Inhibition of C–H and C–O Bond Activation by Surface Oxygen: Stabilization of Surface Phenoxide in the Reaction of Phenol on Oxygen-Precovered Mo(110)

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Abstract: The presence of surface oxygen on Mo(110) is shown to increase the kinetic stability of surface phenoxide formed after saturation phenol exposure with respect to decomposition. Temperature-programmed reaction and X-ray photoelectron spectroscopies have been used to study the reactions of phenol (C_6H_5OH) on oxygen-precovered Mo(110) ($\theta_O = 0.33$). At saturation coverage, surface phenoxide is formed from cleavage of the phenol O–H bond at temperatures below 400 K and is stable on the surface to 650 K, where it undergoes disproportionation to gaseous phenol ($E_d = 42$ kcal/mol) and the decomposition products gaseous water, gaseous dihydrogen, and surface carbon. A trace amount of benzene is also produced from decomposition of surface phenoxide. The hydrogen released by O–H bond cleavage in phenol at low temperature reacts with oxygen in the oxide overlayer to form gaseous water at temperatures below 400 K. Intact molecular phenol is also desorbed at temperatures below 350 K. The atomic oxygen overlayer dramatically stabilizes C–O and C–H bonds in the surface phenoxide species, which are cleaved at ~370 K on the clean Mo(110) surface. The stability of surface phenoxide on the oxygen-precovered surface is dependent on the coverage of phenol-derived surface species, with decomposition occurring at lower temperature for lower phenol exposures. No gaseous phenol is reformed from phenoxide for low phenol exposures.

1. Introduction

Phenol is a bifunctional molecule which may interact with a transition-metal surface through either the oxygen lone pair or the entire π ring system. The reactivity of the surface species formed upon adsorption may be influenced by structure and the coverage of either the species itself or atomic species such as oxygen and carbon. Previously, we studied the reaction of phenol on clean Mo(110)[1] to investigate the nature of the interaction with the surface and the reactivity of surface species formed. Only decomposition to surface carbon, surface oxygen, and gaseous dihydrogen is observed on Mo(110) after desorption of multilayers of phenol and a weakly bound molecular species. Surface phenoxide (C_6H_5O) forms at temperatures below 360 K; however, the phenoxide intermediate begins to irreversibly decompose by 370 K, where both C–H and C–O bonds activate. The activation of C–H bonds in the same temperature region as C–O bonds and the depletion of surface hydrogen through H_2 formation is thought to prevent hydrogenolysis of the phenoxide surface intermediate to benzene.

Oxygen overlayers are known to affect the reactivity of Mo(100) and Mo(110). Studies of the adsorption of Lewis acids and bases on clean and oxygen-precovered Mo(100) show that while the clean Mo(100) surface dissociates many molecules upon adsorption at room temperature, the oxidized surface is much less reactive to dissociation.[2] The presence of atomic oxygen on Mo(100) inhibits C–O bond scission in the formation reaction of gaseous methane from methoxy groups on the surface formed from methanol.[3] The rate of CO dissociation on an oxygen-precovered Mo(110) surface has also been studied[4] and found to be slower than that on the clean surface. Interestingly, in contrast to the case of oxygen, reaction on the sulfided Mo(110) surface exhibits the same CO dissociation kinetics as the clean surface.

The motivation for study of the reaction of phenol on an oxygen overlayer is twofold. Understanding the effect of oxygen on surface kinetics in the reaction of oxygen atom-containing molecules is important since surface oxygen is a reaction product of deoxygenation and may influence further reaction. Secondly, pretreatment with oxygen is a common step in the binding of phenolic adhesives to metals; thus, it is important to determine the influence of oxygen on the reactivity of phenolic species. Temperature programmed reaction and X-ray photoelectron spectroscopies were used in this study to examine the reactions of phenol on Mo(110), the closest packed face of molybdenum, which had been precovered with a 0.33 monolayer atomic oxygen overlayer. The presence of the oxygen overlayer is found to stabilize phenoxide groups on the surface with respect to decomposition to such an extent that recombination to form phenol occurs at temperatures over 600 K. Water, dihydrogen, and trace amounts of benzene are evolved as decomposition products of the phenoxide groups present on the surface. Thus, the presence of atomic oxygen significantly alters the energetics for surface reactions on Mo(110), leading to slower kinetics for decomposition. The reaction of water on the oxygen-precovered Mo(110) surface was also studied to aid in the interpretation of the phenol results and will be discussed first.

2. Experimental Section

All experiments were performed in two ultrahigh vacuum chambers with base pressures of 1.5×10^{-10} Torr. The X-ray photoelectron and most of the temperature-programmed reaction experiments were performed in a chamber described previously.[5] This chamber is equipped with a Physical Electronics 5300 X-ray photoelectron spectroscopy system, a UTI-100C quadrupole mass spectrometer surrounded by a liquid nitrogen cooled shield, and electron optics for Auger electron spectroscopy and low-energy electron diffraction. The mass spectrometer was interfaced with an IBM computer which allowed data collection for up to 10 masses in a single experiment. Auger electron spectroscopy and low-energy electron diffraction were used to monitor crystal cleanness and check surface order. X-ray photoelectron data were analyzed and curve-fitted by using the computer and software provided with the Physical Electronics system. The C(1s), O(1s), and Mo(3d) regions were monitored for collection times of 7, 7, and 2 min, respectively. Clean Mo(110) surface spectra were subtracted from the C(1s) region, since photoemission from molybdenum exhibited structure in this region. The Mo(3d) peak at 227.7 eV was used to calibrate the binding energies of the C(1s) and O(1s) regions. Binding energies are accurate to within ±0.2 eV. For the temperature annealing experiments, a saturation dose of phenol was adsorbed on the crystal at 100 K, flashed to the temperature of interest twice at a heating rate of ~15 K/s, and recooled to 100 K before X-ray photoelectron data were collected. A new phenol dose was used for each X-ray photoelectron spectrum collected in order to minimize beam damage to surface species. There were no changes in the X-ray photoelectron spectra over time for the collection times used (16 min), indicating that beam damage was not occurring. The second chamber, described previously,[6] was used to perform isotopic labeling temperature programmed reaction experiments, to observe low-energy electron diffraction patterns, and to measure Auger peak ratios.

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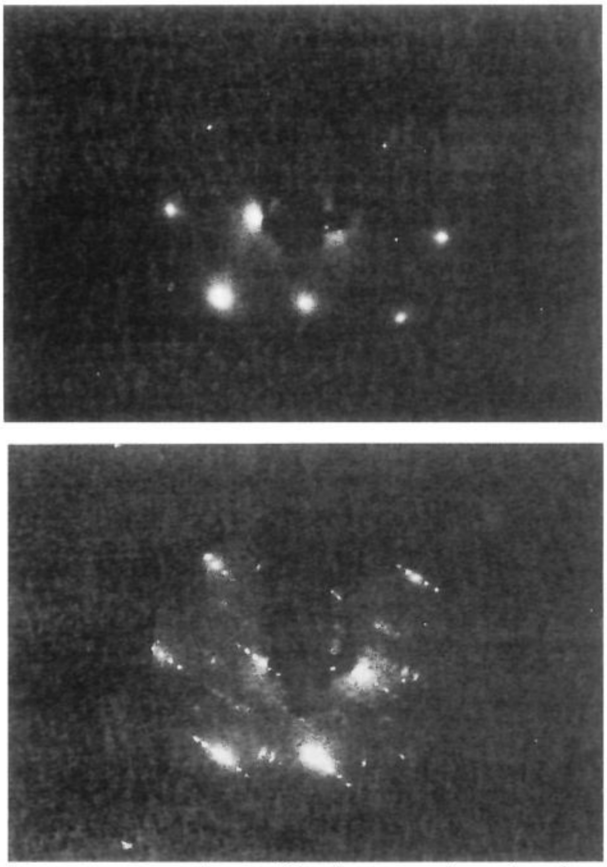

Figure 1. Low-energy electron diffraction patterns observed at a beam voltage of 72 eV of (a) (top) clean Mo(110) and (b) (bottom) 0.33 monolayer oxygen overlayer on Mo(110) used for studies of the reaction of phenol and water.

Preparation of the Mo(110) single crystal was performed in the manner described previously.[6] Phenol was obtained from Mallinckrodt (Loose Crystals, ACS), degassed at 300 K repeatedly, and used without further purification. Deuterium-labeled phenol (phenol-d_6 and phenol-d_5, 98%) was obtained from Cambridge Isotope Laboratories and degassed in the same manner as phenol-h_6. Oxygen (Matheson, Extra Dry, 99.6%) was used to make atomic overlayers and to clean the crystal after temperature-programmed reaction. Oxygen exposure is expressed in units of Torr·s, which refer to the product of the backing pressure of the oxygen in the doser reservoir and the time in seconds the doser is open. Directed dosing was used in all cases so that the chamber pressure was never above 3×10^{-10} Torr during phenol dosing. Phenol exposure is referenced to saturation exposure, which is defined as the exposure after which there is no further increase in the amount of product formation (water, dihydrogen). A crystal dosing temperature of 100 K was used in all experiments unless otherwise noted.

The 0.33 monolayer oxide used in this study was formed by exposing the Mo(110) crystal to 60 Torr·s of oxygen at a crystal temperature of 1200 K. After cooling to 100 K, the low-energy electron diffraction pattern shown in Figure 1b was observed. The coverage of oxygen in the overlayer formed in this manner was calibrated by measuring the area of the O(1s) X-ray photoelectron peak of the oxygen overlayer and comparing it to the total S(2p) area observed for the Mo(110)–p(2 × 2)–S overlayer, which is known to have a coverage of 0.25 monolayers. After correcting for the relative atomic sensitivity factors, this measurement yields a coverage of 0.33 monolayer for the oxygen overlayer. The structure of oxygen overlayers on Mo(110) has been studied previously.[7,8] The low-energy electron diffraction patterns reported for 0.25 and 0.50 monolayer coverages of oxygen[8] are similar to those observed here for the 0.33 monolayer oxygen overlayer and shown in Figure 1. The ratio of the O(KLL) to Mo(MNN) Auger peak-to-peak height is also consistent with those measured previously for this coverage. The oxygen overlayer used here could also be formed by exposing the crystal to oxygen at a temperature of 100 K and annealing to 1200 K. The oxide formed in this manner was found to have a low-energy electron diffraction pattern and reactivity identical with that of the oxide formed at high temperature. The exact coverage of oxygen was found to have very little influence on the peak temperatures observed in temperature-programmed reaction within the range of 0.25-0.50 monolayer of oxygen, although the ratio of decomposition to phenol desorption at high temperature was found to be affected by the oxygen coverage.

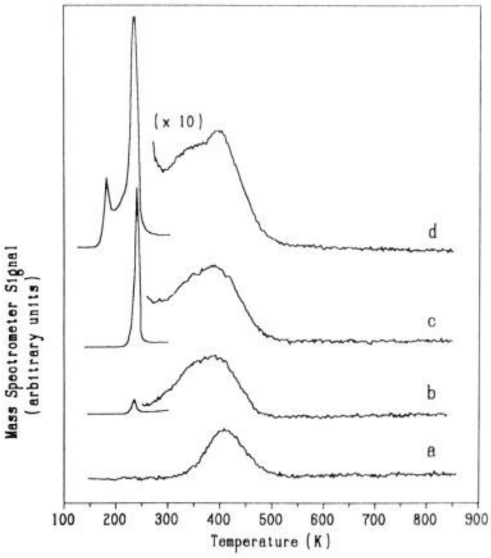

Figure 2. Temperature programmed reaction spectra of water (18 amu) from adsorption of water on the 0.33 monolayer oxygen-precovered Mo(110) surface at 100 K as a function of water exposure. Exposures are (a) 0.1, (b) 0.2, (c) 0.8 and (d) 1.0 of saturation.

3. Results

3.1. Water: Temperature Programmed Reaction and X-ray Photoelectron Studies.

The reaction of water on Mo(110) covered with a 0.33 monolayer oxygen overlayer was studied to aid in interpretation of the phenol data since water is evolved as a product from reaction of phenol. The oxygen overlayer was prepared as described in the Experimental Section and exhibited the low-energy electron diffraction pattern shown in Figure 1b. The temperature programmed reaction spectra of water (18 amu) adsorbed at 100 K obtained as a function of water exposure are shown in Figure 2. Water and dihydrogen are the only gaseous products evolved during reaction. Water is produced in three separable peaks for exposures greater than saturation with maxima at 180, 240, and 400 K. The sharp peak at 180 K is attributed to sublimation of water multilayers since this peak increases indefinitely in intensity with exposure (Figure 2d). Other workers have observed sublimation of water multilayers from Ni(110),[9] Ru(001),[10] and Pt(111)[11] at 155, 170, and 160 K, respectively. The somewhat higher temperature observed in the data shown in Figure 2d is attributed to nonuniform heating of the Mo(110) crystal in this temperature regime (when the filament is first turned on in the temperature programmed reaction experiment). If slower heating rates are used, the temperature of multilayer sublimation is observed to be around 160 K.

The broad water desorption peak centered at 420 K after low exposure shifts to 400 K with increasing exposure and then broadens on the low-temperature side at high exposures (Figure 2). Adsorption of [^{16}O]water (18 amu) on an ^{18}O overlayer shows desorption of both $H_2{}^{16}O$ (18 amu) and $H_2{}^{18}O$ (20 amu) masses in this peak, demonstrating that water desorbing in this peak arises from recombination of species on the surface (data not shown). As the water exposure is further increased (Figure 2), a sharp molecular peak appears at 240 K in the spectrum of water commencing at an exposure ~0.2 of saturation. Saturation of this

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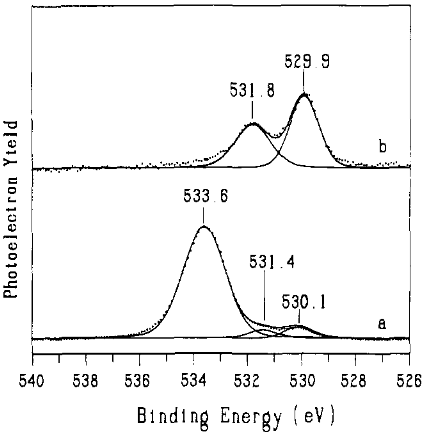

Figure 3. O(1s) X-ray photoelectron spectra of water adsorbed on a 0.33 monolayer oxygen precovered Mo(110) surface at 100 K for (a) multilayer water exposure and (b) saturation water exposure annealed to 300 K.

peak is defined as saturation exposure (1.0). Sharp desorptions of hydrogen-bonded clusters of water have been observed at similar temperatures on oxygen-precovered Ni(110)[9] and other metals. Dihydrogen is also formed from the decomposition of water on Mo(110) in a peak centered at 475 K at low exposures, which shifts smoothly in temperature with exposure to 390 K at saturation exposure (data not shown).

O(1s) X-ray photoelectron spectra collected for multilayers of water adsorbed at 100 K and after annealing a saturation expoosure of water to 300 K are shown in Figure 3. The peak near 530 eV is due to the atomic oxygen overlayer. Multilayers of water were found to have a binding energy of 533.6 eV (Figure 3a). The small peak centered at 531.4 eV is attributed to OH groups in the first monolayer or hydrogen-bonded layers of water on the surface. After annealing to 300 K, a temperature past multilayer sublimation and the sharp 240 K desorption (see Figure 2), two peaks are resolvable in the O(1s) X-ray photoelectron spectrum at 531.8 and 529.9 eV with an area ratio of ~2:3. The 529.9-eV peak is due to the 0.33 monolayer oxygen overlayer as mentioned above. The peak at 531.8 eV is assigned to hydroxyl groups on the oxygen-precovered surface based on the temperature programmed reaction isotopic exchange results presented above, and the agreement of the binding energy observed here with that observed for OH groups on other metals. A study of water adsorbed on Cu(111) assigned O(1s) values of 533.5 eV for water multilayers, 533.3 eV for adsorbed water, and 531.5 eV for hydroxyl groups on the surface.[12] Water adsorption on oxygen-covered Ag(110) has also been studied previously by X-ray photoelectron spectroscopy;[13] the O(1s) binding energy of hydroxyl groups on the surface was found to be 532 eV.

3.2. Phenol: Reaction at Saturation Coverage. Temperature prorammed reaction and X-ray photoelectron spectroscopies were used to study the reaction of phenol adsorbed on a Mo(110) surface which was precovered with 0.33 monolayer of oxygen atoms. The temperature programmed reaction spectrum shown in Figure 4 is obtained after adsorbing a saturation exposure of phenol on the oxygen-precovered surface at a crystal temperature of 100 K. Four gas-phase products are evolved: dihydrogen, water, phenol, and benzene. All masses in the range of 2–150 amu were monitored for reaction products after exposing the oxide to a saturation dose of phenol, but no other gaseous products were detected. Consistent with results found for the clean surface,[1] phenol multilayers sublime from the surface at 210 K. In contrast to reaction on the clean surface where no molecular phenol desorption is observed above 240 K, molecular phenol is desorbed from the oxygen-precovered surface at 650 K. Additionally, high-temperature dihydrogen (β_2) evolves at 725 K on the oxygen-precovered surface, almost 200 K higher than that observed from phenol reaction on the clean surface. H_2 produced from recombination of hydrogen atoms, measured in a separate experiment after dosing the 0.33 monolayer oxygen overlayer with a saturation dose of H_2 (data not shown), occurs at 450 K and produces the additional reaction product H_2O at 400 K. Since the peak maximum of the β_2-dihydrogen is well above 450 K, this dihydrogen must be evolved from decomposition of a stable surface intermediate.

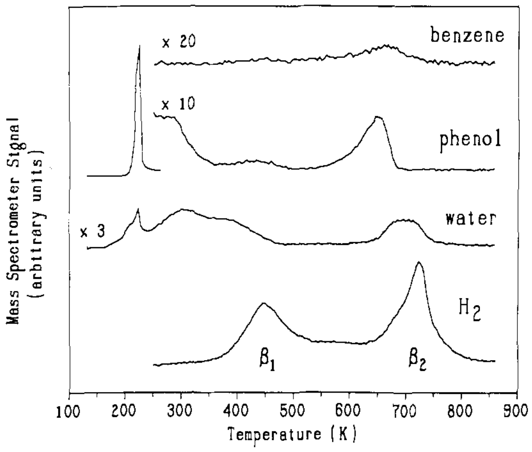

Figure 4. Temperature programmed reaction spectra after exposure of Mo(110) precovered with 0.33 monolayer of atomic oxygen to a saturation exposure of phenol. Four gaseous reaction products are observed: phenol (94 amu), dihydrogen (2 amu), water (18 amu), and benzene (78 amu).

As on the clean surface, decomposition is a significant reaction pathway on the oxygen-precovered surface. Consistent with the observation of the decomposition products, dihydrogen and water (Figure 4), is the presence of atomic carbon after reaction to 850 K in the Auger electron and X-ray photoelectron spectra. Although atomic carbon and oxygen are formed on the surface during temperature-programmed reaction, no desorption of CO arising from recombination of carbon and oxygen is observed during temperature-programmed reaction to 850 K, presumably because CO recombination and desorption do not occur until temperatures around 1000 K on Mo(110).[14] Comparing the peak-to-peak height of the carbon(KLL) Auger transition to the molybdenum (LMM) Auger transitions for the clean and oxygen-precovered surfaces after reaction of a saturation exposure of phenol to 850 K reveals that only 45% as much phenol decomposes on the oxygen-precovered surface as on the clean surface.

Water produced during reaction of phenol on oxygen-precovered Mo(110) arises from recombination of hydrogen with oxygen in the oxygen overlayer at low temperature and decomposition of a stable surface intermediate at high temperature. The origin of the low-temperature water is revealed by reaction of phenol on an ^{18}O overlayer (data not shown). The water desorbed at low temperature from reaction of phenol on the ^{18}O overlayer contains predominantly ^{18}O, although small amounts of ^{16}O-containing water were also detected.[15] If phenol-h_6 is adsorbed on oxygen-precovered Mo(110) followed by deuterium atom adsorption, no deuterium is incorporated into the low-temperature water desorption peaks. Thus, low-temperature water is formed from a hydrogen in phenol (which is shown below to be the alcoholic hydrogen) and oxygen in the overlayer. Also, note that the sharp peak in the water desorption from a multilayer exposure of phenol (Figure 4) at 210 K appears from cracking of phenol in the mass spectrometer to 18 amu.

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[15] The [^{16}O]water arises from very small amounts of oxygen always present on the clean Mo(110) crystal. This was demonstrated by varying the length of time for the ~1900 K anneal used to remove oxygen from the crystal after cleaning and measuring the difference in the ratio of 18 to 20 amu desorption after ^{18}O overlayer formation and phenol reaction. As expected, the shorter the annealing time, the greater the 18:20 amu ratio.

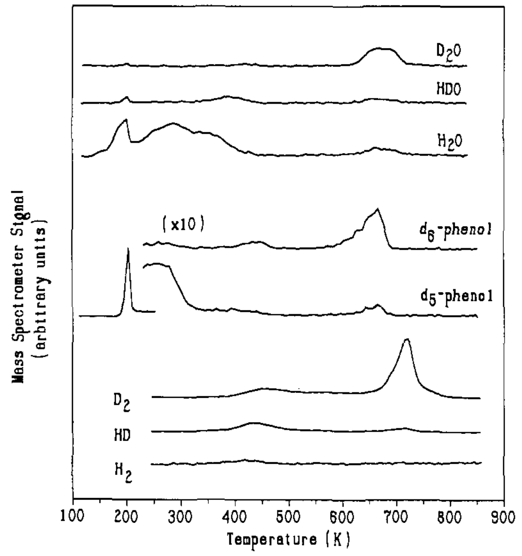

Figure 5. Temperature programmed reaction spectra of H_2 (2 amu), HD (3 amu), D_2 (4 amu), phenol-d_5 (99 amu), phenol-d_6 (100 amu), H_2O (18 amu), HDO (19 amu), and D_2O (20 amu) evolved after a saturation exposure of phenol-d_5 (C_6D_5OH) to the 0.33 monolayer oxygen-precovered Mo(110) surface at 100 K.

The water desorbed at high temperature after saturation phenol exposure must be associated with reaction of a surface species that arises only from phenol. Comparison of the temperature-programmed reaction of water produced in the reaction of phenol (Figure 4) and that from reaction of water (Figure 2d) shows that water alone produces no high-temperature desorption (>500 K) on the 0.33 monolayer oxygen overlayer. The water formed at high temperature from reaction of phenol-h_6 on an ^{18}O overlayer incorporated both ^{16}O and ^{18}O, consistent with decomposition of a surface species containing an intact C–O bond that decomposes to release hydrogen to react with surface oxygen to form [^{18}O]-water or with the ^{16}O present in the C–O bond.

To ensure that the observed water formation arises from reaction of phenol on the oxide surface and not from water impurity in the phenol sample, $H_2{}^{18}O$ was adsorbed at 100 K before and after dosing phenol on the ^{16}O overlayer (data not shown). In neither case did the characteristic water desorption from phenol appear at 20 amu—only desorption similar to that observed from dosing water on the oxygen-precovered surface was observed at 20 amu. Additionally, no water desorption is observed from reaction of phenol on clean Mo(110),[1] making it unlikely that water is present as a sample impurity.

Unlike reaction of phenol on the clean surface, there is an additional reaction pathway on the 0.33 oxygen overlayer surface to desorb phenol and trace amounts of benzene at very high temperature (Figure 4). This reaction occurs only at high coverage (>0.67 of saturation) and is associated with the production of high-temperature dihydrogen and water, suggesting that a stable surface species forms phenol and benzene in competition with nonselective decomposition. Benzene is evolved only in trace amounts from saturation exposures of phenol in a single peak centered at 660 K, a temperature sufficiently different from that of phenol desorption to preclude the assignment of this peak as a cracking fraction of phenol. In addition to the formation of phenol at high temperature, a broad phenol desorption coincident with the desorption of water is observed in the range of ~210–325 K after saturation phenol exposures.

The temperature programmed reaction spectrum of a saturation exposure of phenol-d_5 (C_6D_5OH) on the 0.33 oxygen-precovered surface (Figure 5) shows that the phenol evolved at high temperature arises from recombination of phenoxide groups on the surface and deuterium atoms. The prevalence of phenol-d_6 in the phenol desorption at 650 K demonstrates that C_6D_5O groups on the surface disproportionate to form phenol-d_6, D_2O, D_2, and surface carbon. X-ray photoelectron results presented below show that carbon–oxygen bonds are present to temperatures up to 650 K, supporting the identification of the surface species as phenoxide. This assertion is further supported by labeling experiments in which a saturation exposure of phenol-h_6 is reacted on the 0.33 monolayer ^{18}O overlayer (data not shown). These experiments demonstrate that no ^{18}O is incorporated into the phenol desorbing from the surface at high or low temperature, showing that C–O bond cleavage does *not* occur in the surface species leading to these desorptions.

Table I. X-ray Photoelectron Curve-Fitting Parameters for Phenol on Mo(110) + 0.33 oxygen

		C(1s)		O(1s)	
525 K	binding energy, eV	285.1	283.6	531.6	530.0
	area, count·eV/s	1066	4145	5825	9591
	fwhm, eV	1.2	1.2	1.3	1.3
675 K	binding energy, eV	283.8	283.0	531.4	529.9
	area, count·eV/s	408	1369	2589	10448
	fwhm, eV	1.0	1.0	1.5	1.3
850 K	binding energy, eV		282.7	531.4	530.0
	area, count·eV/s		1554	2200	8784
	fwhm, eV		1.0	1.5	1.3
oxygen	binding energy, eV			531.4	530.0
	area, count·eV/s			2671	9210
	fwhm, eV			1.5	1.3

The low-temperature desorption of phenol arises from intact molecular phenol. Reaction on the oxygen-precovered crystal after dosing a saturation amount of phenol-h_6 at 100 K, followed by a saturation exposure of D_2, evidences no incorporation of deuterium into molecular phenol desorbed below 350 K (data not shown). This assignment is further supported by the results of the phenol/^{18}O overlayer experiment presented above, which demonstrate that no C–O bond cleavage occurs in the low-temperature molecular desorption.

The dihydrogen desorption arising from decomposition of the phenoxide groups present on the oxygen-precovered surface until high temperature (650 K) is generated by the cleavage of C–H bonds. The temperature programmed reaction spectrum of an approximately 1:1 mixture of phenol-h_6 and phenol-d_6 coadsorbed to saturation at 100 K on the Mo(110)–0.33 O surface evidences an isotope effect in the temperature of the β_2-peak maxima of D_2, HD, and H_2. D_2 formation peaks ~5 K higher than HD, and HD at ~5 K higher than H_2. No isotope effect is observed in the leading edge of the β_1 desorption peaks for H_2, HD, and D_2 after reaction of the mixture on the oxygen-precovered crystal consistent with the rate of β_1-dihydrogen formation being limited by recombination of hydrogen atoms on the surface. Also, there is no isotope effect in hydrogen and deuterium desorption from clean Mo(110).[16] The observed isotope effect in the β_2 peak is indicative of the cleavage of C–D and C–H bonds to form dihydrogen arising from the decomposition of a phenoxide intermediate.

Carbon (1s) and oxygen (1s) X-ray photoelectron spectra obtained after saturation exposure of phenol to the 0.33 oxygen monolayer Mo(110) surface show that the C–O bond remains intact to temperatures above 525 K, consistent with formation of surface phenoxide. Data collected after annealing to 525, 675, and 850 K are shown in Figure 6 and summarized in Table I. The C(1s) spectrum obtained after annealing to 525 K [Figure 6a(i)], a temperature below that of the high-temperature phenol, dihydrogen, and water desorptions, can be fit with two peaks corresponding to the inequivalent carbons in the phenyl ring of a phenoxide species. The relative intensity of the two peaks is ~1:4, not 1:5 as expected, when only two peaks are used to fit the data. An alternate fit with three peaks (data not shown) gives the expected intensity ratio since the carbons ortho to the oxygen substituent position are shifted by a small amount from the meta and para carbons. The results of X-ray photoelectron experiments on multilayers of phenol, presented elsewhere,[1] show the splitting of the carbon bound to oxygen and those at other positions in the ring to be 1.7 eV, in close agreement with that of 1.5 eV observed

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here (Table I). The presence of carbon with a binding energy of 285.1 eV indicates that C–O bonds are still intact at 525 K, in agreement with the labeling experiments discussed above. The combination of X-ray photoelectron data and temperature programmed reaction data show that the predominant species on the surface up to and after annealing to 525 K is phenoxide.

At temperatures less than 525 K, the C(1s) spectrum is essentially identical with that shown in Figure 6a(i) (data not shown). After annealing to 675 K, where high-temperature phenol desorption has commenced, a lower binding energy peak at 283.0 eV appears, attributed to the presence of atomic carbon or CH groups on the surface. Thus, C–C bonds are cleaved between 525 and 675 K, consistent with disproportionation of a phenoxide surface species to desorbing phenol and decomposition products. Annealing to 850 K, a temperature where dihydrogen evolution is complete, yields one C(1s) peak at a binding energy of 282.7 eV, attributed to atomic carbon [Figure 6a(iii)]. From Table I, the areas of the curve-fitted C(1s) peaks at 525 and 850 K indicate that ~72% of the carbon present on the surface desorbs between 525 and 850 K.

Figure 6 also shows the corresponding oxygen (1s) X-ray photoelectron spectra obtained from a saturation exposure of phenol on the oxygen-precovered surface. The peak present in all three spectra at 530.0 eV is due to atomic oxygen present in the overlayer. After annealing to 675 and 850 K [Figure 6b(ii) and (iii)], only atomic oxygen is present on the surface. The peak detected at 531.4 eV in these two spectra is attributed to a shake-up of the 530.0-eV atomic oxygen peak, since it is always observed when atomic oxygen is present on the Mo(110) surface, even after annealing to 1000 K.[1] Thus hydroxyl groups on the surface cannot be the origin of this peak since all hydrogen-containing species desorb at temperatures well below 1000 K. Furthermore, readsorption of hydrogen-containing species after annealing and cooling can be ruled out based on the fact that no H_2 or H_2O is desorbed during temperature-programmed reaction performed after X-ray photoelectron data collection. The tail to high binding energy observed here is found to be present on all O(1s) peaks studied on Mo(110) and is attributed to core-hole lifetimes, electron-hole pairs, or phonon creation which asymmetrically broaden core peaks on the high binding energy side.[17] At lower annealing temperatures (525 K and lower) another peak at 531.6 eV is detected [Figure 6b(i)]. The ratio of the areas of the peak centered at 531.6 eV to that of the atomic overlayer peak was found to change on annealing from 225 to 350 to 525 K (data not shown) with the higher binding energy peak decreasing in relative intensity and loss of intensity in the high binding energy side of the 531.6 eV peak tail. The peak at 531.6 eV is attributed to surface phenoxidde since it disappears in the range of 650–700 K, the same temperature at which phenol formation is observed (Figure 4). Recall that reaction of phenol-d_5 shows that all O–H bonds are broken by 525 K, ruling out intact phenol as a possible surface intermediate. However, the binding energy of 531.6 eV observed here for phenoxide is significantly shifted from that proposed for phenoxide on the clean surface (530.8 eV)[1] and measured previously for alkoxide groups on Cu(110): 530.7–531.0 eV.[18] The higher binding energy is attributed to a shift induced by the oxygen overlayer. Previous X-ray photoelectron studies of molecular CO adsorbed on oxygen-precovered Mo(110) showed a shift of the O(1s) peak attributed to CO by ~1 eV higher from that on the clean surface.[4] The physical origin of this shift is unknown, but may be due to an increase in the acidity of Mo atoms caused by the presence of the electronegative oxygen overlayer leading to a more positive charge on oxygen in phenoxide and hence a higher oxygen binding energy.

A rough estimate of the saturation coverage of phenoxide on the 0.33 oxygen-precovered surface may be made by comparing the 525 K O(1s) X-ray photoelectron intensities of the phenoxide and atomic oxygen peaks. The presence of oxygen shake-ups on the atomic oxygen and phenoxide oxygen peaks makes this determination inaccurate; however if we ignore intensity from the shake-ups on both peaks, a rough estimate of the coverage can be made. The intensity of the 531.6-eV phenoxide peak is increased by the atomic oxygen shake-up, but the shake-up from the 531.6-eV peak has not been included in the curve fit shown [Figure 6b(i)] causing a decrease in the measured area of the 531.6-eV peak. The increase caused by the atomic oxygen shake-up is expected to be larger than the decrease caused by the 531.6-eVshake-up, so our estimate is likely to be an upper limit. Comparison of the areas of the two peaks gives a phenoxide coverage of ~0.2 monolayer at 525 K.

In addition to formation of phenoxide groups on the surface that decompose at high temperature, there is also evidence for a minor amount of competing decomposition after saturation phenol exposure on oxygen-precovered Mo(110). The temperature programmed reaction spectrum of phenol-d_5 on the oxygen-precovered surface (Figure 5) shows that some D_2 and HD are formed at temperatures around 450 K, indicative of some cleavage of ring C–D bonds. The amounts of these isotopes produced are small ($\ll$10%), so the *predominant* reaction pathway at saturation exposure is formation of phenoxide groups on the surface. X-ray photoelectron results presented above show no evidence of decomposition below 525 K, confirming that decomposition at low temperature is a very minor reaction pathway. There is also evidence for a small amount of reversible C–D bond activation in the temperature-programmed reaction data: some phenol-d_5 is produced in the high-temperature phenol desorption after reaction of phenol-d_5 (Figure 5). Since this phenol arises from phenoxide reaction at a temperature above that of desorption of recombined surface hydrogen, a small amount of reversible C–H bond activation must be occurring at low temperature.

3.3. Phenol: Reaction at Subsaturation Coverages. The stability of phenoxide is strongly dependent on phenol coverage. Importantly, no gaseous products (phenol, water, dihydrogen, or benzene) are formed in the disproportionation reaction at high temperature for phenol exposures less than 0.25 of saturation. Figure 7a shows the evolution of the decomposition product, dihydrogen, from reaction as a function of phenol exposure. At saturation coverage [Figure 7a(vi)], dihydrogen is formed in two peaks centered at 450 and 740 K, labeled β_1 and β_2, respectively. As a function of exposure, β_1 remains constant with respect to temperature; however, β_2 shifts from ~550 K at an exposure 0.08 of saturation [Figure 7a(i)] to 740 K at saturation. The shift in the temperature of maximum desorption in the β_2 peak with exposure indicates that the surface intermediate that decomposes to produce β_2-dihydrogen and has been identified as phenoxide for saturation exposure is stabilized at high phenol exposures. As mentioned previously, dihydrogen evolved from recombination of H atoms on the oxygen-precovered surface has been found to desorb at ~450 K. High-temperature water and phenol desorption (Figure 7, parts b and c) are found only for initial phenol exposures ≥0.33 and 0.67 of saturation, respectively, suggesting that surface phenoxide is only stabilized with respect to decomposition at phenol coverages at least 0.33 of saturation.

C(1s) and O(1s) X-ray photoelectron data were collected for an exposure 0.25 of saturation, an exposure where no high-temperature phenol is produced [Figure 7(iii)]. The data are not shown here since the signal-to-noise ratio was low at this low coverage, allowing only qualitative interpretation. Both the C(1s) and O(1s) spectra were identical with those obtained for saturation exposures up to 300 K; however, decomposition to atomic oxygen and carbon with a binding energy of 283.0 eV attributable to atomic carbon or CH groups on the surface occurs by 475 K. Thus, the stability of the surface phenoxide species on the oxygen-precovered surface is affected significantly by coverage, with faster decomposition kinetics being observed at low phenol exposures.

4. Discussion

Surface phenoxide is stabilized to ~300 K higher ($\Delta E_a \sim 20$ kcal/mol)[19] than on clean Mo(110) by the presence of oxygen

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atoms after saturation phenol exposure. Based on the temperature programmed reaction and X-ray photoelectron data presented above, we propose the scheme shown in Figure 8 for the reaction of phenol at saturation coverage on the 0.33 monolayer oxygen covered Mo(110). After adsorption of phenol on oxygen-precovered Mo(110) at 100 K, the O–H bond cleaves to form surface phenoxide (C_6H_5O) at low temperature. Competing with phenoxide formation is desorption of intact molecular phenol. Hydrogen released by O–H bond cleavage reacts with oxygen in the oxygen overlayer to form gaseous water at temperatures below 400 K. Dihydrogen is also formed at around 450 K. Surface phenoxide is stable with respect to decomposition up to ~600 K, where it undergoes disproportionation to the decomposition products dihydrogen, water, and surface carbon or reacts with hydrogen released by C–H bond cleavage in other phenoxides to reform gaseous phenol.

The results of isotopic labeling experiments show that low-temperature water desorption arises from hydrogen evolved from O–H bond cleavage and oxygen in the oxygen overlayer. However, the mechanism by which water is formed at low temperature is not known in detail. In particular, it is not known whether OH groups are formed on the surface as intermediates in the water formation reaction. Oxygen (1s) X-ray photoelectron results suggest that OH may be present at low temperature. On annealing from 350 to 525 K, the relative intensity of the high binding energy oxygen (1s) peak attributed to phenoxide (531.6 eV) to that of the atomic overlayer peak decreases. This decrease could be due to formation of water from surface OH groups, which were measured in separate experiments on water to have a binding energy of 531.8 eV on the oxygen-precovered surface.

The coverage of surface species derived from the reaction of phenol on the oxygen-precovered Mo(110) surface is found to have a significant effect on the kinetic stability of the phenoxide intermediate. Temperature programmed reaction and X-ray photoelectron results for subsaturation phenol exposures demonstrate that although phenoxide is probably still formed at lower coverage, it begins to decompose by 475 K for exposures 0.25 of saturation. Thus, slower decomposition kinetics are observed at saturation coverage due to stabilization by other phenoxide intermediates. Similarly, surface phenoxide was also found to be stabilized with respect to decomposition at high coverage after reaction of phenol on Mo(110).[1] Either electronic effects caused by the modification of the surface electronic structure on adsorption of phenoxide or geometric constraints on the surface sites available for decomposition reactions at high coverage may be responsible for the observed stabilization. The second possibility may be explored further if the geometry of phenoxide on the surface can be determined. We have estimated the saturation coverage of phenoxide to be ~0.2 monolayer based on the ratio of the intensities of the 525 K O(1s) peaks of phenoxide and atomic oxygen. At this coverage it would be difficult for phenoxide species to fit onto the surface with the ring parallel to the metal surface unless the layer were azimuthally ordered, assuming van der Waals atomic radii and standard bond lengths for phenyl and C–O bonds. Thus, a different geometry of phenoxide on the surface at high and low coverage could play a role in the observed stabilization at high coverage. The orientation of the phenoxide species on the oxygen-precovered surface is not known; however, near-edge X-ray absorption fine-structure measurements (NEXAFS) are planned that may provide this information.

On both the clean Mo(110) and oxygen-precovered surfaces O–H bond cleavage to form phenoxide is the first step in reaction of phenol. On the clean surface O–H bond cleavage occurs at temperatures below 360 K.[1] The results of temperature programmed reaction experiments on phenol-d_5 (C_6D_5OH) presented here show that hydrogen from the O–H bond is evolved primarily at low temperature in H_2O desorption, consistent with cleavage of the O–H bond between 100 and 400 K on the oxygen-precovered surface. Therefore, in both cases, phenoxide is formed at temperatures below 400 K. In addition, phenoxide is present with other species on the surface for both the clean and oxygen-precovered surface. X-ray photoelectron results for phenol on the clean surface show that, at 300 K, at least two species are present on the Mo(110) surface after reaction of phenol, one of which can be identified as phenoxide. The other species is thought to be either molecular phenol or a second absorption state of phenoxide. On the oxygen-precovered surface, the desorption of intact molecular phenol does not conclude until approximately 350 K, indicating that adsorbed phenol is undergoing competing desorption and formation of surface phenoxide at temperatures lower than 350 K. Additionally, OH groups and/or atomic hydrogen may be present on the oxygen-precovered surface at low temperature.

The reactivity of phenoxide on the two surfaces dramatically differs at temperatures above 350 K. The cleavage of C–H and C–O bonds commences at this temperature on the clean Mo(110) surface, leading to irreversible decomposition to dihydrogen, surface carbon, and oxygen. However, on the oxygen-precovered surface we find that surface phenoxide is stabilized with respect to C–O and C–H bond cleavage to temperatures above 600 K. This corresponds to an increase in the activation energy for decomposition of ~20 kcal/mol. The enhanced stability of phenoxide on the oxygen-precovered surface also results in a change in the product distribution. Specifically, phenol and trace amounts of the hydrogenolysis product, benzene, are formed along with the decomposition product water from reaction on the oxygen-precovered surface.

The presence of atomic oxygen may exhibit several different effects on the reactivity of adsorbed molecules on metal surfaces. Oxygen may act as a Brønsted base by abstracting hydrogen. This effect has been observed in the reaction of higher alcohols to alkoxy surface species on Cu(110),[20] Ag(110),[21] and Pd(111),[22] and for methanol on Ni(111),[23] Pt(111),[24,25] Pd(111),[22] Pd(100),[26] and Rh(111).[27] The formation of water from the abstracted hydroxyl hydrogen and the oxygen in the overlayer is thought to enhance the yield of adsorbed alkoxy on the surface. Oxygen may also withdraw negative charge from metal atoms, increasing the Lewis acidity of the metal atoms. This effect should increase the surface-adsorbate bond energy of species bound to the surface via a Lewis base type interaction. Finally, molecular CO and alkoxy species have been observed to be stabilized with respect to decomposition when oxygen is present, as mentioned previously.[3,18] This effect could be due to either electronic changes arising from the presence of the atomic oxygen or the blocking of surface sites necessary for reaction.

In comparing the reaction of phenol on the clean and oxygen-precovered surfaces of Mo(110) we find evidence for several of the effects mentioned above. Water is produced at low temperature as phenol is converted to phenoxide on the oxygen-precovered surface, in a process similar to that observed in the reaction of alcohols on oxygen-covered group VIII and IB transition metals. It is interesting to note that this reaction is not observed for methanol on oxygen-precovered Mo(100),[3] suggesting that this reaction may have a strong crystallographic dependence for molybdenum.

The presence of atomic oxygen overlayers strongly affects the kinetics for decomposition in the reaction of phenol on the oxygen-precovered Mo(110) surface compared to reaction on the clean surface. However, over the limited oxygen-precoverage range investigated (0.25–0.50 monolayer), the exact oxygen precoverage

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(19) The assumptions used here are that the activation energy for phenol desorption is an upper bound on the activation energy for the phenoxide disproportionation reaction; the disproportionation reaction is a first-order process; the preexponential factor is 10^{13} s^{-1}.

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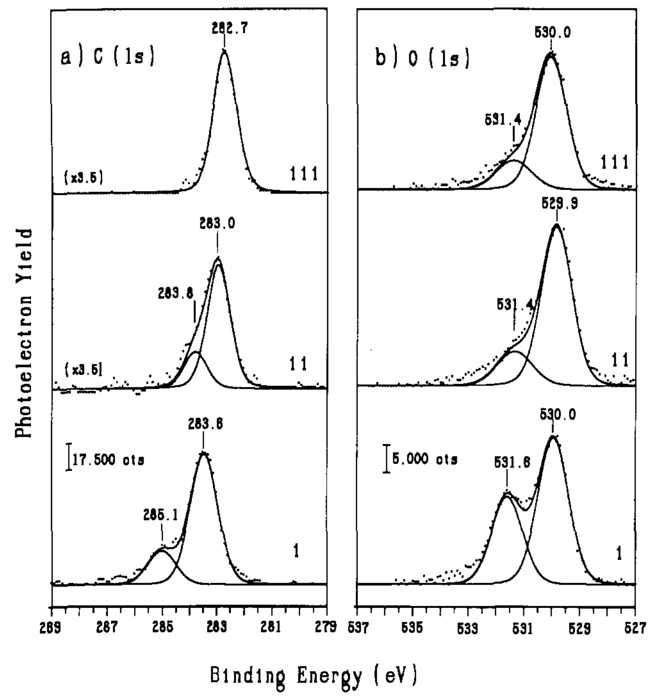

Figure 6. X-ray photoelectron spectra of phenol adsorbed on 0.33 monolayer oxygen-precovered Mo(110) surface at 100 K and annealed to (i) 525, (ii) 675, and (iii) 850 K. C(1s) data are shown in (a) and the corresponding O(1s) data in (b).

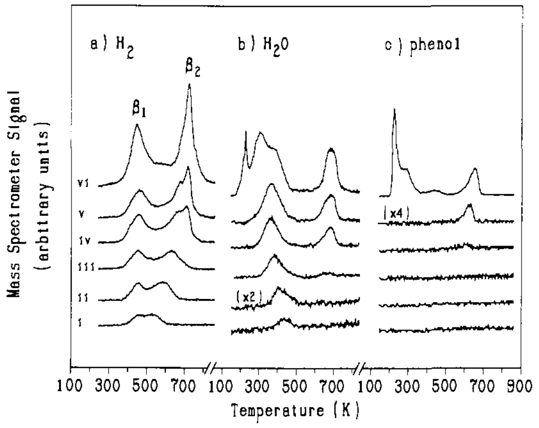

Figure 7. Temperature programmed reaction spectra of (a) dihydrogen (2 amu), (b) water (18 amu), and (c) phenol (94 amu) evolved during reaction of phenol on 0.33 monolayer oxygen-precovered Mo(110) after adsorption at 100 K as a function of phenol exposure. The phenol exposures shown are the following: (i) 0.08, (ii) 0.17, (iii) 0.25, (iv) 0.33 (v) 0.67, and (vi) 1.00 of saturation.

was not found to affect the temperature to which the phenoxide species was stabilized before decomposing for saturation phenol exposures. Thus, the presence of only a small amount of surface oxygen induces the significant stabilization with respect to decomposition observed for high phenol coverages. It is not likely that differences in phenoxide coverage on the clean and oxygen-precovered surface are responsible for this stabilization, since X-ray photoelectron results suggest that the saturation coverage after desorption of molecular phenol at low temperature is similar on both surfaces.

It is difficult to determine whether the disproportionation reaction observed at high temperature on the oxygen-precovered surface is initiated by C–O or C–H bond cleavage in surface phenoxide. Although the results of the phenol-h_6/phenol-d_6 mixture experiment show that the evolution of high-temperature dihydrogen arising from decomposition of the phenoxide surface species exhibits an isotope effect, demonstrating that dihydrogen evolution arises from C–H bond cleavage, no information regarding whether C–H or C–O bond cleavage initiates disproportionation is provided by this experiment. Previous studies of the C_1 through C_3 alcohols on clean and oxygen-precovered Cu(110)[18] show that the decomposition temperature of surface alkoxides can be correlated with the C–H bond strength for hydrogens on the carbon bonded directly to oxygen, suggesting that C–H bond cleavage controls alkoxide decomposition. In the case of phenol on oxygen-precovered Mo(110), the fact that phenol desorption is observed in significant amounts rather than only nonselective decomposition suggests that selective cleavage of one C–H bond occurs first, leading to phenol formation. However, decomposition of some surface phenoxides via either C–H or C–O bond activation could modify the surface kinetics sufficiently to favor phenol formation and desorption.

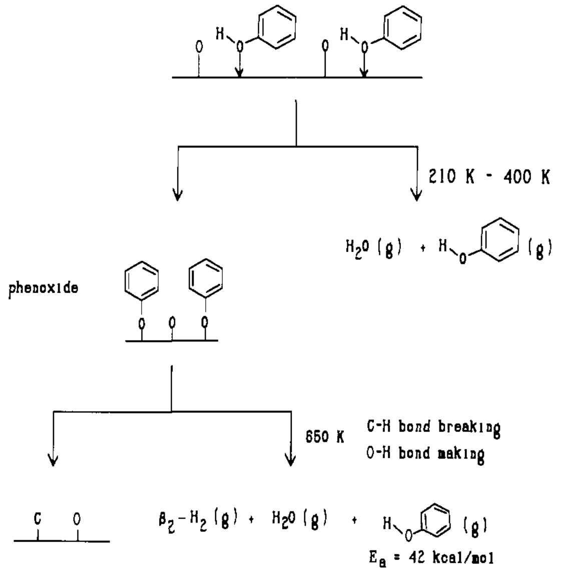

Figure 8. Reaction scheme for phenol on 0.33 monolayer oxide Mo(110) surface after adsorption at 100 K at saturation phenol exposure.

Further studies leading to a better understanding of the effect of oxygen overlayers on the reactivity of Mo(110) are planned. Both electronic and geometric effects, such as the structure of surface species, may play a role in the increased stability of surface phenoxide in the presence of surface oxygen. Near-edge X-ray absorption fine-structure measurements of surface phenoxide wiil provide important information about the structure of the species on the surface and the effect of structure on the observed reactivity. Finally, a comparison of the reaction of other alcohols on the same surface may provide insight into the relationship between C–O and C–H bond strength and reactivity of the oxygen-precovered surface. In particular, it will be interesting to see if the production of water at low temperature is unique to the reaction of phenol, which is known to be a relatively strong Brønsted acid in comparison to other alcohols.

5. Conclusions

Surface phenoxide is stabilized to temperatures ~300 K higher than on the clean Mo(110) surface by the presence of 0.33 monolayer of atomic oxygen. At low-temperature and saturation coverage, phenol undergoes competing molecular desorption and formation of surface phenoxide. Water is produced at low temperature from the hydrogen released in cleavage of the O–H bond and the oxygen in the oxide. Surface phenoxide disproportionates to gaseous phenol and the decomposition products water, dihydrogen, and surface atomic carbon at temperatures above 600 K. Reaction on the oxygen-precovered surface exhibits much slower kinetics for C–O and C–H bond activation than reaction on the clean surface. Furthermore, decomposition kinetics are found to be much faster at lower phenol coverages, with no formation of gaseous phenol observed, indicating self-stabilization of phenoxide at high coverage.

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