Changing Reactivity of a Bimetallic Surface via Oxidation: Reactions of Methanol on Oxygen-Covered Co Thin Films

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Methanol reaction on oxygen-covered Co thin films deposited on Mo(110) exhibits selectivity different from reaction on the pure Co overlayers. The presence of oxygen favors partial oxidation to formaldehyde over decomposition to CO and H_2. Other products evolved from methanol reaction on the Co−oxygen overlayer are CO, methyl radicals, H_2O, H_2, and methanol. In addition to inhibition of C−H bond breaking, oxidation also decreases the activity of the Co surface toward C−O and O−H bond scission, leading to a reduction in total reactivity. Furthermore, electron energy loss data show that the methoxide intermediate is stable up to high temperatures ($\sim$450 K). The dependence of product yields on oxygen and Co coverages indicates that formaldehyde production occurs on oxygen-covered Co and does not result from oxygen-induced restructuring of the Co overlayer. These studies of oxygen-covered Co thin films on Mo(110) demonstrate that the activity of a bimetallic surface can be altered by the extent of oxidation in a manner similar to oxidation of bulk transition metals.

Introduction

The chemistry of methanol on transition-metal surfaces is an important area of research since it probes the microscopic reverse and secondary pathways in catalytic partial oxidation processes. Both Co and Mo play important roles in the catalysis of oxygen-containing molecules. For example, the partial oxidation of methanol to formaldehyde is carried out over Mo oxides promoted by mid-transition metals such as Fe,[1,2] while the synthesis of methanol from CO and H_2 is catalyzed by Co particles on an oxide support.[3] Furthermore, Mo-based materials with Co added as a promoter comprise commercial deoxygenation catalysts.[4]

Previous studies of alcohol chemistry on bulk transition metal surfaces, such as Fe(001),[5,6] Mo(110),[7] Pd(111),[8] and (2 × 1)-Pt(110),[9] have demonstrated that oxidation can be used as a means of altering reaction selectivity. Although these studies show potential for selectively modifying catalytic activity, it is important to investigate the influence of oxygen modifiers in bimetallic systems, since the commercial catalysts often consist of more than one metal. It is possible that oxygen modification of thin films will be different from bulk materials because of their different geometric and electronic properties. Herein we report that the addition of oxygen to thin Co films deposited on Mo(110) changes the selectivity for methanol reaction. Selective dehydrogenation producing formaldehyde is favored on the oxidized Co overlayer, whereas only nonselective dehydrogenation to CO and H_2 occurs on the pure Co overlayer. Oxygen decreases the surface activity for C−H, C−O, and O−H bond breaking and stabilizes the methoxide intermediate to $\sim$450 K. Thus, oxidation is used as a means of altering reaction selectivity on the bimetallic Co−Mo surfaces.

The structure[10,11] and reactivity[12−15] of Co overlayers on Mo-(110) have previously been investigated in detail. In the absence of oxygen, the Co overlayer grows pseudomorphically up to a coverage of 1.0 ML, and at 1.3 ML, a more closely packed structure with the same lattice constant as Co(0001) is formed.

Studies of alcohols on Co overlayers have shown that there is no change in chemistry upon varying the Co coverage from 0 to 1.3 ML, except that significant reaction on exposed Mo(110) still occurs for the 1.0 ML overlayer.[13−15]

Our earlier work involving the characterization of the oxygen-on-Co overlayers demonstrated that exposing the 1 ML Co overlayer to a saturation dose of oxygen at 100 K results in oxygen bound to Co.[16] A comparison of the Co(2p) region for this unannealed oxidized Co thin film with that of bulk Co oxides (CoO, Co_3O_4) suggests that the oxidation state of the Co could be a mixture of +2 and +3.[17,18] The lack of attenuation of the Co(2p) signal at temperatures below 600 K indicates that there is *not* a substantial amount of aggregation into three-dimensional islands over the temperature range for methanol reaction. However, subsequent annealing above 600 K causes Co−O bond breaking and Co aggregation into three-dimensional islands as oxygen migrates to the Mo surface.[16]

Experimental Section

Experiments were performed in two separate ultrahigh-vacuum chambers, which have been described previously,[19−21] each with base pressures of $<1 \times 10^{-10}$ Torr. Both chambers are equipped with a computer-controlled UTI mass spectrometer for temperature-programmed reaction experiments and low-energy electron (LEED) optics for characterizing the Co overlayers. Furthermore, one chamber has a computer-controlled high-resolution energy loss spectrometer (LK2000) and a cylindrical mirror analyzer (CMA) for detecting Auger electrons. Sample cleaning and preparation procedures are described elsewhere.[12,20]

Electron energy loss data were collected for approximately 30 min using a primary beam energy of 3 eV at a resolution of $60-64$ cm^{-1}. The crystal was biased to −100 V during temperature-programmed reaction in order to prevent electron-induced reactions caused by the mass spectrometer. The heating profile used in these experiments was not completely linear but was extremely reproducible; between 250 and 700 K the heating rate was 7 ± 3 K/s.

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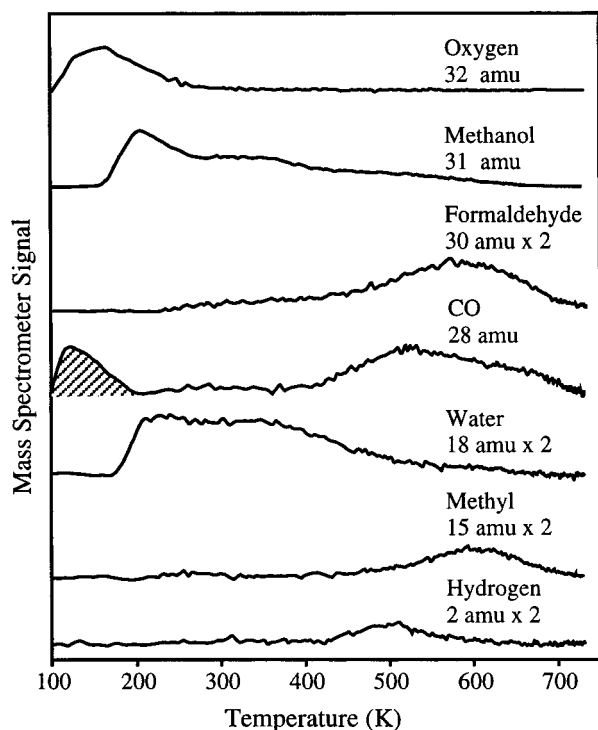
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Figure 1. Temperature-programmed reaction data for methanol on the fully oxidized 1.3 ML Co overlayer. The shaded region represents background CO desorption.

The preparation and characterization of Co overlayers have been described previously.[12,13,16] X-ray photoelectron, temperature-programmed desorption, and LEED data indicate that Co–Mo alloying is unlikely under these Co coverage and preparation conditions. The fully oxidized Co overlayers were prepared by depositing Co at 100 K and annealing to 760 K for 60 s; the surface was then exposed to oxygen for 60 s at a chamber pressure of 1×10^{-9} Torr and sample temperature of 100 K, with the crystal approximately 3 mm away from the stainless steel directed dosing tube.[20,22] The other oxygen-on-Co overlayers were prepared by exposing the Co overlayers to oxygen at a chamber pressure of 1×10^{-9} Torr for 15, 30, 60, and 90 s at 100 K, with the crystal ∼8 mm away from the directed doser.

Methanol (Aldrich, 99.9%) and methanol-d_4 (99.8% d, Cambridge Isotope Laboratories) were used as received. Samples were stored in glass bottles and subjected to several freeze–pump–thaw cycles before use. Sample purities were checked by mass spectrometry.

Results

Formaldehyde (580 K), CO (520 K), methyl radicals (600 K), water (160–500 K), methanol (200 and ∼350 K), and H_2 (500 K) are the gaseous products evolved from the temperature-programmed reaction of methanol on the fully oxidized Co film ($\theta_{Co} = 1.3$ ML) (Figure 1). Some O_2 (32 amu) is also evolved at 175 K and is attributed to desorption of molecular oxygen bound to oxidized Co.[23] All masses up to 80 amu were monitored, and no other gaseous products were detected.[24] Specifically, the absence of 26 and 27 amu signals demonstrates that C_2 hydrocarbon products are not formed. Furthermore, the absence of 43, 44, and 58 amu signals rules out acetaldehyde and acetone as products. The lack of CO desorption around 1200 K from atomic recombination indicates that nonselective decomposition does not occur.

Products were identified based on a quantitative analysis of the mass spectrometer fragmentation patterns. Formaldehyde

evolution was identified from the 29:30 amu ratio of 1.25, which is the same within experimental error to that measured for an authentic sample of formaldehyde, 1.35. The ratio of the corresponding ions (30:32) for the reaction of methanol-d_4 was also 1.25, confirming the product assignment as formaldehyde-d_2. The 28 amu signal attributed to CO evolution was corrected for the cracking contribution from formaldehyde using the 28:30 amu ratio reported in the literature.[25] The assignment of the 15 amu signal to methyl radical production was confirmed by the reaction of methanol-d_4, which produced CD_3 (18 amu); notably, no 16 amu signal was detected. The 30:31 amu ratio of 0.80 for methanol evolution is correct for an authentic sample of methanol, and the 34:36 amu ratio from methanol-d_4 reaction is also correct for methanol-d_4. The H_2O (18 amu) peak at 160 K was corrected for the contribution from methanol multilayer desorption, since the methanol sample itself contained a small amount of H_2O and the temperatures for methanol and H_2O sublimation are similar. The 18 amu intensity was ∼10% that of the 32 amu intensity in the cracking pattern of methanol. The D_2O (20 amu) evolution profile from methanol-d_4 reaction was the same as the corrected H_2O evolution profile from methanol-d_0 reaction. Note that the small H_2 (2 amu) signal is not from background H_2 adsorption, since D_2 (4 amu) is also observed from methanol-d_4 reaction.

The product distribution from methanol reaction on the 1.3 ML Co film depends strongly on oxygen coverage (Figure 2). As the oxygen coverage is increased to saturation, the amount of methanol reaction decreases to ∼25% of that on the pure Co overlayer, based on relative CO and formaldehyde yields;[26] CO and H_2 are the only gaseous products from methanol reaction on the pure Co overlayer.[14] The H_2 yield decreases as a function of oxygen coverage. Likewise, the H_2O yield[27] is greatest at the lowest oxygen coverage (15 s exposure) and decreases with further oxygen exposure. The change in molecular CO yield below 760 K with increasing oxygen exposure is also consistent with an inhibition of C–H bond activation by adsorbed oxygen on the Co; the peak temperature for molecular CO evolution shifts from ∼430 K on the pure Co film to ∼520 K on the fully oxidized Co film. The rise in formaldehyde yield with increasing oxygen coverage indicates a change in reaction selectivity from nonselective decomposition producing CO and H_2 to selective dehydrogenation producing formaldehyde. There is also an increase in methyl radical yield as a function of oxygen exposure, illustrating that methyl formation is associated with the oxygen-covered surface.

The initial increase in molecular CO yield at low oxygen coverage is attributed to reduced surface activity for C–O bond scission in the presence of oxygen (Figure 2). The decrease in recombinant CO production at higher oxygen exposures confirms that less C–O bond dissociation occurs as the oxygen coverage is increased. Previously, we have demonstrated that CO evolution around 1200 K due to atom recombination results from C–O bond dissociation, which is attributed to reaction at exposed Mo and defect sites in the Co overlayer.[14]

The product yields as a function of Co coverage for saturation exposures of oxygen show that C–O bond retention products are favored on oxidized Co while C–O bond scission products are favored on oxidized Mo(110) (Figure 3). Both the formaldehyde[28] and CO yields increase with increasing Co coverage, while the methyl radical production decreases. Studies of methanol chemistry on oxygen-covered Mo(110) have demonstrated that methyl radical is the major gaseous product.[29] The formation of methyl radicals on the oxidized 1.3 ML Co overlayer therefore suggests that defect sites in the close-packed
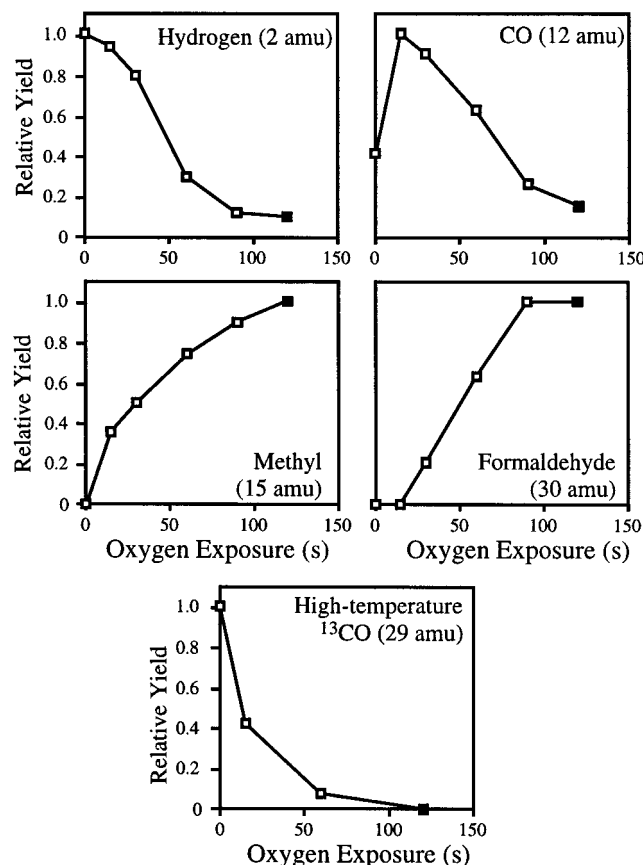
Figure 2. Product yields for methanol reaction on oxygen-on-Co (1.3 ML) overlayer as a function of oxygen exposure. The shaded data points represent the yields for reaction on 1.3 ML of Co with a saturation oxygen exposure; this oxygen-on-Co overlayer was prepared under different dosing conditions than the other overlayers shown and is therefore not part of the oxygen exposure time scale.[27] The yields were normalized by dividing by the maximum value in each plot except in the H_2 case.[45] Carbon monoxide was monitored at 12 amu because of the significant contribution to 28 amu from formaldehyde. The data for the high-temperature CO yield was collected in a separate series of experiments using $^{13}CH_3OH$ to minimize the contribution from background CO.
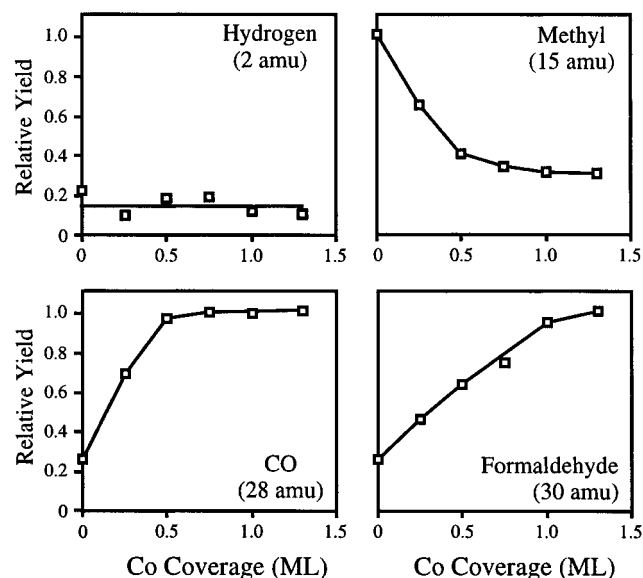

Figure 3. Product yields for methanol reaction on oxygen-on-Co overlayers with a saturation oxygen exposure as a function of Co coverage. The yields were normalized by dividing by the maximum value in each plot.

Co overlayer allow methanol reaction to occur on oxygen-covered Mo(110). Alternatively, oxygen-induced structural changes in the Co overlayer upon heating may also increase the number of exposed oxygen-covered Mo sites.

Electron energy loss data for methanol on the oxidized 1.0 ML Co overlayer heated to 250 K indicate that methoxide is present on the surface, but the presence of some molecular methanol cannot be ruled out (Figure 4c). The losses at 1063, 1454, and 2908 cm^{-1} are assigned to ν(C−O), δ(CH$_3$), and ν(C−H) modes, respectively, for methoxide, methanol, or a combination of the two.[14,30] The absence of a distinct mode at ∼3200 cm^{-1} from ν(O−H) does not conclusively rule out methanol as an intermediate because the O−H stretch is often weak. However, ν(O−H) for molecular methanol on the 1.3 ML Co overlayer *has* been observed at 100 K.[14] Unfortunately, the region near δ(O−H) for methanol (∼700 cm^{-1}) is obscured by the metal−O stretches from the Co−oxygen overlayer. The modes at 3609 and 1600 cm^{-1} are characteristic of molecular H$_2$O on the surface. The 1600 cm^{-1} loss is attributed to δ(H−O−H), based on studies of H$_2$O on Fe(100),[31] Pd(100),[32] and Ag(110),[33] and the mode at 3609 cm^{-1} is assigned to ν(H−O−H) for non-hydrogen-bonded H$_2$O.[31] The frequency for ν(H−O−H) is strongly dependent on the extent of hydrogen bonding and shifts to lower energy at higher H$_2$O coverages.[31−34]

The losses from molecular H$_2$O vibrations, accompanied by H$_2$O evolution between 160 and 500 K, demonstrate that some O−H bonds of methanol are broken to form methoxide. Note that this surface H$_2$O is *not* a contaminant because H$_2$O is not observed on the pure Co overlayer or Mo(110) after heating methanol to 250 K. It is also possible that a hydroxyl species on the surface contributes to the 3609 cm^{-1} loss. Although ν(O−H) for hydroxyl is typically lower than ν(O−H) for molecular water, the O−H stretch for non-hydrogen-bonded hydroxyl on Fe(100) has been observed around 3600 cm^{-1}.[31]

The vibrational peaks associated with H$_2$O/OH disappear after heating methanol on the oxidized Co overlayer to 500 K (Figure 4d), and the resulting spectrum is consistent with a methoxide species. The lack of intensity around 2000 cm^{-1} from ν(CO) illustrates that CO evolution, which commences at ∼450 K, is reaction-limited rather than desorption-limited. The absence of methanol desorption above 500 K suggests that methanol is not present on the surface at this temperature. However, the losses below 1000 cm^{-1} cannot be used to make definitive assignments because this region is again obscured by the metal−O modes from the Co−oxygen overlayer heated to 500 K. The modes at 1454 and 2937 cm^{-1} are attributed to δ(CH$_3$) and ν(C−H), respectively, based on assignments for methoxide on Mo(110)[30] and on the 1.3 ML Co overlayer.[14] The spectrum of methanol-d_4 after heating to 500 K confirms these assignments (Figure 4e) since losses at 2081 and 2236 cm^{-1} are attributed to ν(C−D) and 2δ(CD$_3$), while the shoulder at 1129 cm^{-1} can be assigned to δ(CD$_3$). The loss at ∼980 cm^{-1} in the spectrum of both methanol-d_4 and methanol-d_0 is partially assigned to ν(C−O), but the Co−oxygen overlayer itself has a relatively intense mode at 989 cm^{-1} from oxygen at terminal sites.[16]

The electron energy loss data at 500 K show that formaldehyde is not a surface-stable intermediate. Studies of η^2(C,O) formaldehyde on Pd(111) indicate that ν(C=O) should appear at 1420 cm^{-1}.[35] The absence of a mode at this energy for methanol-d_4 heated to 500 K demonstrates that η^2(C,O) formaldehyde-d_2 is not formed. Furthermore, the lack of intensity at 1695 cm^{-1} from ν(C=O) in both methanol-d_0 and -d_4 reaction indicates that η^1(O) formaldehyde(-d_2) is not produced, based on studies of η^1(formaldehyde) on Rh(111).[36]

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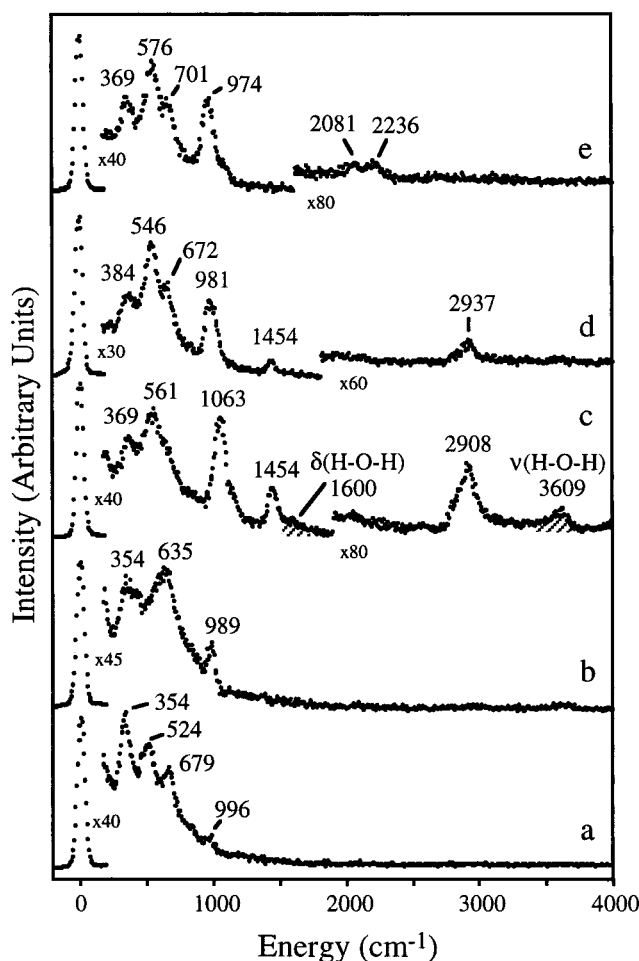*J. Phys. Chem. B, Vol. 102, No. 1, 1998* **109**

Figure 4. Electron energy loss data for methanol on the 1.0 ML Co overlayer exposed to a saturation dose of oxygen at 100 K after (a) heating to 250 K; (b) heating to 500 K; and the Co−oxygen overlayer at 100 K after exposure to a saturation dose of (c) methanol-d_0, heated to 250 K; (d) methanol-d_0, heated to 500 K; and (e) methanol-d_4, heated to 500 K. The full width at half-maximum of the elastic peak was 60−64 cm^{-1} in all cases.

Discussion

The addition of oxygen to the Co thin films deposited on Mo(110) alters the selectivity for methanol reaction by passivating the Co surface toward C−H, C−O, and O−H bond breaking. The substantial (∼25%) decrease in the total amount of reaction and the persistence of molecular methanol up to 400 K reflect an inhibition of O−H bond breaking on the oxidized Co films. Furthermore, the presence of oxygen stabilizes methanol binding to the Co surface, allowing methanol to remain on the surface up to 400 K. The change in product distribution as a function of oxygen exposure illustrates that selective C−H bond scission to produce formaldehyde is favored on oxidized Co, whereas nonselective decomposition to CO and H$_2$ is the major reaction pathway on the pure Co overlayer.[14] The increased temperature for C−H bond breaking reflects decreased dehydrogenation activity. On the oxygen-covered Co overlayer, methoxide is stable below 450 K, based on electron energy loss data and the fact the that onset of CO evolution occurs around this temperature, whereas on the pure Co overlayer, methoxide decomposes below 350 K.[14] Oxidation of the Co overlayer also eliminates the C−O bond dissociation pathway. CO dissociation on the pure Co overlayer has been attributed to reaction at defect sites,[14] suggesting that oxidation of these defects results in suppression of C−O bond breaking.

The reactions of methanol on oxygen-covered Co thin films (1.3 ML) deposited on Mo(110) occurs predominantly on the oxidized Co, not on exposed Mo. Previous X-ray photoelectron studies show that the Co−O bonds basically remain intact up to 600 K, and there is no detectable attenuation of the Co(2p) signal due to aggregation of Co into three-dimensional islands.[16] Furthermore, the increase in formaldehyde yield as a function of increasing Co coverage illustrates that formaldehyde production on the fully oxidized 1.3 ML Co overlayer primarily arises from reaction on oxygen-covered Co, not oxygen-covered Mo-(110). Notably, formaldehyde is not formed from reaction on the pure Co overlayer. Formaldehyde is also not produced from methanol reaction on a surface consisting of three-dimensional Co islands and highly oxidized Mo(110), which is formed by heating the Co-on-oxygen overlayer to 965 K.[16,37] Thus, the temperature-programmed reaction data for methanol demonstrate that significant oxygen migration from Co does not occur below ∼600 K, which is consistent with our previous X-ray photoelectron studies.[16]

Structural changes small enough to not be detectable by X-ray photoelectron spectroscopy may occur upon heating the oxidized Co overlayer, contributing to methyl evolution around 600 K. Although methyl radical formation decreases as a function of increasing Co coverage, it persists even on the close-packed (1.3 ML) oxidized Co overlayer. The onset of Co island formation at ∼600 K during temperature-programmed reaction may cause more Mo−O sites to be exposed, and methyl radicals are the product associated with methanol reaction on oxygen-covered Mo(110).[29] Some methyl radical formation may also be attributed to defects initially present in the Co overlayer which leave oxygen-covered Mo(110) exposed, since studies of alcohol reaction on the pure 1.3 ML Co overlayers have shown that C−O bond scission products associated with reaction on Mo result from such defects in the Co overlayer.[13−15]

The broad product evolution peaks for formaldehyde, CO, water, and methanol in the temperature-programmed reaction of methanol on oxidized Co are most likely related to the heterogeneity of the highly oxidized Co overlayer. The broad features in the low-energy region in the electron energy loss spectrum for the Co−O overlayer (Figure 4) suggest that oxygen is bound at a number of different sites. Based on electron energy loss studies of oxygen on Mo(110),[38] the loss at 996 cm^{-1} could be attributed to terminal oxygen while the 354, 524, and 676 cm^{-1} losses could be attributed to oxygen at the higher coordination sites. Likewise, the large full width at half-maximum (∼2 eV) for the O(1s) peak in the X-ray photoelectron spectrum at 100 K reflects multiple oxygen species on the surface.[16] Minor structural changes, which are not detected by X-ray photoelectron spectroscopy, in the Co overlayer upon heating may also contribute to the surface heterogeneity.

Alcohol reactivity on the pure[13−15] and oxidized Co thin films deposited on Mo(110) is similar to that on modified bulk midtransition metal surfaces. Specifically, the presence of electronegative adsorbates such as oxygen or sulfur inhibits nonselective C−H bond scission such that formaldehyde is produced on Fe(100)−O,[5,6] oxygen-covered Pd(111),[8] (2 × 1)-Pt(110)−O,[9] Fe(100)−c(2 × 2)-S,[39] and Ni(100)−c(2 × 2)-S;[40] decreased total reactivity on the modified surfaces is also observed due to inhibition of O−H bond breaking. On oxygen-covered Pt(110)[41] and Fe(110)[42] formaldehyde is not produced from methanol reaction, but decreased C−H bond activation leads to methoxide stabilization to higher temperatures compared to the clean surface. The reduced surface activity is attributed to a combination of electronic modification and site blocking

for the Fe(100)−O case[5,6,39] and to site blocking for Ni(100)−S[40] and Fe(100)−S.[39]

The reduced activity of the Co thin films in the presence of oxygen may be due to either site blocking or electronic surface modification. Preliminary results for methanol reaction on sulfur-covered Co films show that sulfur reduces total reactivity, perhaps by site blocking, but does not favor partial oxidation of methanol to formaldehyde over decomposition. Since sulfur is larger than oxygen but less electronegative, site-blocking effects are expected to be more significant for the sulfur case, while electronic effects would be less important. This suggests that electronic modification of the Co overlayer contributes to oxygen-promoted selective dehydrogenation. Furthermore, our investigations of ethanol reactivity on Co-on-oxygen and Co-on-sulfur overlayers on Mo(110) illustrate that the reactivity of the Co thin film can be electronically modified by electronegative adsorbates such as oxygen or sulfur.[7] Density functional calculations for the Co−oxygen system are planned to help address this question. These studies of bimetallic Co−Mo surfaces with oxygen added as a modifier demonstrate that methanol reaction selectivity can be altered via surface oxidation.

While our studies indicate that the reactivity of Co thin films is modified by oxygen in a fashion similar to many bulk mid-transition metals, this may not generally be the case. Notably, formaldehyde is not produced in methanol reaction on oxygen-covered Pd thin films (1 ML),[43] whereas $H_2C=O$ is formed from methanol on oxygen-covered Pd(111).[8] On the oxidized Pd monolayer, CO and CO_2 are formed instead. These results indicate that oxygen did not passivate the Pd monolayer toward nonselective C−H bond breaking. Thus, the reaction of methanol is strongly dependent on the Pd coverage and the thermal treatment of the oxidized layers. In particular, oxidation of the Pd monolayer at 1000 K resulted in formaldehyde production from methanol in a process analogous to bulk Pd-(111).[43] These data suggest that the Pd film aggregates into three-dimensional islands at high temperature when oxygen is present, similar to Co on oxidized Mo(110).[16] The contrast between the Pd and Co thin films indicates that additional studies are necessary to discern which properties will control the chemical behavior of metal thin films.

Conclusions

The selectivity for methanol reaction on Co thin films deposited on a Mo(110) substrate can be modified by oxygen in a manner similar to bulk mid-transition metals. Specifically, C−H, C−O, and O−H bond scission is inhibited in the presence of oxygen. On the oxidized Co overlayers, selective dehydrogenation to produce formaldehyde is favored over CO production, which is the major reaction pathway on the pure Co overlayer. The oxidized Co−Mo surfaces exhibit methanol chemistry characteristic of reaction on both oxidized Co and oxidized Mo.

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(22) The oxygen coverage was estimated as ∼2 ML based on the O(1s) X-ray photoelectron signal.[16] The absolute coverage calibration was determined using p(4 × 1) sulfur overlayer known to correspond to a coverage of 0.5 ML[44] and the C(1s):S(2p) and O(1s):C(1s) ratios calculated from the decomposition of thiophene and methanol, respectively, on Mo-(110).

(23) $^{18}O_2$ evolution (36 amu) was observed when the Co−O overlayer was prepared with oxygen-18.

(24) Some 16 amu signal was observed, most likely from methyl radicals reacting on mass spectrometer shield, since CD_3H (19 amu) and not CD_4 (20 amu) was observed in the reaction of CD_3OD.

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(26) Since molecular and recombinant CO are the only C-containing product formed from methanol reaction on the pure Co overlayer, the integrated CO signal from temperature-programmed reaction is used as a measurement of the total reactivity. Similarly, the yields for formaldehyde and CO were used as a measurement of the total reactivity of the oxidized 1.3 ML Co overlayer. The estimated total reactivity is a lower limit since the methyl radical yield was not included in this calculation. Methanol desorption is not considered to contribute to total reactivity. The relative mass spectrometer sensitivities for formaldehyde and CO were determined by leaking in a fixed pressure of authentic CO and formaldehyde samples, in separate experiments, and comparing the signal intensities.

(27) The yield of H_2O is not shown because the 18 amu signal could not be reliably integrated, due to the water contribution associated with methanol sublimation.

(28) Some formaldehyde is produced even on the pure ∼1.0 ML oxygen overlayer on Mo(110). The formaldehyde yield is quite sensitive to the oxygen coverage and preparation conditions.

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(45) Because the level of H_2 production on the highly oxidized surface was very low, the H_2 yields were normalized by dividing by the yield from reaction on the pure Co overlayer, to illustrate that variations in the H_2 signal are from scatter due to experimental error.