact that, while the synthesis of c-Mo₂C phases by various methods, with either Mo or C vacancies have been reported in the literature, first-principles DFT calculations predict the formation of stoichiometric Mo₂C at temperatures above about 620 K.³⁴ The experimental

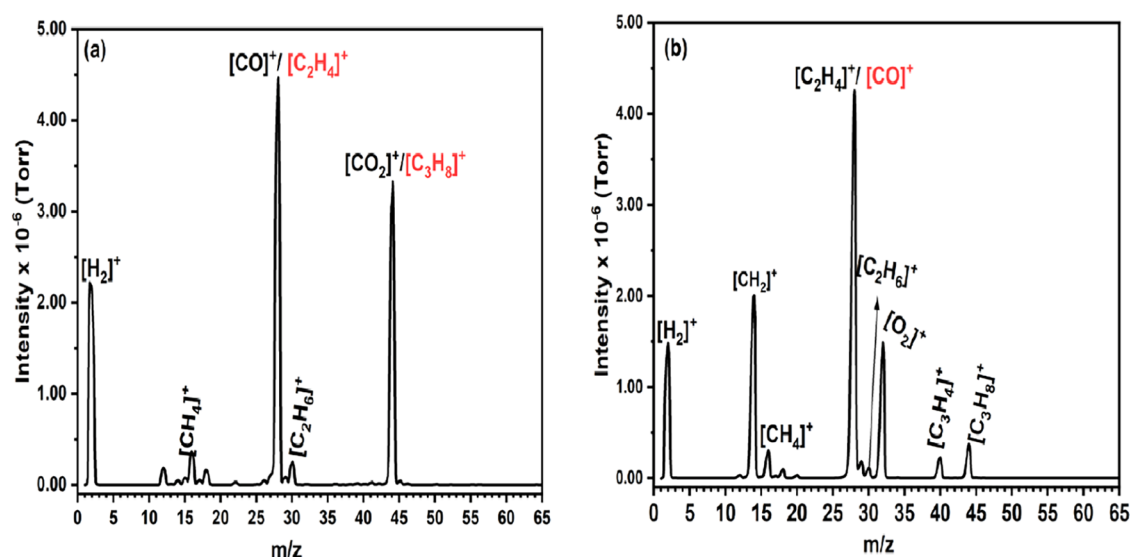


Figure 2. (a) Mass spectrum of ambient-exposed c-Mo_{1.3}C and (b) ambient-exposed c-Mo₂C during exposure to CO+H₂ at 523 K sample temperature, P_{CO}/P_{H₂} = 2, and total pressure = 8×10^{-4} Torr. For m/z 44 and m/z 28, primary peak assignments, based on the propane cracking pattern (Figure S8 Supporting Information), are given in black and secondary species in red. See text.

results reported here are thus in agreement with the theoretical predictions regarding the synthesis temperature required for the stoichiometric c-Mo₂C.

The crystallite sizes are 3 nm for the c-Mo_{1.3}C film and 8 nm for the c-Mo₂C film as determined by Williamson–Hall analysis of the GIXRD results.³⁵ This finding is consistent with the visually lower signal-to-noise ratio observed for the c-Mo_{1.3}C film (Figure S4a, Supporting Information) compared to that of the c-Mo₂C film (Figure S4b, Supporting Information). The much smaller crystallite sizes compared to film thickness indicate polycrystalline nanostructures, which is typical for cubic Mo carbides and has been observed by other researchers.^{31,33,36,37} Thus, the *in situ* AES (Figure S3, Supporting Information) and GIXRD spectra (Figure S4, Supporting Information) indicate that sputter deposition at 300 K yielded a c-Mo_{1.3}C film, whereas deposition at 700 K yielded a stoichiometric c-Mo₂C film.

SEM/EDX data for the c-Mo_{1.3}C and c-Mo₂C films are displayed in Figures S5 and S6 (Supporting Information), respectively. In both cases, the data indicate uniform spatial distribution of Mo and C, as well as of O. The latter can be attributed in part to the FTO substrate, although XPS data (see below) will indicate a minor contribution from MoO₂ distributed uniformly through both films. AFM measurements, shown in Figure S7 (Supporting Information), indicate RMS roughness values of 70 nm for c-Mo_{1.3}C and 50 nm for c-Mo₂C.

XPS spectra acquired after ~3 h of ambient exposure are displayed for c-Mo_{1.3}C in Figure 1a–c and for c-Mo₂C in Figure 1d–f. These XPS data show that both catalyst films are predominantly Mo carbide (formal Mo(II) oxidation state), with significant Mo 3d_{5/2} components at 228.1 eV (Mo(II))^{21–23} and corresponding carbidic C 1s features at 283.1 eV.^{17,20,22} Both ambient-exposed films also contain Mo 3d_{5/2} features corresponding to Mo(IV) and Mo(V) oxides at 230.2 and 232.3 eV, respectively,^{18–23} and O 1s features near 530.4 eV, corresponding to lattice O of the Mo oxides.^{38,39} Both films also exhibit significant O 1s intensities at 531.9 and 534.0 eV, attributed to adsorbed OH and H₂O, respectively.^{38,39} Additionally, the atomic ratios for Mo(II) to carbidic carbon

are 1.3 for the c-Mo_{1.3}C film (Figure 1a,c) and 2.0 for the c-Mo₂C film (Figure 1d,f)—in close agreement with the *in situ* AES spectra (Figure S3, Supporting Information). Notable differences between the two ambient-exposed films, however, are a much higher relative intensity ratio of Mo(V) to Mo(II) of ~0.8 and the presence of an observable Mo(VI) feature at 233.6 eV^{18–23} in the Mo 3d_{5/2} spectrum of ambient-exposed c-Mo_{1.3}C (Figure 1a) with Mo(VI)/Mo(II) intensity ratio ~0.3. In contrast, the Mo 3d spectrum of c-Mo₂C (Figure 1d) displays a much smaller relative Mo(V)/Mo(II) intensity ratio of ~0.2 and no observable evidence of Mo(VI). Thus, the data in Figure 1 show that the surface of the c-Mo_{1.3}C film is readily oxidized to Mo(VI) upon ambient exposure, whereas the c-Mo₂C film is more oxidation-resistant, being oxidized only to Mo(V) under the same conditions. As will be shown below, this oxidation resistance contributes significantly to the FTS activity of the ambiently exposed c-Mo₂C film.

Reactions of Ambient-Exposed Films with CO and H₂

In this section, the behaviors of ambient-exposed c-Mo_{1.3}C and c-Mo₂C catalyst films in FTS are compared under identical model reaction conditions (temperature of 523 K; CO and H₂ partial pressure ratios of 2:1 and total pressure of 8×10^{-4} Torr).

The steady-state mass spectrum for CO + H₂ flow reacting on ambient-exposed c-Mo_{1.3}C (Figure 2a) shows peaks corresponding to CH₄⁺ and/or atomic O⁺ (m/z 16), C₂H₆⁺ (m/z 30), H₂O⁺ (m/z 18), and preferential formation of a species with m/z 44. The assignment of this peak primarily to CO₂⁺ rather than to the propane parent ion (C₃H₈⁺; Figure 2a) is based on the cracking pattern of C₃H₈ (Figure S8, Supporting Information) at the same temperature and pressure in the CTMS chamber where this reaction was performed but with no catalyst surface. From the cracking pattern of C₃H₈ in Figure S8 (Supporting Information), the ratio of the intensities of the peak at m/z 28 to the peak at m/z 44 is ~16.9. In contrast, the data in Figure 2a indicate that the m/z 28: m/z 44 peak intensity ratio is substantially lower (~1.4). This situation is, of course, complicated by the fact that the m/z 28 feature corresponds to both principal features in the C₃H₈ cracking

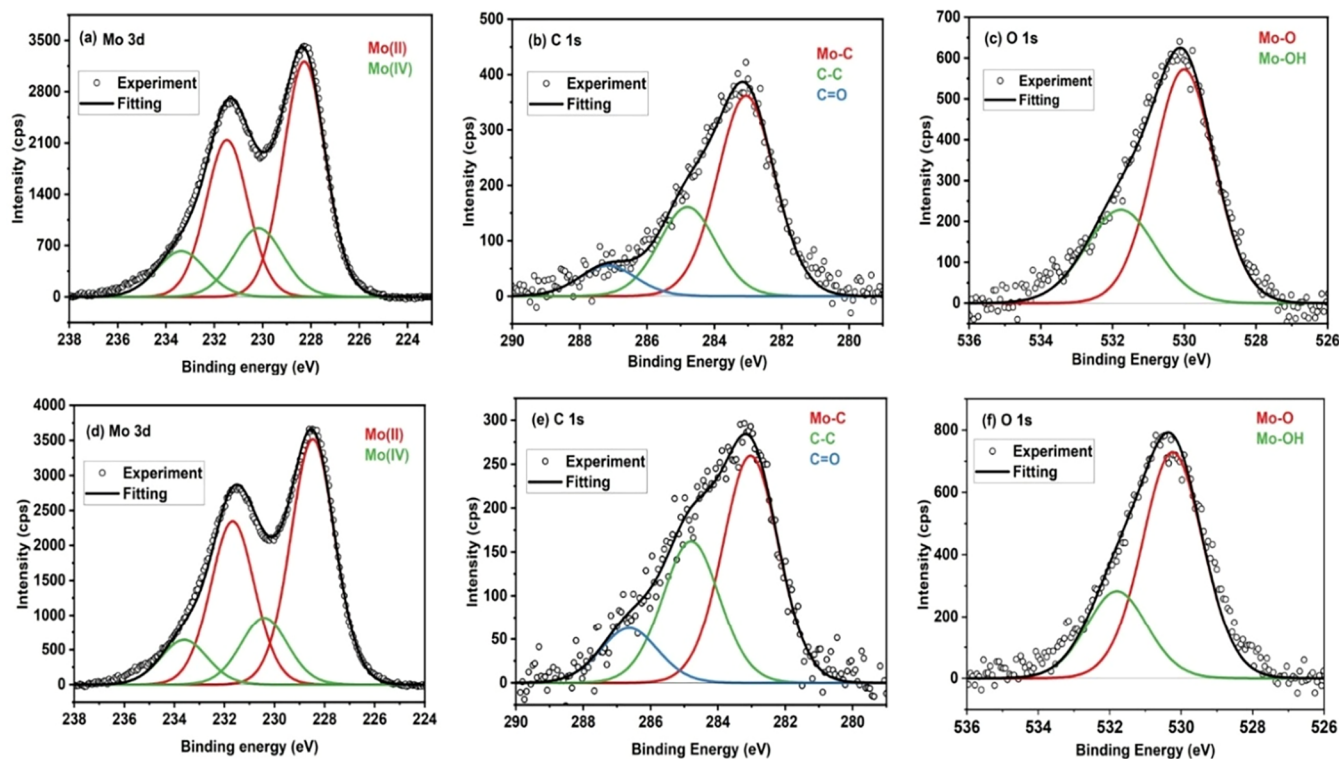


Figure 3. XPS spectra for sputter-cleaned $c\text{-Mo}_{1.3}\text{C}$; (a) Mo 3d, (b) C 1s, and (c) O 1s; (d–f) corresponding spectra for sputter-cleaned $c\text{-Mo}_2\text{C}$.

pattern: C_2H_4^+ (Figure S8, Supporting Information), as well as to CO^+ . However, the relatively high intensity of the m/z 44 feature in Figure 2a, if due predominantly or even substantially to C_3H_8 , would lead to a far higher m/z 28 intensity (by almost an order of magnitude), even without counting the contribution from CO, than is observed. Thus, the m/z 44 feature observed in Figure 2a for ambiently exposed $c\text{-Mo}_{1.3}\text{C}$ is assigned primarily to the parent ion of CO_2 and not to that of C_3H_8 , although the presence of the latter cannot be entirely excluded. In contrast, the data in Figure 2b, for ambient-exposed $c\text{-Mo}_2\text{C}$, display a relative m/z 28: m/z 44 intensity of ~ 18 , much closer to that of ~ 17 observed in the C_3H_8 cracking pattern (Figure S8, Supporting Information) and therefore indicative of significant C_3H_8 formation. Similarly, the m/z 28 feature (Figure 2b) can thus be attributed in large part to the C_2H_4^+ feature of the C_3H_8 cracking pattern.

This assignment is corroborated in part by smaller features in the CTMS of ambient-exposed $c\text{-Mo}_2\text{C}$ (Figure 2b) at m/z 14 and m/z 40—assignable on the basis of the C_3H_8 cracking pattern (Figure S8) to CH_2^+ and C_3H_4^+ , respectively—that are not observed in the CTMS for ambient-exposed $c\text{-Mo}_{1.3}\text{C}$ (Figure 2a). Thus, while the precise ratio among various species contributing to a specific m/z feature cannot be determined from CTMS features in Figure 2 alone, it is clear that the presence or absence of Mo(VI) surface oxide significantly alters the mass spectrum and thus FTS products. The mass spectrum observed in the presence of Mo(VI) ($c\text{-Mo}_{1.3}\text{C}$, Figure 2a) clearly has fewer peaks assignable to alkanes than that observed in the absence of Mo(VI) ($c\text{-Mo}_2\text{C}$, Figure 2b), which exhibits strong evidence of C_3H_8 formation as well as the formation of shorter alkanes.

Importantly, the formation of O_2 (m/z 32) is also observed for ambient-exposed $c\text{-Mo}_2\text{C}$ (Figure 2b), consistent with direct scission of the CO bond (but see below). No such

feature is observed, however, for ambient-exposed $c\text{-Mo}_{1.3}\text{C}$ (Figure 2a). Thus, reaction of $\text{CO} + \text{H}_2$ on the ambient-exposed $c\text{-Mo}_{1.3}\text{C}$ catalyst surface yields primarily CO_2 and some H_2O , with no evidence of direct CO bond scission (i.e., O_2 formation). In contrast, the corresponding reaction on the ambient-exposed $c\text{-Mo}_2\text{C}$ surface yields C_3H_8 and shorter alkanes, significant amounts of O_2 , and a smaller amount of H_2O .

The variation of the partial pressures of selected FTS products with reaction time at constant temperature (523 K), CO and H_2 partial pressures, is displayed in Figure S9a (Supporting Information) for ambient-exposed $c\text{-Mo}_{1.3}\text{C}$ and in Figure S9b (Supporting Information) for ambient-exposed $c\text{-Mo}_2\text{C}$. The data displayed show that, for both ambient-exposed surfaces, the partial pressures of the FTS products are relatively constant over the time measured. Therefore, the time dependence data in Figure S9 (Supporting Information) indicate that the FTS turnover occurs at a steady state, rather than being transient, on the catalyst films for the reaction conditions employed here. The data therefore indicate that ambient-exposed $c\text{-Mo}_2\text{C}$, with Mo(V) and lower oxides, effectively catalyzes CO bond scission and C–C coupling to complete the FTS under these reaction conditions. In contrast, ambient-exposed $c\text{-Mo}_{1.3}\text{C}$ (which has Mo(VI) surface oxides) exhibits much weaker activities in FTS than $c\text{-Mo}_2\text{C}$, yielding primarily CO_2 , without O_2 formation, or other evidence of significant CO bond scission.

In situ XPS spectra obtained for both surfaces after the reaction discussed above (Supporting Information, Figures S10 and S11) indicate that the exposures to such reaction conditions induced negligible changes in either Mo oxidation states or adventitious C surface coverage. Therefore, the data shown in Figures 1 and 2 and in S9 and S11 (Supporting Information) indicate that ambient-exposed $c\text{-Mo}_2\text{C}$, under

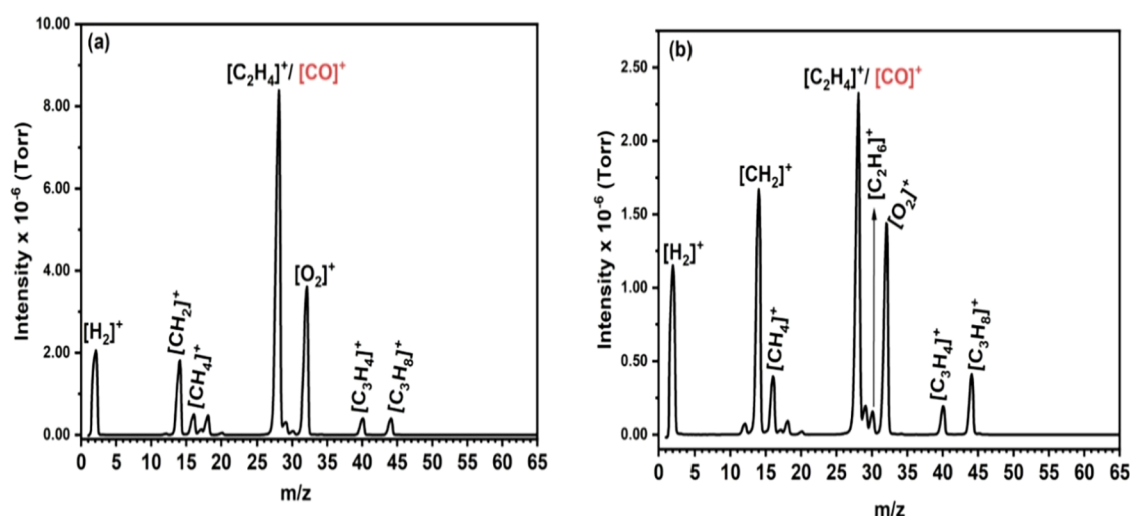


Figure 4. (a) Mass spectrum of sputter-cleaned c-Mo_{1.3}C and (b) sputter-cleaned c-Mo₂C during exposure to CO+H₂ at 523 K sample temperature, $P_{\text{CO}}/P_{\text{H}_2} = 2$, and total pressure = 10^{-4} Torr. For m/z 44 and m/z 28, primary peak assignments, based on the propane cracking pattern (Figure S8 Supporting Information), are given in black and secondary species in red. See text.

these reaction conditions, is a stable catalyst surface to produce C₃H₈ and possibly other hydrocarbons through FTS. FTS on most catalysts requires high pressure (>10 bar) to maintain high *C_xH_y coverage needed for C–C coupling, and *operando* deactivation due to carbon deposition and/or active-site oxidation is common.^{40,41} The above data demonstrate the ability of c-Mo₂C to catalyze CO hydrogenation to non-C₁ alkanes at mild practical temperatures (~250 °C) and moderate vacuum conditions employed in this surface science study. The data also indicate that c-Mo_{1.3}C behaves similarly but is not as resistant to oxidation as Mo(VI), which inhibits FTS. The thermal stability of c-Mo₂C, even at temperatures of >600 °C, has been demonstrated in the literature^{28,42} and therefore further indicates that c-Mo₂C has the potential to be a stable, selective FT catalyst. While the thermal stabilities of Mo-deficient c-Mo_{2-x}C phases have not, to our knowledge, been demonstrated, the greater oxidation resistance and demonstrated thermal stability of the stoichiometric phase emphasize both the promise of c-Mo₂C as an FT catalyst and the importance of obtaining appropriate stoichiometry during synthesis.

Reactions of Ar Ion Sputter-Cleaned Films with CO and H₂

After the CTMS studies described above, and subsequent *in situ* transfer back to the XPS chamber without ambient exposure, both catalyst films were exposed to Ar ions (5×10^{-5} Torr Ar, 3 keV energy) for a total of 1 h to remove surface oxides, carbon, and other contaminants induced by exposure to ambient or the reaction condition. XPS spectra acquired after Ar ion cleaning are shown in Figure 3a–c for c-Mo_{1.3}C and in Figure 3d–f for c-Mo₂C. The data in Figure 3 show that, after Ar ion-induced removal of surface oxides and much adventitious C, the XPS spectra of the two catalyst films are quite similar. The Mo 3d spectrum of sputter-cleaned c-Mo_{1.3}C (Figure 3a) shows, however, that there remains a significant amount of Mo(IV) oxide present, with a similar relative intensity vs the Mo(II) carbide feature as observed prior to sputter cleaning (Figure 1a). A similar observation is also made for the sputter-cleaned c-Mo₂C surface (Figure 3d) compared to the ambient-exposed surface (Figure 1d). This indicates that Mo(IV) oxide (formally MoO₂) is not confined to the surface

region of either film but instead is distributed throughout the surface/near-surface region for both films.

CTMS spectra during the FTS on both sputter-cleaned catalyst films, acquired under the same reaction conditions as the ambient-exposed films, are displayed in Figure 4. Corresponding variations of the partial pressures of selected FTS products with time are shown in Figure S12 (Supporting Information).

The data in Figure 4a demonstrate that the removal of surface oxides by Ar ion bombardment induces a significant change in the catalytic activity of the c-Mo_{1.3}C film. The intensity ratio of the m/z 28: m/z 44 peaks has increased from ~1.4 (Figure 2a) to ~16, much closer to that observed for the cracking pattern of C₃H₈, ~16.9 (Figure S8, Supporting Information), and similar to that observed for both ambient-exposed and sputter-cleaned c-Mo₂C, ~18. For this reason, the feature at m/z 28 in Figure 4a is now assigned primarily to the C₂H₄⁺ cracking product from C₃H₈, the most intense feature in the C₃H₈ cracking pattern (Figure S8, Supporting Information). This indicates significant C₃H₈ formation. A similar logic holds for the assignments of the m/z 28 and m/z 44 features for c-Mo₂C (Figure 4b). The data in Figure 4a also indicate the formation of O₂ at the sputter-cleaned c-Mo_{1.3}C surface, at a rate qualitatively comparable to that observed on the sputter-cleaned c-Mo₂C surface (Figure 4b), based on the relative intensity ratios between the O₂⁺ peak and hydrocarbon peaks. Thus, the data in Figure 3 indicate that the removal of ambient-induced surface oxides by Ar ion bombardment yields comparable XPS spectra for both c-Mo_{1.3}C and c-Mo₂C. The data in Figure 4 also indicate that both films are now active for FTS to form C₃H₈ although relative peak intensities vary slightly. The data in Figure S12 (Supporting Information) show that, for both films, the partial pressures of C₃H₈ and O₂ reaction products remain roughly constant during the exposure to the reaction condition, indicative of stable catalyst reactivity under these conditions. In summary, the data in Figures 1–4 indicate that c-Mo₂C is FTS-active both in the presence and absence of ambient-induced surface Mo(V) oxides, but no Mo(VI) is formed under any studied conditions. In contrast, c-Mo_{1.3}C is FTS-active only upon removal of the ambient-induced Mo(VI) surface oxide.

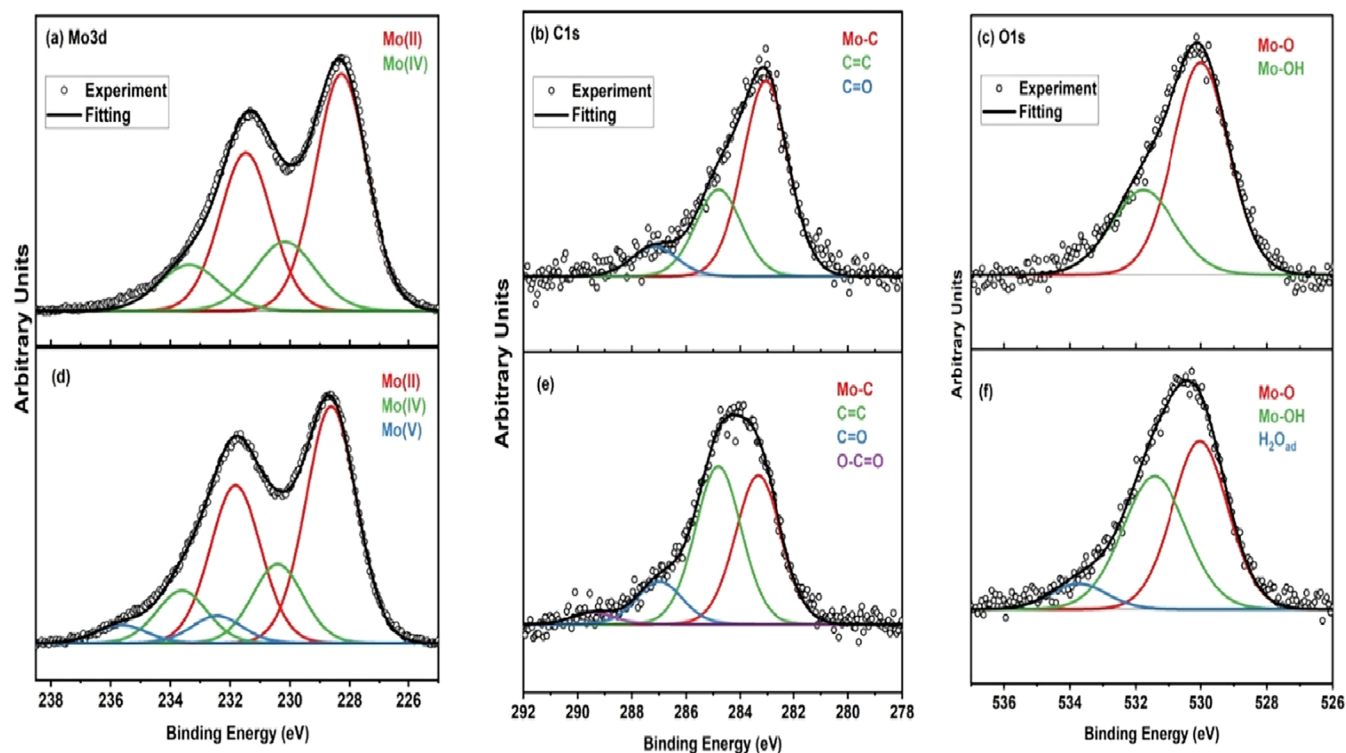


Figure 5. XPS spectra for sputter-cleaned c-Mo_{1.3}C: (a) Mo 3d, (b) C 1s, and (c) O 1s before reaction with CO and H₂ (same data as in Figure 3a–c); (d–f) corresponding spectra after reaction with CO and H₂.

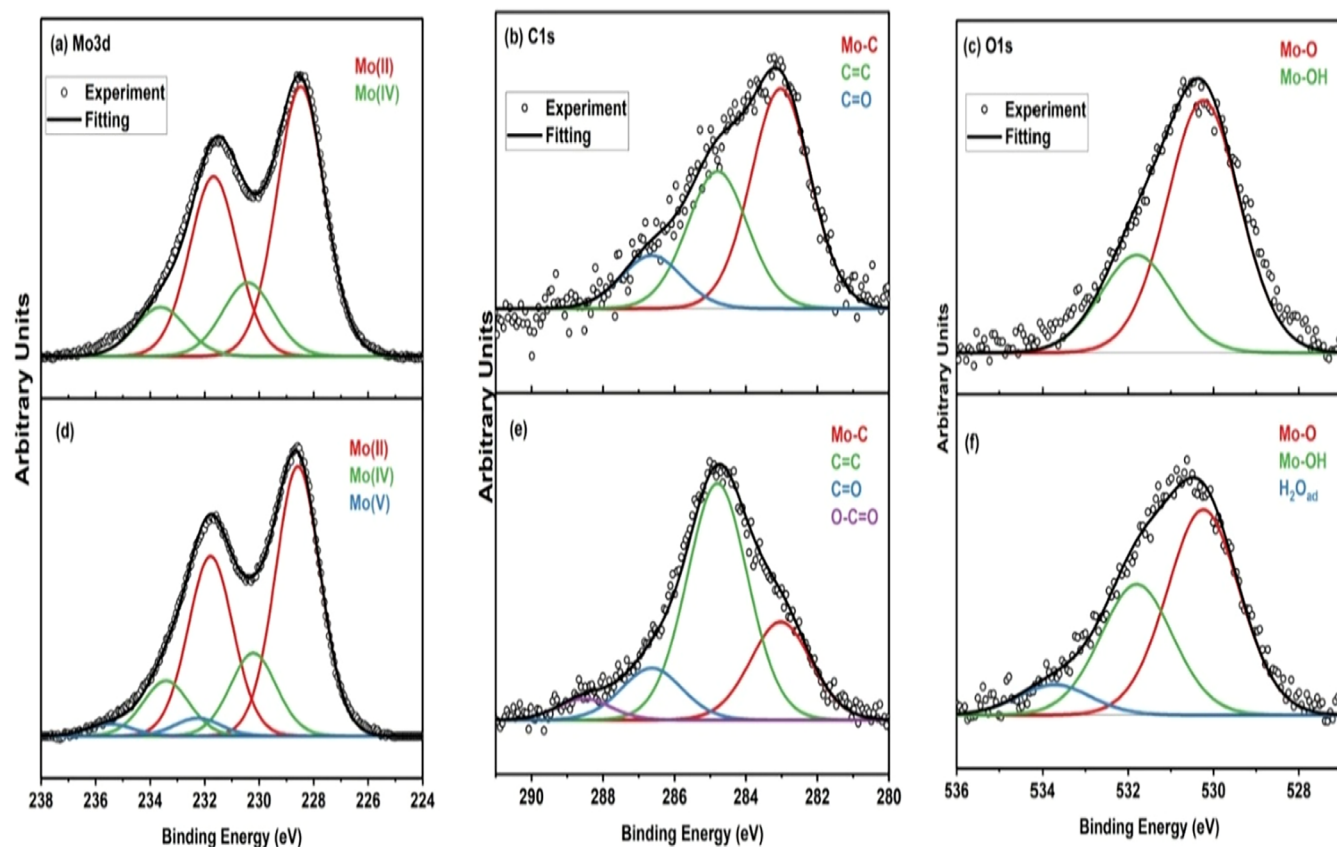


Figure 6. XPS spectra for sputter-cleaned c-Mo₂C: (a) Mo 3d, (b) C 1s, and (c) O 1s before reaction with CO and H₂ (same data as in Figure 3d–f); (d–f) corresponding spectra after reaction with CO and H₂.

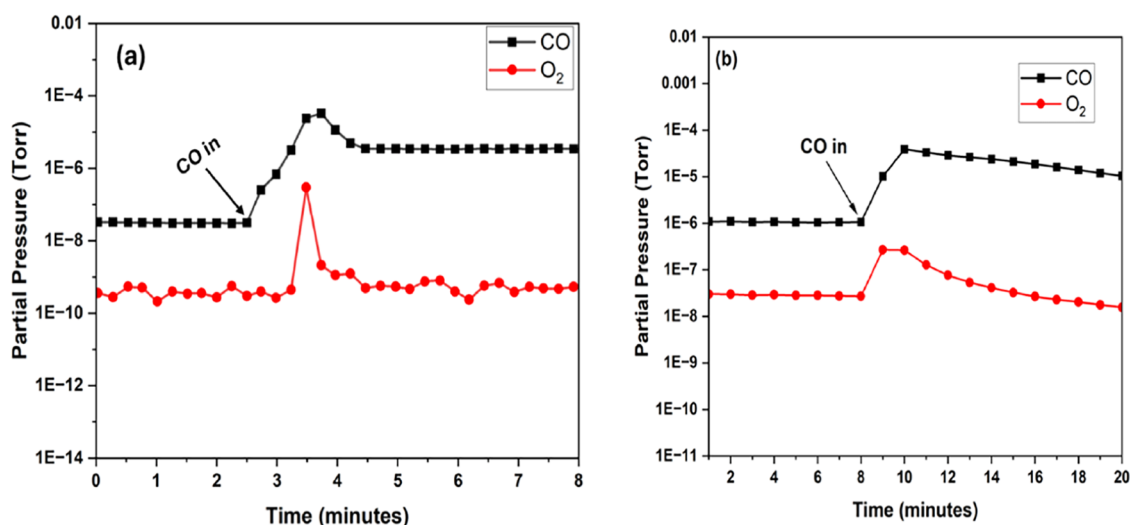


Figure 7. Time-dependent plots showing evidence of CO bond scission on (a) sputter-cleaned c-Mo₂C and (b) ambient-exposed c-Mo_{1.3}C during CO exposure (without H₂).

XPS spectra are shown in Figure 5 for sputter-cleaned c-Mo_{1.3}C acquired before (Figure 5a–c) and after (Figure 5d–f) the reaction at 523 K. Similar data are shown in Figure 6 for the c-Mo₂C film. (Note that the data in Figure 5a–c are the same as in Figure 3a–c, and the data in Figure 6a–c are the same as in Figure 3d–f but are reproduced for the convenience of the reader.)

For both c-Mo_{1.3}C and c-Mo₂C, changes in the Mo 3d spectra indicate that the above reaction conditions, while of mild temperature, pressure, and limited duration, have induced some reoxidation of the catalyst film surface to Mo(V). No evidence of Mo(VI) formation was observed for either film in the absence of ambient exposure. As expected, exposure of both Ar ion sputter-cleaned carbide films to the above-described FTS reaction conditions yields enhanced surface adventitious carbon formation (C 1s binding energy 284.8 eV; Figures 5e and 6e) as well as increased surface hydroxylation (O 1s ~ 532 eV; Figures 5f and 6f) due to reaction intermediates in the FTS formed by CO and H₂ dissociation.

The data in Figures 3 and 4 thus demonstrate that Ar ion sputtering of c-Mo_{1.3}C to remove surface oxides significantly alters the reactivity in CO hydrogenation at 523 K, resulting in a mass spectrum and product distribution similar to that exhibited by both the ambient-exposed and sputter-cleaned c-Mo₂C surfaces.

The presence of Mo(IV) in the XPS spectra of both films before and after sputter cleaning is consistent with this species being dispersed throughout the subsurface of both films, rather than concentrated in the surface region. For this reason, the differences in reactivities of the two ambient-exposed catalyst films cannot be ascribed to the presence of MoO₂. The data in Figures 5 and 6 indicate that the reactions described above induce some reoxidation of the surfaces of both sputter-cleaned c-Mo_{1.3}C and c-Mo₂C, with formation of Mo(V). In neither case, however, is Mo(VI) formation observed on sputter-cleaned film after FTS catalysis under the reaction conditions employed here.

The above data (Figures 1–6) thus demonstrate that the presence of Mo(VI) surface oxide is directly correlated with the loss of FTS activity (*non-C₁ alkane formation*). While the formation of Mo(V) is observed on both Ar-ion sputtered films during

the reaction, Mo(VI) does not form on either film surface under the reaction conditions. Only ambient exposure induces Mo(VI) formation and only on c-Mo_{1.3}C, resulting in a loss of FTS activity. This finding corroborates the results of Patterson et al. and Kountoupi et al. on powdered Mo_{1–x}C nanoparticles under industrially relevant FTS conditions.^{8,11}

Studies of CO Bond Scission

The hydrogenation of CO on metal carbides is known or proposed to occur by a number of different reaction mechanisms.^{11,43} Of interest, of course, is whether direct C≡O bond scission, in the absence of hydrogen, can occur under the reaction conditions used here. In order to examine this possibility on both highly FT-active and inactive surfaces, CTMS studies were carried out at 523 K, in the presence of 10^{−4} Torr CO only, on both sputter-cleaned c-Mo₂C and ambient-exposed (and hence oxidized) c-Mo_{1.3}C. In both cases (Figure 7), transient O₂ desorption was observed upon CO exposure, indicating direct C≡O bond scission without the assistance of H₂. In the case of sputter-cleaned c-Mo₂C (Figure 7a, red trace), the immediate rise in partial pressure of O₂ upon CO exposure is pronounced but is followed by rapid decay of the O₂ peak intensity with prolonged CO exposure time. Similar behavior is observed for air-exposed c-Mo_{1.3}C (Figure 7b, red trace) although the initial increase in the O₂ partial pressure is much less pronounced. The data in Figure 7 indicate that on c-Mo_xC surfaces, direct dissociation of CO that leads to desorption of O₂ can occur, even in the absence of H₂. The rapid decay of O₂ partial pressure with CO exposure time is consistent with the poisoning of active surface sites due to the rapid accumulation of surface C in the absence of H₂. This hypothesis is also consistent with the mass spectrometry data in Figures 2, 4 and 7, as well as Figures S9 and S12 (Supporting Information), indicating extended O₂ formation with time when H₂ is cofed with CO, on FTS-active c-Mo₂C surfaces (both ambient-exposed and sputter-cleaned), as well as on sputter-cleaned, FTS-active c-Mo_{1.3}C surfaces, as under this condition, surface C is constantly removed by reacting with *H to form alkanes. The above findings are also consistent with reported DFT calculations,⁴³ indicating that the dissociation of adsorbed CO species is favored at surface Mo-terminations but only at low CO surface occupancies.

Although we cannot determine the C–C coupling mechanism on c-Mo_xC films with confidence, the fact that significant amounts of O₂ are formed from CO dissociation, and that no alcohol-indicating MS fragments are present (Figure 2b), implies that *CH_x–*CH_x coupling is the dominating coupling pathway, i.e., CO dissociates prior to C–C coupling. This is intuitive as the vacuum-pressure reaction operates at low surface coverages and thus C–C coupling rates, and Mo_xC materials are well-known for facile CO dissociation.⁴³

CONCLUSIONS

The data presented above demonstrate that DC magnetron sputter deposition from a commercial Mo₂C target onto an FTO substrate yields, at 700 K, a stoichiometric fcc Mo₂C film (“c-Mo₂C”), whereas at 300 K, a Mo-deficient fcc film; c-Mo_{1.3}C, with the phases identified by GIXRD (Figure S4, Supporting Information) and the Mo/C stoichiometries determined by *in situ* AES (Figure S3, Supporting Information) in close agreement with *ex situ* XPS (Figure 1). Importantly, the c-Mo₂C film exposed to ambient conditions exhibits less Mo(V) oxide than the c-Mo_{1.3}C sample and no Mo(VI) oxide (Figure 1). This results in quite different reactivities (Figure 2b), with the ambient-exposed c-Mo₂C film exhibiting relative amu 28/amu 44 mass spectrum intensities characteristic of C₃H₈ formation and O₂ formation indicative of direct C≡O bond scission without hydrogen interaction, as shown in Figure 7. In contrast, ambient-exposed c-Mo_{1.3}C exhibits no O₂ formation (Figure 2a) and an amu 28/amu 44 mass spectrum intensity ratio too low by an order of magnitude to indicate C₃H₈ formation. However, the removal of ambient-induced surface oxides from both films yields mass spectra that are very similar, with amu 28/amu 44 intensity ratios indicative of C₃H₈ formation, along with O₂ formation indicative of direct CO bond scission (Figures 3 and 4).

In situ XPS and CTMS data demonstrate that the presence of a Mo(VI) surface oxide significantly alters the catalytic reactivity of the c-Mo_{1.3}C surface in CO hydrogenation, shifting the selectivity from alkanes (FTS) + O₂ to significant CO₂ formation (Figure 2a). In contrast, both c-Mo₂C and c-Mo_{1.3}C films, in the absence of Mo(VI) oxide, produce similar mass spectra, indicating the formation of O₂, C₃H₈ (Figures 2b and 4), and shorter alkanes. Thus, the formation of Mo(VI) surface oxide—occurring only on the nonstoichiometric film—is directly connected with the suppression of FTS reactivity and enhancement of CO₂ formation.

Importantly, the above results corroborate and provide insight regarding previous findings for CO hydrogenation, under industrial conditions, on nonstoichiometric cubic Mo carbide nanoparticles.⁸ A comparison of the results on thin films presented here to those for nanoparticles published previously⁸ indicates that stoichiometric c-Mo₂C nanoparticles are potential FTS catalysts. Indeed, nonstoichiometric c-Mo carbide nanoparticles should also be active, provided that any ambient-induced surface Mo(VI) oxide can be removed.

An important issue remaining to be resolved, however, is the extent to which such catalytic and oxidation-resistant trends with Mo/C stoichiometry are exhibited by other forms of molybdenum carbide, such as β-Mo₂C. Studies of such thin films and the extent of their correspondence to the catalytic behaviors of β-phase Mo₂C nanoparticles are in progress in our laboratories.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.5c07904>.

Schematics of UHV system for *in situ* XPS and CTMS studies; additional AES and XRD data; additional SEM and AFM data; fragmentation pattern of C₃H₈ in the CTMS chamber; variation of reaction products with time during CTMS studies; additional XPS data; table of comparison for experimental XRD data and PDF cards (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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