ABSTRACT: Controlled C–O bond scission is an important step for upgrading glycerol, a major byproduct from the continuously increasing biodiesel production. Transition metal nitride catalysts have been identified as promising hydrodeoxygenation (HDO) catalysts, but fundamental understanding regarding the active sites of the catalysts and reaction mechanism remains unclear. This work demonstrates a fundamental surface science study of Mo2N and Cu/Mo2N for the selective HDO reaction of glycerol, using a combination of model surface experiments and first-principles calculations. Temperature-programmed desorption (TPD) experiments showed that clean Mo2N cleaved two or three C–O bonds of glycerol to produce allyl alcohol, propanal, and propylene. The addition of Cu to Mo2N changed the reaction pathway to one C–O bond scission to produce acetol. High-resolution electron energy loss spectroscopy (HREELS) results identified the surface intermediates, showing a facile C–H bond activation on Mo2N. Density functional theory (DFT) calculations revealed that the surface N on Mo2N interacted with the H atoms in glycerol and blocked some Mo sites to enable selective C–O bond scission. This work shows that Mo2N and Cu/Mo2N are active and selective for the controlled C–O bond scission of glycerol and in turn provides insights into the rational catalyst design for selective oxygen removal of relevant biomass-derived oxygenates.

KEYWORDS: Glycerol, Hydrodeoxygenation, Nitrides, TPD, HREELS, DFT

1. INTRODUCTION

The transition from a fossil fuel-based economy to a more sustainable one supported by various renewable energy technologies has attracted much research attention in recent years.1,2 Many different approaches for replacing fossil fuels have been developed, among which biodiesel production is especially promising because this process turns agricultural and animal wastes into a valuable fuel.3 During biodiesel production, glycerol is a major byproduct. The continuing growth of biodiesel production yields a large amount of relatively inexpensive glycerol,4 which has been identified as one of the top 12 biomass building blocks that can be converted into high-value chemicals and materials.5 Therefore, implementing technologies for upgrading glycerol can significantly benefit the overall process economics. The multiple –OH functional groups in glycerol allow for the conversion into a variety of value-added compounds. So far, many approaches for upgrading glycerol have been identified.6–9 Glycerol can be upgraded through enzymatic conversion,6,7 carboxylation,8,9 dehydration,10,11 etherification,12,13 hydrogenolysis/hydrodeoxygenation (HDO),14–16 reforming,17,18 and oxidation.19,20 HDO is a particularly interesting route among these pathways that yields a variety of valuable chemicals, such as propylene, allyl alcohol, propanal, and acetol. On the one hand, the selective scission of specific C–O bonds in glycerol, while preserving others, remains a key challenge for the highly functionalized glycerol molecule. On the other hand, the presence of multiple –OH groups within glycerol also makes it a suitable model compound for studying higher sugars. Previously, we have demonstrated Cu/Mo2C as a promising HDO catalyst that allows for controllable C–O bond scission of glycerol16 and 1,2- and 1,3-propanediol.21 By tuning the Cu coverage on Mo2C, selective cleavage of one, two, and three C–O bonds of glycerol can be achieved on the Cu site, Cu/Mo2C interface site, and Mo2C site of the catalytic surface, respectively.

Transition metal nitride catalysts, in particular Mo2N, have demonstrated excellent activity and selectivity for the removal of heteroatoms, such as N, O, and S.22–24 However, the active
sites and reaction mechanism for the Mo$_2$N-catalyzed HDO reaction of biomass-derived oxygenates are still unclear. In this work, we present the first fundamental surface science study on the selective HDO reaction of glycerol over Mo$_2$N and Cu-modified Mo$_2$N. A combination of model surface experiments and density functional theory (DFT) calculations was used in order to understand the detailed reaction mechanism and active sites. Temperature-programmed desorption (TPD) experiments revealed that Mo$_2$N could cleave two or three C−O bonds of glycerol, while Cu/Mo$_2$N cleaved one C−O bond, suggesting the feasibility of tuning the product selectivity with Cu modification. High-resolution electron energy loss spectroscopy (HREELS) measurements showed that C−H bond activation was more favorable on Mo$_2$N, while Mo$_2$C interacted more strongly with the O atoms in glycerol. DFT calculations revealed detailed binding configurations and energetics of the different glycerol C−O bond cleavage pathways. It is worth noting that Mo$_2$N alone could cleave two C−O bonds to form allyl alcohol and propanal, which was only achievable on the Cu/Mo$_2$C interface. Furthermore, the comparisons between Mo$_2$N and Mo$_2$C, as well as between Cu/Mo$_2$N and Cu/Mo$_2$C provide insights into the design of more efficient nitride- and carbide-based catalysts for controlling C−O bond scission reactions.

One advantage of transition metal nitrides over the carbide analogues is related to the correlation between experimental results and DFT modeling. During the synthesis of nitride catalysts, surface N can desorb in the form of N$_2$, thus avoiding the accumulation of large amount of N on the surface. This synthesis procedure yields a clean N-terminated surface, which allows one to realize the full potential of DFT calculations over model catalyst surfaces for guiding rational catalyst design. In contrast, during the synthesis of powder Mo$_2$C catalysts, carbon layers can accumulate on the Mo$_2$C surface, lowering the activity of the surface and inhibiting the direct correlation between experimental results and DFT calculations. Even though transition metal carbides and nitrides both show unique chemical and catalytic properties, fundamental surface science studies have been focused mainly on the former. The current work represents the first surface science study over transition metal nitride surfaces, Mo$_2$N and Cu/ Mo$_2$N, for the reaction pathways of organic molecules such as glycerol. These fundamental studies should provide insights into controlling the C−O, C−C, and C−H bond scission using nitride catalysts.

2. MATERIALS AND METHODS

2.1. Synthesis and Characterization of Mo$_2$N Thin Films

Mo$_2$N thin films were synthesized on 0.1 mm thick polycrystalline Mo (Alfa Aesar, 99.95%) foils cut into 1 cm × 2 cm rectangles. The cut foils were sonicated for 5 min in ethanol to remove surface oils, washed in deionized (DI) water, sonicated for 5 min in 1 M NaOH to remove surface oxides, and received a final wash in DI water prior to being loaded into a horizontal quartz tube furnace. Nitridation was conducted under a 150 cm$^3$/min flow of 100% ammonia, where the furnace temperature was ramped from 298 to 1123 K at a linear rate of 7 K/min and kept at 1123 K for 10 h. The sample was then gradually cooled under the same gas condition to room temperature. The furnace was purged with Ar, and nitride foils were removed.

The Mo$_2$N foils were characterized using both X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). An ultrahigh vacuum (UHV) chamber equipped with XPS was used to quantify the Mo/N ratios under a base pressure of 2 × 10$^{-9}$ Torr. XPS measurements were conducted using a PHI 5600 XPS equipped with a hemispherical analyzer and an Al X-ray source. XRD measurements were conducted using a Cu Kα X-ray source in a PANalytical XPERT3 Powder X-ray diffractometer that measured both symmetric and 3° glancing incidence (GI) scans.

2.2. UHV Model Surface Experiments

TPD and HREELS experiments were conducted in stainless-steel UHV chambers that have been previously described. The as-synthesized Mo$_2$N thin film was spot-welded to the chamber via two tantalum heating posts for resistive heating as well as cooling with liquid nitrogen. The surface was prepared in a similar manner as described in our previous work. To synthesize Cu-modified Mo$_2$N, the clean Mo$_2$N surface was exposed to a heated Cu source to facilitate the physical vapor deposition (PVD) process. The Cu coverage was controlled by the deposition time and current and verified by the Cu/ Mo atomic ratio from Auger electron spectroscopy (AES) measurements following the method developed by Cumpson et al. Upon the completion of surface preparation, the surface was cooled to 200 K and exposed to 5 Langmuir (L, 1 L = 10$^{-6}$ Torr·s) of H$_2$ and then 4 L of glycerol with the surface facing the directional dosing tube. The surface was then heated up at a linear rate of 3 K/s in front of the mass spectrometer that recorded the desorption of gas-phase products. In the HREELS experiments, the prepared surface was exposed to a desired amount of reactant and cooled to below 200 K before the first spectrum was taken. Subsequent spectra were recorded after heating the surface to specific temperatures and cooled to below 200 K. All gases (H$_2$, O$_2$, Ne) were used without further purification. The reactant (glycerol, 99.5%, Sigma-Aldrich) was purified by a series of freeze–pump–thaw cycles to the sample cylinder. The synthesis and experiment of the Mo$_2$C/Mo(110) surface used for comparison was described previously.

2.3. DFT Calculations

The deoxygenation mechanism of glycerol was examined on the γ-Mo$_2$N(111) surface using DFT calculations. All structural optimizations and energy calculations were performed with the Vienna ab initio simulation package (VASP 5.4). The calculation methodology relied on a generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof formalism (PBE) along with Grimme’s D3 dispersion correction. A cutoff energy of 500 eV was selected for the plane-wave basis. Following the procedure explained by Henson and co-workers, the structure of bulk fcc γ-Mo$_2$N was constructed by removing 50% of the nitrogen atoms from the perfect fcc structure in the 100/010 direction to obtain a ratio of Mo:N = 2:1. The optimized structure became tetragonal with cell parameters of 4.24 and 3.97 Å with the selected level of theory. These values are in good agreement with the experimental value of 4.16 Å from the X-ray diffraction and 4.19–4.23 Å from previous DFT calculations with different levels of theory. Experimentally, a nitridified Mo thin film was used due to the difficulty of manufacturing Mo$_2$N single crystals. The nitridized Mo thin film should contain a mixture of low-index surfaces, with the stoichiometry verified by XPS to be Mo$_2$N. Here, we chose the N-terminated Mo$_2$N(111) surface for the mechanistic study because the (111) surface is one of the major exposed surfaces of the Mo$_2$N catalysts and the N-terminated (111) surface has been reported to be thermodynamically more stable than the Mo-terminated (111) surface. The (2 × 2) surface unit cell with cell parameters of (11.98 Å × 9.95 Å × 22.17 Å) considered here consists of 7 atomic layers of Mo$_2$N and a 1 Å vacuum added in z-direction. In order to create a nonpolar slab, both sides of the slab were terminated by an N-layer. A Monkhorst-Pack (MP) 44 k-point mesh was used for all atoms were fully relaxed except for the bottom two atomic layers of Mo$_2$N during structural optimization. Dipole and quadrupole corrections to the energy were taken into account using a modified version of the Makov and Payne method and Harris–Foulke-type corrections were included for the forces. The climbing image-NEB and dimer methods were used to optimize all transition state (TS) structures. In addition, we examined the effect of DFT functional on the glycerol HDO reaction by reoptimizing all the intermediates and TS structures with the meta-GGA SCAN+rVV10 JACS Au pubs.acs.org/jacsau XXX, XXX, XXX-XXX

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functional, which has been shown to predict accurate geometries and energies of diversely bonded molecules and materials.50

3. RESULTS AND DISCUSSION

3.1. Characterization of Mo2N Thin Films

Symmetric and GI-XRD were used in combination to determine the nitride phase in the bulk and near the surface. The XRD pattern of the synthesized Mo2N thin film was compared to those of bcc Mo, hexagonal MoN, and fcc Mo2N from the Inorganic Crystal Structure Database (ICSD). In Figure S1a, the symmetric XRD reflections of bcc Mo (ICSD 52267) were more intense than reflections of hexagonal MoN (ICSD 245232) and fcc Mo2N (ICSD 172802). The presence and intensity of the parent metal diffraction peaks indicated that Mo, MoN, and Mo2N coexisted in the bulk phase. Surface-sensitive GI-XRD further informed the nitride phase near the surface region of the thin film. When the GI-XRD angle was fixed at 3 degrees, the relative intensity of Mo2N reflections increased with respect to those of parent bcc Mo. These results indicated that Mo2N was present on the foil surface as a thin film, consistent with the findings of past studies on transition metal carbide analogues.51,52 XPS was used to further characterize the Mo/N stoichiometry of the surface nitride phase (Figure S1b,c). An N:Mo ratio of ~1.9 was obtained on the basis of the curve fitting, which suggested the presence of Mo2N near the surface region. The detection depth of our XPS with an Al Kα source was at least 2 nm according to the inelastic mean free path53 of the kinetic energies of photoelectrons for the Mo(3d) peaks between 232.2 and 235.3 eV and N(1s) peak at 396.7 eV. This suggested that there should be more than 6 layers of Mo2N on

Figure 1. Comparison of temperature-programmed desorption spectra of (a) propylene (39 amu), (b) propanal (29 amu), (c) allyl alcohol (57 amu), and (d) water (18 amu) from H2 predosed Mo2N and Mo2C surfaces after exposing the surfaces to 4 L of glycerol.
the surface. Therefore, the influence of the Mo and MoN underneath should be negligible. Details about the estimation of the XPS detection depth can be found in the Supporting Information.

3.2. Reaction Pathways on Mo2N and Cu/Mo2N from TPD Experiments

In order to identify the unique properties of Mo2N, TPD experiments were performed to compare the reaction pathways of glycerol over the Mo2N and Mo2C surfaces. The preparation and experimentation of the Mo2C surface were described previously. In all TPD experiments, the surface was exposed to 5 L of H2O, followed by 4 L of glycerol. The results showed that both Mo2N and Mo2C could break all the C−O bonds in glycerol to form propylene. In addition, Mo2N could also break two C−O bonds of glycerol to produce propanal and allyl alcohol. Figure 1 compares the desorption of propylene, propanal, and allyl alcohol from Mo2N and Mo2C after exposing the surfaces to glycerol. From Figure 1a, it is apparent that propylene was produced on both surfaces. On Mo2C, the propylene peak had an onset temperature of around 300 K and a peak temperature of 389 K. On Mo2N, the propylene peak had an onset temperature at about 350 K and peak temperature at 480 K. This suggested that both surfaces were active for breaking all C−O bonds of glycerol. Figure 1b,c show the desorption of propanal and allyl alcohol from Mo2N and Mo2C. Although these HDO products were not detected from Mo2C, propanal desorption was observed from Mo2N, with a peak temperature of 480 K. Allyl alcohol was also formed over Mo2N, with a desorption peak temperature of 419 K. While Mo2C only catalyzed the scission of all three C−O bonds of glycerol to produce propylene, Mo2N was active for breaking two or three C−O bonds of glycerol to form allyl alcohol, propanal, and propylene. Figure 1d compares the desorption of water from Mo2N and Mo2C. Both surfaces showed a common peak temperature at 459 K. However, a long tail was also observed on Mo2C. It is likely that more O atoms were deposited on Mo2C from producing propylene after the scission of three C−O bonds of glycerol, while both two and three C−O bond scissions occurred on Mo2N. Overall, the average H2O desorption temperature was lower on Mo2N, suggesting a more facile O removal. Since the surface was held at 200 K when exposed to glycerol, the amount of molecularly adsorbed water from impurity in glycerol was negligible, as will be discussed in the HREELS results later.

In order to probe the effect of Cu addition on the reaction pathways, TPD experiments of the Mo2N surfaces with different Cu coverages were performed. From these experiments, two distinct sites were identified, the Mo2N site and the Cu site. The reaction pathways of glycerol on the Cu/Mo2N surfaces are summarized in Scheme 1. On the Mo2N site, glycerol underwent three C−O bond scissions to form propylene, or two C−O bond scissions to produce allyl alcohol and propanal. On the Cu site, glycerol only proceeded through one C−O bond scission to form acetol. Figure 2a–d show the different products observed on the Cu/Mo2N surfaces with different coverages of Cu. In Figure 2a, propylene desorption peaks were observed on all surfaces spanning from 350 to 650 K, with a peak temperature of 480 K. An additional cracking pattern of 41 amu was included in the Supporting Information (Figure S2) to verify the production of propylene. The 41 amu peaks had similar peak shapes and desorption temperatures as the 39 amu peaks, which were different from the 29 amu (propanal), 57 amu (allyl alcohol), or 74 amu (acetol) peaks. As the Cu coverage was increased, the propylene peak area decreased, suggesting that propylene was formed on the Mo2N site. Figure 2b shows the desorption of propanal, with a peak temperature of 480 K. The peak area of propanal also decreased with the increase of Cu coverage, suggesting that propanal was produced on the Mo2N site. There was another sharp peak at 373 K, which was part of the cracking pattern of another product, acetol. The concurrent increase of the 373 K peak areas in Figure 2b (29 amu) and Figure 2d (74 amu), while retaining a similar peak area ratio (see Table S2 in Supporting Information), as the Cu coverage was increased suggested that both peaks were cracking patterns from acetol desorption. As the relative intensity of different masses measured by the UTI mass spectrometer in this study had been adjusted for optimal data resolution, the relative intensity ratio of different masses presented herein may differ from those shown in the NIST database. In Figure 2c, the desorption of allyl alcohol was observed with a peak temperature of 419 K, which was significantly lower than that of the propanal (480 K), with the difference being explained with the reaction energetics from DFT calculations in Section 3.4. Similar to the propylene and propanal, the allyl alcohol peak area also decreased as the Cu coverage was increased, suggesting that all three molecules were produced on the Mo2N site. Figure 2d shows the desorption of acetol, a product formed after only one C−O bond scission of glycerol. In contrast to all the other products, the activity of acetol increased with the Cu coverage, suggesting that acetol was formed on the Cu site of the surface. This result is similar to that on the Cu site of the Cu/Mo2C surface. With the addition of Cu, the reaction pathway shifted to a more facile pathway involving only one C−O bond scission forming acetol, as evidenced by the lower desorption temperature of 373 K than that of the propylene, allyl alcohol, and propanal formation pathways.

Quantification of product concentrations from the glycerol reactions on the corresponding surfaces has been performed using procedures described previously, and the results are shown in Figure 3 and Table S1 in the Supporting Information. The total product concentrations from surfaces with interfacial Cu coverages were comparable to those on the Cu/Mo2C system, while those from the Mo2N and thick Cu/Mo2N surfaces were higher than those on Mo2C and thick Cu/Mo2C. A change in product distribution was noticed as the Cu coverage was varied. On Mo2N, the product distribution
consisted of 51% propylene, 23% propanal, and 26% allyl alcohol. As the Cu coverage was increased, the concentrations of propylene, propanal, and allyl alcohol decreased. In the meantime, acetol production continued to increase and became dominant on the thick Cu surface.

3.3. Surface Intermediates from HREELS Measurements

HREELS experiments were performed to identify the adsorption and surface intermediates during the reaction of glycerol over Mo$_2$N and Cu-modified Mo$_2$N, as well as to compare with those on Mo$_2$C and Cu-modified Mo$_2$C surfaces. The vibrational mode assignment was listed in Table 1. Glycerol was dosed to the surfaces at 200 K and subsequently heated to the indicated temperatures. All spectra were recorded after the surfaces were cooled back to 200 K. After dosing glycerol at 200 K, the spectra were similar on all surfaces, consistent with the $\nu$(CO) mode (1060 cm$^{-1}$), $\delta$ (CH$_2$) mode (1436 cm$^{-1}$), and $\nu$(CH) mode (2866 cm$^{-1}$) being the characteristic vibrational modes of glycerol$^{16}$ (Figure 4a), indicating molecular adsorption of glycerol on all the surfaces. The absence of the $\delta$(HOH) mode of molecular water previously observed$^{55,56}$ on C/Mo(110) and C/W(110) between 1630 and 1644 cm$^{-1}$ also suggested that there was negligible amount of molecular water on the surfaces from exposure to glycerol at 200 K. Upon heating to 300 K (Figure 4b), a clear difference was noted between the Mo$_2$C and Mo$_2$N surfaces at the $\delta$(CH$_2$) mode (1423 cm$^{-1}$). On Mo$_2$N, the $\delta$(CH$_2$) mode decreased and was weaker compared with the $\nu$(CO) mode (1060 cm$^{-1}$), suggesting that the C–H bonds in...
glycerol were preferentially activated. In contrast, on Mo2C, the intensity of the $\delta(\text{CH}_2)$ mode did not change significantly. Also observed was the presence of hydroxyl groups ($\nu(\text{OH})$) on Mo2N at 3309 cm$^{-1}$, which were absent on Mo2C. This suggested that some hydroxyl groups were preserved on Mo2N, while Mo2C tended to break all the O–H bonds. A red shift of $\nu(\text{CO})$ from 1060 cm$^{-1}$ was also observed on Mo2C but not on Mo2N or any other surfaces, indicating that Mo2C interacted strongly with the C–O bonds in glycerol. When the surfaces were heated to 400 K (Figure 4c), the decrease of $\delta(\text{CH}_2)$ mode at 1423 cm$^{-1}$ was more significant on Mo2N than on Mo2C, further demonstrating the interaction between Mo2N with the C–H bonds in glycerol. In addition, the $\nu(\text{OH})$ mode on Mo2N decreased significantly, indicating that more O–H bond scission had occurred. It should be noted that the O–H bond scission happened at a higher temperature on Mo2N than on Mo2C, with the $\nu(\text{OH})$ mode being absent on the latter surface by 300 K. This suggested that Mo2N interacted less strongly with the O–H bonds in glycerol as compared with Mo2C. It was also noticed that when Mo2N was modified by 0.5 ML Cu, the extent of attenuation of the $\delta(\text{CH}_2)$ mode intensity (1423 cm$^{-1}$) became less, indicating that Cu weakened the interaction between the surface and the C–H bonds in glycerol. Furthermore, the thick Cu/Mo2N 400 K spectrum appeared to be similar to that of the thick Cu/Mo2C surface, where no significant C–H bond activation was observed. Overall, the HREELS results demonstrated that the C–H bond activation on Mo2N was facile, while the O–H bond and C–O bond activations were more favorable on Mo2C. The addition of Cu weakened these interactions on both Mo2N and Mo2C. DFT calculations in the following section further revealed that surface N on Mo2N interacted with glycerol, which helped to activate certain O–H bonds and played an indirect role in activating the C–H bond, whereas Mo2C interacted strongly with the O moiety in glycerol.

### Table 1. Vibrational Mode Assignment of Glycerol$^a$

| mode | frequency (cm$^{-1}$) |
|------|---------------------|
| $\nu$(MO) | 564 | 570 |
| $\tau$(OH) | 631 | 631 | 671 |
| $\nu$(CO) | 1060 | 1060 | 1060 |
| $\rho$(CH$_2$) | 1322 | 1322 | 1356 |
| $\delta$(CH$_2$) | 1423 | 1423 | 1430 |
| $\nu$(CH) | 2846 | 2846 | 2873 |
| $\nu$(OH) | 3309 | 3309 | 3248 |

$^a$$\nu$ – stretching, $\tau$ – torsion, $\rho$ – rocking, $\delta$ – deformation. $^b$Ref 16.

glycerol were preferentially activated. In contrast, on Mo2C, the intensity of the $\delta(\text{CH}_2)$ mode did not change significantly. Also observed was the presence of hydroxyl groups ($\nu(\text{OH})$) on Mo2N at 3309 cm$^{-1}$, which were absent on Mo2C. This suggested that some hydroxyl groups were preserved on Mo2N, while Mo2C tended to break all the O–H bonds. A red shift of $\nu(\text{CO})$ from 1060 cm$^{-1}$ was also observed on Mo2C but not on Mo2N or any other surfaces, indicating that Mo2C interacted strongly with the C–O bonds in glycerol. When the surfaces were heated to 400 K (Figure 4c), the decrease of $\delta(\text{CH}_2)$ mode at 1423 cm$^{-1}$ was more significant on Mo2N than on Mo2C, further demonstrating the interaction between Mo2N with the C–H bonds in glycerol. In addition, the $\nu(\text{OH})$ mode on Mo2N decreased significantly, indicating that more O–H bond scission had occurred. It should be noted that the O–H bond scission happened at a higher temperature on Mo2N than on Mo2C, with the $\nu(\text{OH})$ mode being absent on the latter surface by 300 K. This suggested that Mo2N interacted less strongly with the O–H bonds in glycerol as compared with Mo2C. It was also noticed that when Mo2N was modified by 0.5 ML Cu, the extent of attenuation of the $\delta(\text{CH}_2)$ mode intensity (1423 cm$^{-1}$) became less, indicating that Cu weakened the interaction between the surface and the C–H bonds in glycerol. Furthermore, the thick Cu/Mo2N 400 K spectrum appeared to be similar to that of the thick Cu/Mo2C surface, where no significant C–H bond activation was observed. Overall, the HREELS results demonstrated that the C–H bond activation on Mo2N was facile, while the O–H bond and C–O bond activations were more favorable on Mo2C. The addition of Cu weakened these interactions on both Mo2N and Mo2C. DFT calculations in the following section further revealed that surface N on Mo2N interacted with glycerol, which helped to activate certain O–H bonds and played an indirect role in activating the C–H bond, whereas Mo2C interacted strongly with the O moiety in glycerol.

The reaction mechanism of the glycerol HDO is examined computationally on the N-terminated Mo2N(111) surface using DFT to understand the experimentally observed trend in product selectivity. In our earlier work, the glycerol HDO mechanism was examined at different active sites of a Cu/Mo2C model surface. The calculated reaction energy profiles predicted
that the Mo sites are very active for cleaving all three C–O bonds of glycerol producing propylene and the Cu/Mo2C interface sites prefer to cleave two C–O bonds forming allyl alcohol and propanal. In contrast, the Cu sites are active for cleaving only one C–O bond leading to the formation of acetol. Our current experimental studies on the Cu/Mo2N surface (Figure 3) reveal that the product yield of acetol increases with increasing Cu coverage, suggesting that acetol is produced mainly on the Cu surface. HREELS observations also reveal that the surface intermediates on thick Cu/Mo2N and thick Cu/Mo2C surfaces are similar. These results indicate that the Cu sites supported on both Mo2C and Mo2N behave similarly and that the glycerol HDO mechanism on the Cu sites supported on Mo2N is expected to be very similar to that of the Mo2C supported Cu surface that was examined in detail in our earlier reports. However, the products observed on the clean Mo2N and Mo2C surfaces clearly differ for the glycerol HDO. While propylene is the only main product observed on the Mo2C surface, formation of allyl alcohol and propanal is also observed in addition to propylene on the Mo2N surface. Thus, in the present study, we examine the deoxygenation pathways of glycerol on the N-terminated Mo2N(111) surface and compared the results with our earlier work on the Mo2C(0001) surface with the aim of understanding the difference in reaction mechanism on these two surfaces.

The elementary reaction pathways calculated for the glycerol deoxygenation reaction on the Mo2N surface are illustrated in Figure 5. The zero-point energy corrected reaction energies and activation barriers for the elementary reactions calculated with PBE+D3 and SCAN+rvv10 functionals are summarized in Table S3, and the corresponding structures are depicted in Figure S3 and S4 of the Supporting Information. The available adsorption sites on the N-terminated Mo2N(111) surface are the surface Mo sites (*Mo) and surface N sites (*N). Only H atoms are found to adsorb on the N sites and all the other intermediate species adsorb on the Mo sites. While adsorption of an H atom on the surface N atom is favored by only 0.03 eV compared with the Mo site, adsorption of C and O atoms on the Mo sites are favored by 0.54 and 2.99 eV, respectively, relative to adsorption on the N site. As shown in the inset of Figure 5, glycerol thus prefers to adsorb on the Mo2N surface with two oxygen atoms interacting with the surface Mo sites and the H atoms of two O–H groups exhibiting strong H-
bonding interactions with the surface N atoms. The binding energy calculated with PBE+D3 functional (−1.56 eV) suggests that the adsorption of glycerol on the N-terminated Mo2N surface is about 0.6 eV less stable than on the Mo2C surface16 where glycerol binds with all three oxygen atoms. In agreement with the results on the Mo2C surface, activation barriers calculated for the initial O–H and C–OH bond cleavages of glycerol on the Mo2N(111) surface (Table S3) suggest that the O–H bond dissociations are preferred over C–OH bond dissociations. In general, the SCAN+rVV10 functional predicts a slightly stronger adsorption of glycerol and its dissociated products by 0.2–0.3 eV compared with the PBE+D3 functional (Table S3). However, the trends observed for the reaction/activation energies of competing elementary reactions are very similar between these two functionals, and thus, in the following, we discuss PBE+D3 data. Our calculations (Figure S5) predict lower activation barriers for transferring H atoms from the OH groups to the nearest surface N atoms relative to the transfer to the nearest Mo sites and the secondary O–H bond scission to the surface N atom ($E_{ZPE}^{act} = 0.11$ eV, 2B) is both kinetically and thermodynamically preferred over the primary O–H scission ($E_{ZPE}^{act} = 0.53$ eV, 2C). The secondary O–H cleavage process producing an alkoxide species (CH$_2$OH−CHO−CH$_2$OH*, 2B) is exothermic by −1.46 eV, which is very similar to that on the Mo$_2$C(0001) surface.16 It should be noted here that the reactant and product states depicted in Figure S5 and also in the elementary reactions of Table S3 of the Supporting Information constitute one discrete state, although they are written as having multiple species for clarity; that is, the dissociated atoms/fragments stay on the surface and the energy calculations include the lateral interactions between these species.

The terminal O–H bond cleavage of the alkoxide species (2B → 3B) was found to be the next favorable elementary reaction with an activation barrier of 0.42 eV, which is much lower than the C–H (2B → 3C) and C–O (2B → 3D) bond scissions at the secondary carbon. The O–H or C–OH dissociations at the second terminal −OH, that is not bonded to the surface Mo, are not possible since the dissociated O/ OH species cannot bind on the Mo site, which is blocked by a surface N atom (Figure S3−S4). At this terminal carbon of 2B, a concerted cleavage of the C–H and O–H bonds, producing the CH$_2$O−CHO−CH$_2$OH* (3A) intermediate, is possible with an activation barrier of 0.61 eV, which is only 0.19 eV higher than the most favorable O–H scission process (2B → 3B). However, formation of 3A is thermodynamically less favorable by 0.85 eV compared with 3B. Another concerted pathway, which includes C–O cleavage at the secondary carbon and C–OH cleavage at the terminal carbon, leads to the formation of allyl alcohol (2B → 3E). This step is thermodynamically more favorable by 0.41 eV than the O–H cleavage; however, the required activation barrier for this step is 0.47 eV higher than the O–H cleavage. It appears that the favorable pathway for the formation of allyl alcohol is a concerted cleavage of two C−O bonds from the intermediate CH$_2$OH−CHO−CH$_2$O* (3B), which possesses a lower activation barrier ($E_{ZPE}^{act} = 0.63$ eV) than the C–H bond scissions at the middle (3B → 4C) or terminal (3B → 4D) carbon atoms. Here again, the possibility of the concerted cleavage of C–H and O–H bonds at the third carbon of 3B, producing the CHO−CHO−CH$_2$O* (4A) intermediate, was examined, and it was found that the activation barrier of this process is only 0.1 eV higher than the concerted C–O cleavage reaction of 3B producing allyl alcohol (4B). SCAN+rVV10 functional calculations also predicted very similar activation barriers for 3B → 4A (0.86 eV) and 3B → 4B (0.89 eV) suggesting that both processes are kinetically equally favorable. Overall, this result is consistent with the observation from HREELS experiments that the C–H bonds of glycerol can be activated over Mo$_2$N, whereas only the O–H and C–O bonds are activated over Mo$_2$C.

In the next step, the intermediate CHO−CHO−CH$_2$O* (4A) is converted to acrolein (CHO−CH = CH$_2$ 5A) via a concerted C–O cleavage with an activation barrier of only 0.31 eV. The lower activation barrier observed for the concerted C–O cleavages of CHO−CHO−CH$_2$O* (4A) relative to that of CH$_2$OH−CHO−CH$_2$O* (3B) is due to the presence of a carbonyl group (HC = O) at the terminal position of intermediate 4A, which promotes the C–O cleavage at the neighboring position. Allyl alcohol (4B) can also undergo a concerted C–H and O–H cleavages at the terminal carbon with an activation barrier of only 0.1 eV producing acrolein (5A). While the concerted TSs of the elementary reactions, 2B → 3A, 3B → 4A, and 4B → 5A exhibit mainly the characteristics of C–H bond dissociations (Figure S4 of the Supporting Information), the O–H bond dissociation occurs without any barrier in these cases and takes place simultaneously with a C–H bond dissociation. Acrolein (5A) is easily converted to propenal (7A) via hydrogenation and the preferred pathway for the hydrogenation of acrolein was found to be the abstraction of an H atom by the terminal −CH$_2$ from the surface N (5A → 6A; $E_{ZPE}^{act} = 0.20$ eV) followed by the abstraction of a second H atom by the middle −CH group from the surface Mo site (6A → 7A; $E_{ZPE}^{act} = 0.19$ eV). In another possible pathway, allyl alcohol (4B) can undergo O−H bond scission on the neighboring Mo site to produce CH$_2$O−CHO = CH$_2$.5B. Although the activation barrier of this process is 0.09 eV higher than the acrolein formation process (4B → 5A), it is thermodynamically more favored by 0.56 eV. Our NEB calculations suggested that the formation of acrolein from 5B via C−H dissociation requires an activation barrier as high as 1.7 eV, and thus, we did not consider this pathway. Instead, the C–O cleavage of the intermediate 5B was found to be the next favorable process with an activation barrier of 0.49 eV and an exothermicity of another 0.51 eV. The formation of propylene from intermediate 6B is completed by the hydrogenation of the terminal −CH$_2$ group ($E_{ZPE}^{act} = 0.35$ eV). The calculated activation barriers suggest that converting allyl alcohol to propenal is kinetically more favorable than to propylene; however, the formation of propylene is thermodynamically more favorable by 1.36 eV than propenal because of the deposition of an additional O atom on the Mo$_2$N surface. A “path following” technique is used to identify the minimum energy pathway presented in Figure S5, where the elementary step with the lowest activation barrier is selected as the branch point for the next mechanistic step. The identified pathway is consistent with our earlier study on glycerol decomposition on the β-Mo$_2$C(0001) surface16 and literature reports on ethanol decomposition on the α-Mo$_2$C(100) surface28 and ethylene glycol decomposition on the β-Mo$_2$C(0001) surface.39 All of these studies have suggested that the Mo-sites preferentially dissociate O−H bonds prior to C−O and C−H bond cleavages. Thus, other pathways that exhibit higher activation barriers early in the
reaction network should not have any contribution to the overall rate of reaction.

Because of the strong preferential adsorption of oxygen on the Mo sites, glycerol and its dissociated products adsorb on the Mo sites of Mo2N through the oxygen atoms, and surface N atoms do not play a role in the C–O cleavage process. While the carbon of C3H6 intermediate can adsorb on the surface N atoms after C–O or C–H cleavage, the formation of the products, allyl alcohol, propylene, and so on, requires cleaving the C–N bonds that exhibits more than 0.5 eV higher activation barriers compared with the C–O cleavage processes. Thus, the DFT results suggest that the surface N atoms only play a direct role in the activation of O–H bonds. Overall, the activation barriers for O–H and C–O bond cleavages on the Mo2N surface are slightly higher than those on the Mo2C surface but lower than the ones calculated for the Cu monolayer supported on the Mo2C surface. However, the C–H bond dissociation is favored on the Mo2C supported Cu monolayer compared with the Mo2N surface.

In order to correlate the computational predictions with experimental TPD observations, Figure 6 illustrates the Gibbs free energy profiles calculated with PBE+D3 functional for the minimum energy pathways of the glycerol decomposition on the N-terminated Mo2N(111) model catalyst surface ($T = 350$ K; $P_{\text{gas}} = 7.6 \times 10^{-7}$ Torr). All energies are with reference to the sum of the energies of gas phase glycerol and the initial catalyst model. The numbering of intermediate states corresponds to the states in Figure S5, and the respective bond dissociations (/) and associations (+) are shown at the transition states.

Free energy profiles calculated at the experimental reaction conditions ($T = 350$ K and $P_{\text{gas}} = 7.6 \times 10^{-7}$ Torr, based on the pressure of glycerol and $H_2$ used in TPD experiment) for the minimum energy pathways of glycerol decomposition on the Mo2N surface. The favorable pathway involves two consecutive O–H bond cleavages followed by two concerted C–O bond scissions leading to the formation of allyl alcohol (4B). Calculated free energies further suggest that the desorption of allyl alcohol is favorable at low temperatures, agreeing with the allyl alcohol desorption peak observed at 419 K (Figure 1c) that is lower than the desorption temperatures of propional and propylene. Our earlier work on the Cu/Mo2C(0001) model surface suggested that glycerol undergoes three consecutive O–H bond cleavages with very low activation barriers ($\leq 0.2$ eV) followed by three consecutive C–O bond cleavages, leading to the preferred production of propylene on the Mo sites (Figure S5 in the Supporting Information). Since the third O–H dissociation is blocked by the presence of surface N atoms on the Mo2N surface, this catalyst prefers to produce allyl alcohol. Very small activation barriers associated with the initial C–H/O–H bond scissions (0.10 eV) or O–H scission (0.19 eV) of the terminal $-CH_2OH$ of allyl alcohol (4B) suggest that allyl alcohol can undergo further reaction on the Mo2N surface to produce propanal and propylene. This correlates well with the TPD results displaying desorption peaks for propanal and propylene at a higher temperature of 480 K (Figure 1), that is, it suggests that these two products are produced from allyl alcohol. Free energy profiles (Figure 6) further indicate that the formation of propylene from allyl alcohol is thermodynamically more favorable than the formation of propanal, which could explain the higher selectivity of propylene (51%) observed experimentally compared with propanal (23%), as shown in Table S1. The relatively similar activation free energies observed for the concerted C–H/O–H bond scissions with respect to their competing reaction pathways suggest that the C–H bonds of glycerol dissociated products are activated over the Mo2N surface which agrees with the HREELS experimental results. When the temperature was changed from 200 to 300 K, a decrease in the intensity of the $\delta(CH_2)$ mode and the presence of a $\nu(OH)$ mode was observed on the HREELS spectra of Mo2N, whereas the $\nu(OH)$ modes disappeared and the intensity of $\delta(CH_2)$ remained unchanged over Mo2C. Similar activation barriers predicted by computations for C–H activation (3B $\rightarrow$ 4A) and formation of allyl alcohol with one $-OH$ preserved (3B $\rightarrow$ 4B) could explain the changes observed in the HREELS spectra of Mo2N. Since the preferable pathway for glycerol activation on Mo2C is three consecutive O–H bond cleavages followed by three C–O bond scissions, the HREELS spectra of Mo2C exhibited no change in the $\delta(CH_2)$ mode of Mo2C and the $\nu(OH)$ modes disappeared quickly upon heating.

The strong exothermcity observed for both O–H and C–O bond scissions of glycerol on the Mo2N surface implies that the dissociated O atoms can bind strongly on this surface even in the presence of neighboring N atoms. A comparison of the free energy profiles for the conversion of glycerol to propylene on the Mo sites of the Cu/Mo2C(0001) surface, and the N-terminated Mo2N(111) surface (Figure S5 in the Supporting Information) indicates that the adsorption of O and H atoms on Mo2N is slightly weaker than on Mo2C. The conversion of glycerol to propylene results in the deposition of 3 oxygen and 2 hydrogen atoms on the catalyst surface. Although the final state with adsorbed O and H atoms for the Mo2N surface is found to be about 2 eV less stable relative to the one on the Mo2C surface, the reaction remains strongly exergonic by $-6.58$ eV on the Mo2N surface. Based on DFT calculations, Dlugogorski and co-workers also observed stable O atoms adsorbed on the N-vacant Mo sites during NO reduction and H atoms adsorbed strongly on the surface N sites during H2 dissociation on the Mo2N(111) surface. Experimental studies performed by He et al. revealed the transformation of $\gamma$-Mo2N into a Mo2O3N phase in the presence of NO, and this phase can be reduced back to $\gamma$-Mo2N by $H_2$. Thus, in Table 2, the removal process of adsorbed oxygen atoms on the Mo2N surface by $H_2$ to form $H_2O$ is reported. The calculated activation barriers and reaction energies revealed that the formation of OH from adsorbed O atoms is favored only by
the direct dissociation of gas phase H₂ onto O rather than transferring H atoms adsorbed on the surface Mo or N sites. Similarly, H₂O formation preferably occurs via the disproportionation reaction of two neighboring OH rather than transferring H atoms to OH from the neighboring Mo or N sites. These results are consistent with our earlier work on the Cu/Mo₂C surface and also experimental reports on Mo₂C and Mo₂N, suggesting that the adsorbed O on the Mo sites can be removed by excess H₂. Although the activation barriers calculated for the most favorable pathways of the OH (ΔE_{ZPE}^* = 0.58 eV, reaction (3)) and H₂O formation (ΔE_{ZPE}^* = 0.38 eV, reaction (6)) processes on the Mo₂N surface are about 0.2 eV higher than the corresponding processes on the Mo₂C surface, H₂O desorption from two adsorbed OH (ΔE_{ZPE}^* = 1.22 eV calculated from reactions (6) and (7)) on the Mo₂N surface is thermodynamically favored by 0.16 eV relative to the Mo₂C surface. Thus, the oxygen removal process appears to be more facile on the Mo₂N surface, which is consistent with the lower average desorption temperature of H₂O from Mo₂N (Figure 1d). As shown by Porosoff et al. in the CO₂ reduction reaction with Mo₂C and He et al. in the NO decomposition reaction with Mo₂N, oxycarbides and oxynitrides (Mo₂O⁻½,Mo⁻½) did form under reaction conditions, but could be reduced with sufficient H₂. Future studies should focus on the stability and oxidation states of Mo₂N powder catalysts under reaction conditions relevant to glycerol hydrodeoxygenation, particularly in the liquid phase.

4. CONCLUSIONS

In conclusion, this work demonstrates for the first time of surface science studies of Mo₂N for the selective HDO of glycerol. TPD experiments showed that Mo₂N had similar activity to Mo₂C, with added reaction pathways resulting from the N modification of the surface. Both Mo₂N and Mo₂C cleaved all the C–O bonds in glycerol to form propylene. In addition, Mo₂N could also break two C–O bonds to produce allyl alcohol and propanal, which was only achievable on the Cu/Mo₂C interface. The addition of Cu to Mo₂N shifted the reaction pathway to only one C–O bond scission forming acetol. HREELS results demonstrated that C–H bond activation was possible on Mo₂N, while Mo₂C interacted more strongly with the O atoms in glycerol. DFT results obtained from the glycerol decomposition on the N-terminated Mo₂N(111) surface were in good agreement with experimental observations. The comparison of these results with our earlier mechanistic study on the Mo₂C surface provides evidence that the Mo₂N surface can exhibit a comparably similar activity relative to the Mo₂C surface for the glycerol HDO. Both surfaces interact strongly with the O atoms in glycerol to selectively cleave the C–O bonds while preserving the C–C bonds. Importantly, the surface N atoms of Mo₂N play a critical role in determining the mechanism and product selectivity, such as activating the H atoms in glycerol and blocking specific Mo sites to facilitate the two C–O bond scission and C–H activation pathways. This fundamental study can be further extended to reactor studies using industrial-relevant powder catalysts. Compared with the synthesis of Mo₂C that accumulates carbon on the surface, the synthesis of Mo₂N leaves a well-defined N-terminated surface that allows for better correlation between experimental results and model surface calculations. Overall, this work sheds light on the fundamental understanding of the unique properties of transition metal nitrides in controlling the selective C–O bond scission of glycerol and relevant biomass-derived oxygenates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00403.

Product concentrations (molecule per metal atom) from glycerol on Mo₂N and Cu/Mo₂N with corresponding Cu coverages, peak area ratios of the 29 and 74 amu peaks from Mo₂N surfaces modified with different coverages of Cu, zero-point energy corrected reaction energies (ΔE_{ZPE}) and forward activation barriers (E_{ZPE}^*) for the elementary steps considered in the glycerol decomposition mechanism on the N-terminated Mo₂N(111) catalyst model, molybdenum nitride thin film XRD patterns and molybdenum nitride X-ray photoelectron spectroscopy (XPS), desorption of propylene (41 amu) after exposing Mo₂N surfaces modified with different coverages of Cu, intermediate and transition state structures involved in the glycerol decomposition mechanism on the N-terminated Mo₂N(111) catalyst model, free energy profiles for the minimum energy pathways of glycerol conversion to propylene on the N-terminated Mo₂N(111) and at the Mo sites of Cu/Mo₂C(0001) catalyst model, stability of carbon species on the N-terminated Mo₂N(111) surface (PDF).

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Table 2. Zero-Point Energy Corrected Reaction Energies (ΔE_{ZPE}) and Activation Barriers (E_{ZPE}^*) Calculated with PBE +D3 Functional for the Removal of Adsorbed Oxygen Atoms from the N-Terminated Mo₂N(111) Catalyst Model

| reaction | ΔE_{ZPE} (eV) | E_{ZPE}^* (eV) |
|----------|---------------|-----------------|
| (1) O_{Mo} + H₂O → H₂O_{Mo} + ^*_Mo | 0.59 | 0.75 |
| (2) O_{Mo} + H₂O → OH_{Mo} + ^*_Mo | 0.58 | 0.58 |
| (3) O_{Mo} + H₂(g) → OH_{Mo} + H_{Mo} | 1.42 | 1.42 |
| (4) OH_{Mo} + H₂(g) → H₂O_{Mo} + ^*_Mo | 0.62 | 0.62 |
| (5) OH_{Mo} + H₂ → H₂O_{Mo} + O_{Mo} | 0.60 | 0.60 |
| (6) OH_{Mo} + H₂O(g) → H₂O_{Mo} + O_{Mo} | 0.58 | 0.58 |
| (7) H₂O_{Mo} → H₂O_{Mo} + ^*_Mo | 0.42 | 0.42 |

**Note:** a^*_Mo and ^*_N correspond to the empty surface Mo site and surface N site, respectively on the Mo₂N surface.
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NOTES

The authors declare no competing financial interest.

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