Alcohol Chemistry as a Probe of Mixed-Metal Phases: Reactions of 2-Propanol on Cobalt-Covered Mo(110)

D. A. Chen and C. M. Friend*

Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138 Received: July 22, 1996; In Final Form: September 9, 1996[®]

The reactions of 2-propanol on cobalt-covered Mo(110) have been investigated in an effort to test for special reactivity associated with mixed Co–Mo phases. 2-Propanol reacts via 2-propoxide on a continuous Co overlayer supported on Mo(110), as shown by X-ray photoelectron and infrared spectroscopies. Carbon monoxide, acetone, propene, and hydrogen are the only gaseous products, while carbon and oxygen remain on the surface after temperature-programmed reaction up to 760 K. The acetone and CO production increase whereas propene and propane production decrease as the Co coverage is increased from 0 to 1.5 monolayers (ML). This is consistent with independent reactions occurring on both Co and Mo, since 2-propanol is known to produce propene and propane on Mo(110). The C–O bond retention products (acetone and CO) are attributed to reaction on the Co overlayer. Infrared and temperature-programmed reaction studies confirm that the evolution of CO is desorption limited and that decomposition to CO competes with acetone formation at 330 K. Acetone is produced via selective cleavage of the β C–H bond (adjacent to the oxygen), as shown by selective isotopic labeling experiments. The observed C–O bond retention on Co is consistent with the intermediate strength of the Co–O bond compared to other M–O bonds for transition metals. There is no evidence for aggregation of the Co overlayer induced by 2-propoxide, and therefore the observed reactivity is that of the dispersed Co overlayer.

Introduction

The reactions of alcohols on transition metal surfaces are of interest because oxygen-containing molecules are present in liquid fuelstocks and in adhesives used for metal bonding. Furthermore, the reaction of alcohols on transition metal surfaces serves as a model for the catalytic oxidation of alcohols to ketones and aldehydes as well as the microscopic reverse of the Fischer-Tropsch synthesis of hydrocarbons from CO and hydrogen (syngas). Cobalt in particular is used as Fischer-Tropsch catalyst to convert syngas into primary alcohols and aldehydes.¹ Thus, the identification and characterization of intermediates formed from the reaction of alcohols is important for understanding the mechanism of oxygenate synthesis from CO and hydrogen.² Mixed-metal materials are of particular interest because they offer the potential for reactivity different from the individual constituents, either via alteration in geometric structure due to interactions between the metals or via electronic effects that may lead to synergy between the two metals. Indeed, synergistic effects between Co and Mo have been proposed based on theoretical studies to explain Co promotion in hydrodesulfurization catalysis.³ Furthermore, substantial differences in the adsorption properties of carbon monoxide have been reported for thin metal films, such as Pd on Nb(110),⁴ which have larger lattice constants than the bulk materials. Similar results have been reported for CO adsorption on several other thin metal films supported on refractory metals.4-10

Herein, we discuss the reactions of 2-propanol on Co-covered Mo(110). Cobalt overlayers on Mo(110) have been previously investigated in detail, and the lattice spacing was found to depend on Co coverage.^{5,11–15} For coverages less than 1 ML, the Co overlayer grows pseudomorphically, and a (1×1) low-energy electron diffraction (LEED) pattern is observed. This overlayer is strained due to the higher symmetry and smaller

lattice constant for Co(0001) (2.51 Å) compared to Mo(110) (3.15 \times 2.73 Å), and the atoms are 27% less densely packed than for Co(0001).¹² At a coverage of 1 ML, the overlayer undergoes a phase transition, which results in an (8 \times 2) LEED pattern as the Co atoms compress along the [001] direction to form a surface structure that is only 2% less densely packed than Co(0001). Cobalt islands form on top of the first uniform layer upon annealing overlayers with coverages greater than 1.3 ML.¹¹ Hence, the Co-on-Mo(110) system provides an excellent means for studying structural effects, as well as a means for probing reactivity associated with mixed Co–Mo sites, which are formed at low Co coverages.

Cobalt overlayers were chosen for these studies because of both the proposed synergistic effects between Co and Mo in heteroatom removal catalysis and the anticipated qualitative differences in alcohol reactivity on Co versus Mo. Qualitative differences in Co and Mo reactivity would facilitate deconvolution of chemical processes occurring on the two metals, thus making the Co-on-Mo(110) system ideal for investigations of reactivity as a function of overlayer structure and composition. Previous work has shown that alkoxides, including 2-propoxide, undergo C-O bond scission on Mo(110).^{16,17} Specifically, 2-propanol reacts via 2-propoxide to form propene, propane, and hydrogen on Mo(110), along with surface carbon and oxygen from decomposition.^{16,17} The C–O bond scission in 2-propoxide is driven by the strong Mo-O bond. In contrast, alkoxides react with C-O bond retention on mid- and latetransition metals, which have intermediate metal-oxygen bond strengths.^{2,17–22} For example, CO is evolved from the reactions of alcohols on Rh(111),²¹ Fe(100),²² and Ni(100).¹⁸ Accordingly, C-O bond retention is anticipated for alkoxide reaction on Co, based on the similarity of the Co–O (91. \pm 3.2 kcal/ mol), Fe–O (93.3 \pm 4.1 kcal/mol), and Rh–O (96.8 \pm 10 kcal/ mol) bond strengths.^{24–26} Indeed, this study shows that acetone and CO are the primary gaseous products of 2-propanol reaction on uniform Co layers ($\theta_{Co} \ge 1$ ML).²⁷ Furthermore, the

[®] Abstract published in Advance ACS Abstracts, October 15, 1996.

dependence of the product distribution on Co coverage indicates that the reactivities of Co and Mo are additive, not synergistic, and that there are no significant differences in the chemistry of the Co layers with different lattice constants.

Experimental Section

Experiments were performed in two ultrahigh-vacuum chambers, which have been described previously, $^{28-31}$ each with a base pressure of $\leq 2 \times 10^{-10}$ Torr. Both chambers were equipped with a UTI-100C quadrupole mass spectrometer and electron optics for low-energy electron diffraction. The mass spectrometer was interfaced with a Compaq 486 computer that allowed data collection for up to 10 masses in a single experiment.³² One chamber was equipped with a Physical Electronics 5300 X-ray photoelectron system. X-ray photoelectron data were analyzed and fit on an Apollo DN 3500 workstation using the software provided. The O(1s), C(1s), Co-(2p), and Mo(3d) spectra were collected in consecutive scans over 10, 10, 6, and 2 min intervals, respectively, using a bandpass energy of 17.9 eV. The binding energies were referenced to the Mo(3d_{5/2}) peak at 227.8 eV. For the X-ray photoelectron spectra of 2-propanol on 1 ML of Co, background spectra for 1 ML of Co were subtracted from the O(1s) and C(1s) regions. The second chamber was equipped with a single-beam, cleanair-purged Fourier transform infrared spectrometer (Nicolet, Series 800). All FT-infrared reflection absorption spectra were averaged over 1000 scans using an MCT A detector at 2 cm⁻¹ resolution. Sample spectra were ratioed against a background spectrum after heating the crystal to 760 K and allowing it to cool to 150 K.

Cobalt was deposited on the surface by passing current through three braided tungsten wires that were wrapped around a Co wire (99.999% purity), as described elsewhere.^{14,15} Cobalt was deposited on the crystal at 100 K, and the overlayer was annealed to 760 K for 60 s before 2-propanol exposure. The Co coverage was calibrated using LEED since there is a sharp phase transition at 1 ML, which causes a change from a (1 × 1) to an (8 × 2) pattern for coverages \leq 1 ML; the Co(2p) X-ray photoelectron signals increased linearly with dosing time and were reproducible to within 4%. There is no evidence for Co–Mo alloy formation based on LEED, X-ray photoelectron, and temperature-programmed reaction data.^{14,15,33}

2-Propanol (Fischer Scientific, 99+%), (CH₃)₂CDOH, (CD₃)₂-CHOH, (CD₃)(CH₃)CHOH, and (CD₃)₂CDOD (99% D, Cambridge Isotope Laboratories) were used as received. The samples were stored in glass bottles and subjected to several freeze-pump-thaw cycles prior to use. The purities of the samples were confirmed by mass spectrometry.

Results

Temperature-Programmed Reaction Data. 2-Propanol forms acetone, CO, H₂, and a small amount of propene during temperature-programmed reaction on an ordered 1 ML Co overlayer (Figure 1a).³⁴ Nonselective decomposition to adsorbed carbon, oxygen, and gaseous hydrogen is a competing process, as determined by X-ray photoelectron spectroscopy. No other reaction products were detected in a comprehensive search of all masses up to 80 amu. Specifically, no propane is formed since the 29 amu signal is insignificant, and no ethane, ethylene, acetylene, or methane is evolved, based on the absence of 30, 26, 25, and 16 amu signals, respectively.^{35,36} The temperature-programmed reaction data also indicate that CO evolution is desorption-limited, given that CO evolves from both Co(0001)³⁷ and the Co overlayers at 425 K.



Figure 1. Temperature-programmed reaction of 2-propanol on (a) 1 ML of Co on Mo(110) and (b) clean Mo(110). The representative masses for each product are uncorrected for the cracking contributions from other products. The shaded region in the 28 and 41 amu signal represents the contribution from acetone fragmentation.

For high exposures of 2-propanol on Co overlayers ($\theta_{Co} \ge 1$ ML), two low-temperature desorption states at 160 and 210 K are also observed (Figure 1a). The 160 K peak is attributed to sublimation of condensed 2-propanol since its intensity increases without bound as the 2-propanol exposure increases. The peak at 210 K is observed at exposures lower than those required for multilayer condensation and reaches maximum intensity at the minimum exposure required for appearance of the multilayer peak. The 210 K peak is attributed to molecular desorption since no deuterium is incorporated into 2-propanol- d_0 when deuterium is present on the surface. Specifically, the 46:45 amu signal is 3:200, the same as for the 2-propanol- d_0 sample.

Isotopic labeling studies indicate that the β C–H(D) bond (adjacent to the oxygen) is selectively cleaved during acetone formation (Scheme 1). Only acetone- d_0 (43 and 58 amu) is produced from (CH₃)₂CDOH whereas only acetone- d_6 (46 and

SCHEME 1



64 amu) results from (CD₃)₂CHOH. Furthermore, there is a kinetic isotope effect when deuterium is substituted for hydrogen at the β position, as in (CH₃)₂CDOH and (CD₃)₂CDOD. For example, the peak temperature of acetone evolution is ~20 K higher than for (CH₃)₂CHOH and (CD₃)₂CHOH.

The kinetic isotope effect further indicates that acetone evolution at 330 K is reaction-limited. Acetone itself mainly decomposes on the Co overlayers although there is some desorption below 200 K. Furthermore, in the reaction of a 1:5 mixture acetone- d_6 and 2-propanol, only acteone- d_0 is evolved at 330 K, while all of the acetone- d_6 desorbs below 200 K.

Isotopic labeling studies also show that the small amount of propene formed on the 1 ML Co film occurs via selective dehydrogenation of one of the methyl groups, by a mechanism similar to that reported for 2-propanol reaction on Mo(110).¹⁷ The reaction of (CH₃)₂CDOH produces propene- d_1 as the major propene product, and the 42:41 amu ratio is the same as the 41:40 ratio for an authentic sample of propene- d_0 . The absence of propene- d_0 from (CH₃)₂CDOH reaction clearly shows that the C-H(D) bonds at the γ position are selectively cleaved. Similarly, the reaction of (CD₃)₂CHOH yields propene- d_5 , not propene- d_6 , ruling out an isotope effect.³⁸ Deuterium and 2-propanol coadsorption experiments further demonstrate that there is no H-D exchange in the intermediate that gives rise to propene.³⁹

The product distribution for 2-propanol reaction depends on the Co coverage in a manner that indicates additive, not synergistic, reactivity of Co and Mo. As reported previously, C-O bond cleavage is promoted on Mo(110) (Figure 1b). When Co is deposited on the Mo(110), the yields of products associated with Mo(110) (propane and propene) monotonically decrease, and those associated with the Co overlayer (CO and acetone) increase (Figure 2). Furthermore, there are no significant shifts in the evolution temperatures of the carboncontaining products, indicating that there is no significant perturbation of the chemistry of one metal by the other.

Careful scrutiny of the propene formation curves as a function of Co coverage suggests that a minor amount of propene is formed from reaction on mixed Co-Mo sites (Figure 3). Specifically, for Co coverages below 0.5 ML, there are two propene peaks (β_1 , β_2) at 410 and 455 K. The β_1 peak (410 K) is attributed to reaction on Mo, based on the correspondence in peak temperature to propene formed on Mo(110). The intensity of the β_1 peak and the total propene yield decrease with increasing Co coverage, whereas the β_2 peak intensity reaches a maximum at 0.25 ML. The decrease in total intensity of the propene signal with increasing Co coverage reflects the competition between propene evolution and the formation of products containing intact C–O bonds. A minor amount of β_2 propene ($\sim 6\%$ of the propene signal from reaction on Mo(110)) is formed at 1.5 ML of Co. This suggests that the β_2 peak might arise from reaction at a mixed Co-Mo sites and that a small fraction of 2-propanol is still able to access the Mo surface on the continuous Co overlayer, perhaps via defect sites.

X-ray Photoelectron Studies. The X-ray photoelectron spectrum of 2-propanol on 1 ML of Co clearly shows that the C–O bond remains intact after heating to 250 K and is consistent with a 2-propoxide intermediate (Figure 4). The



Figure 2. Relative yields of various products as a function of Co coverage for the reaction of 2-propanol on Co-covered Mo(110). Integrated signals were divided by the largest value in the data set so that the vertical range is from zero to unity in all cases. The representative signals for each product were corrected for the cracking contribution from other products.³⁶ The error was calculated from the standard deviation determined by five different experiments. Data for all Co coverages were collected in a single day.



Figure 3. Temperature-programmed reaction of 2-propanol on Co overlayers as a function of Co coverage for propene (41 amu). The shaded regions represent cracking contributions from acetone (not shown).

O(1s) binding energy of 531.8 eV is characteristic of intact C–O bonds. The lack of intensity at 530.3 eV, which is the binding energy of atomic oxygen on 1 ML of Co, indicates that the C–O bond is not broken. Intact O–H bonds are expected to have a higher O(1s) binding energy. For example, condensed 2-propanol has an O(1s) binding energy of 533.4 eV. The C(1s) spectra are likewise consistent with formation of 2-propoxide on the 1 ML Co overlayer below 250 K. Specifically, there are two C(1s) states at 286.3 and 284.9 eV with a relative area of 1:1.9. The 286.3 eV peak is attributed to the oxygen-bound



Figure 4. X-ray photoelectron data for the (a) O(1s) region and (b) C(1s) region after heating 2-propanol condensed on 1 ML of Co to (i) 250, (ii) 400, and (iii) 760 K.

carbon, and the 284.9 eV peak is attributed to the methyl carbons.⁴⁰ The ratio of approximately 1:2 substantiates these assignments; 2-propoxide on Mo(110) has C(1s) binding energies at 286.5 and 285.1 eV also with a relative area of 1:2. No atomic carbon is observed after heating 2-propanol condensed on 1 ML of Co to 250 K.

At 400 K, the appearance of an O(1s) peak at 530.2 eV, characteristic of atomic oxygen, indicates that C–O bond cleavage has occurred (Figure 4). However, the persistence of the 531.8 eV peak shows that there are still intact C–O bonds. The 531.8 eV peak could be from CO, given that the O(1s) binding energy of CO on 1 ML of Co is \sim 532 eV. The major peak in the C(1s) region after heating to 400 K is from atomic carbon at 282.9 eV. The 285.8 eV peak is most likely due to

CO, which has a binding energy at 285.7 eV on 1 ML of Co but may also have a contribution from the C–O bond in 2-propoxide. The additional peak at 284.4 eV is consistent with intact C–C bonds but is too low in energy to be from 2-propoxide.

X-ray photoelectron spectra obtained after heating to 550 K indicate that only atomic carbon and oxygen are present (data not shown). The O(1s) state at 530.3 eV and the C(1s) peak at 282.8 eV are characteristic of atomic oxygen and carbon species, respectively. No further changes occur upon heating to 760 K (Figure 4).

The amount of 2-propoxide on the surface at 250 K decreases with increasing Co coverage. At a Co coverage of 1.5 ML, the total amount of reaction is \sim 73% of that on Mo(110), as calculated from the C(1s) signal at 250 K.^{41,42} The estimated coverage of 2-propoxide on 1 ML of Co is \sim 0.2 ML based on a comparison of the C(1s) signal intensity to that of 2-propoxide on Mo(110), which has a coverage of 0.3 ML.⁴³ This suggests that molecular desorption and 2-propoxide formation are competing processes.

X-ray photoelectron studies also indicate that 2-propanolinduced aggregation of the 1 ML Co overlayer is not significant below 500 K. There is no measurable shift in the $Co(2p_{3/2})$ binding energy upon adsorption of 2-propoxide on the 1 ML Co overlayer at 250 K. The peak position and intensity of the Mo signal do not change in either case. The $Co(2p_{3/2})$ binding energy shifts by +0.2-0.3 eV upon heating 2-propanol on the 1 ML Co overlayer to 375 K, consistent with the deposition of atomic oxygen at this temperature; the $Co(2p_{3/2})$ peak to shifts +0.3 eV relative to the pure Co overlayer after depositing ~ 0.2 ML of oxygen on 1 ML of Co at 100 K. Although large oxygen exposures (~ 1 ML) previously have been shown to cause aggregation of the Co overlayer upon heating,¹⁴ the attenuation of the Co(2p) signal resulting from Co aggregation is minimal below 500 K.

Infrared Studies. The infrared spectrum of 2-propanol heated to 250 K on 1 ML of Co is consistent with 2-propoxide formation, based on its close resemblance to that of 2-propoxide on Mo(110) (Figure 5). Increasing the Co coverage from 1.0 to 1.5 ML results in only minor differences in the spectra of both 2-propanol and (CD₃)₂CHOH at 250 K. This suggests that there are no dramatic changes in the bonding caused by variations in the Co overlayer lattice constant. The 2-propoxide intermediate on Mo(110) has been observed previously using electron energy loss and X-ray photoelectron spectroscopies.¹⁶ The infrared data suggest that the O-H bond of 2-propanol is broken by the Co monolayer as well, since the ν (O–H) mode is not observed. While it is possible that the ν (O–H) mode would be absent in infrared data due to orientation effects, we have recently shown that the ν (O-H) mode of HOCH₂CH₂O-Mo(110) can be detected with both infrared and electron energy loss spectroscopies.⁴⁴ The correspondence between infrared spectra on the Co monolayer and Mo(110) also indicates that the molecular framework remains intact after O-H bond scission. The spectra of (CD₃)(CH₃)CHOH, (CD₃)₂CHOH, and (CD₃)₂CDOD heated to 250 K on 1 ML of Co correspond to those of the respective 2-proposide on Mo(110).

Based on the close correspondence in the infrared spectra of the various isotopic forms of 2-propoxide on Mo(110) and 1 ML of Co, the mode assignments are assumed to be similar to the Mo(110) case. Model calculations are planned to establish detailed mode assignments.⁴⁵ The major difference in the spectra for 2-propoxide on the Co overlayer and Mo(110) is the increase in the full width at half-maximum (fwhm) of the ν (C–O) mode. In particular, the 935–925 cm⁻¹ mode is



Figure 5. Infrared reflection—absorption spectra for a saturation exposure of 2-propanol after heating to 250 K on (i) Mo(110) and (ii) 1 ML of Co for the (a) low-frequency region and (b) C–H stretching region.

broader and splits into two peaks, both of which are slightly higher in energy than on Mo(110) (919 cm⁻¹). This change is not simply due to a coverage effect; saturation coverage on 1 ML of Co is reduced by ~25% compared to Mo(110), and a 25% reduction in coverage on Mo(110) caused a *decrease* in fwhm and a shift to *lower* energy. Hence, we attribute the broadening to heterogeneity of the surface. Similarly, the ν -(C–O) for (CD₃)(CH₃)CHO–, (CD₃)₂CHO–, and (CD₃)₂-CDO– are broadened on the 1 ML Co overlayer compared to on Mo(110).

The infrared data also confirm that CO is formed from 2-propoxide reaction on Co-covered Mo(110) at temperatures below 375 K and remains on the surface up to ~400 K. CO is identified based on the development of a new peak in the infrared spectrum at 1975 cm⁻¹ upon heating 2-propanol or (CD₃)(CH₃)CHOH condensed on 1 ML of Co to 375 K (Figure 6); the absence of a significant isotopic shift confirms the assignment as ν (C=O). Furthermore, the stretching frequency for CO adsorbed on 1 ML of Co was independently measured as 1975 cm⁻¹ for a subsaturation coverage, and the frequency of CO coadsorbed with 2-propanol (2-propanol:CO = 5:1) on



Figure 6. Infrared reflection—absorption spectra showing the $\nu(C\equiv O)$ region. Data were collected after heating a saturation exposure of 2-propanol to 375 K on (a) Mo(110) and (b) 1 ML of Co. Spectrum c is for a subsaturation exposure of CO on 1 ML of Co at 100 K.

1 ML of Co heated to 375 K is 1968 cm^{-1,46} The intensities of the ν (C=O) modes observed from the decomposition of 2-propanol depend on Co coverage. For example, the relative intensity of the ν (C=O) mode is greater on 1.5 ML Co than on 1 ML of Co although the frequencies are virtually identical (1978 and 1975 cm⁻¹, respectively). These results are generally consistent with the increase in CO yield as a function of Co coverage and indicate that there is not a substantial change in mechanism upon varying the amount of Co deposited.

The infrared data further suggest that some intact 2-propoxide remains on the surface as CO is formed. The spectrum at 375 K is nearly identical to that of a low coverage of 2-propanol on 1 ML of Co heated to 250 K, with the addition of the ν (C=O) peak. Subsaturation exposures of 2-propoxide- d_0 and (CD₃)-(CH₃)CHO- on 1 ML of Co show that the C-O stretching modes shift to lower frequency by as much as 10–15 cm⁻¹ as a function of 2-propoxide- d_0 and (CD₃)(CH₃)CHO- on Mo-(110).^{47,48} This dependence of ν (C-O) on coverage has also been reported for methoxide on Mo(110)³⁰ and is attributed to decreased dipole-dipole coupling at lower coverages.

The infrared spectrum of 2-propanol on 1 ML of Co, heated to 400 K, demonstrates that most products have left the surface because the intensities of all the modes are decreased to near the noise level. These results are consistent with temperatureprogrammed reaction data which show that all products except β_2 -propene are evolved below 400 K. At 425 K, only small peaks at 1090 and 2970 cm⁻¹ are observed. The low intensities preclude identification of the remaining intermediate(s) and further indicate that the intermediate giving rise to β_2 propene at 450 K is minor.

Discussion

The reactions of 2-propanol on Co monolayers supported on Mo(110) are qualitatively different than on Mo(110) and similar to those on other mid-transition metal surfaces, in that most C–O bonds are retained on uniform Co overlayers. Specifically, the reaction of 2-propanol on 1 ML of Co yields acetone and CO, whereas reaction on Mo(110) produces propene and propane. Hydrogen and surface carbon and oxygen are



Figure 7. Proposed reaction scheme for 2-propanol on a uniform Co overlayer.

produced on both surfaces. Infrared and X-ray photoelectron studies both demonstrate that reaction proceeds via 2-propoxide on both the Co overlayers and Mo(110). Importantly, Co aggregation does *not* play a role in the reactions of 2-propanol on the Co overlayer. Studies of the Co overlayer on Mo(110) have shown that the oxygen (0.25 ML) and Co segregate, but only above 500 K.

The qualitative difference in chemistry on the Co overlayer versus the Mo substrate is explained by periodic trends in the metal-oxygen bond strengths. All of the metal-oxygen bond energies for the group 8 transition metals are between 91 and 97 kcal/mol.^{24,26} Accordingly, 2-propanol reaction on the Co overlayer is very similar to that on Ni(100), Fe(100), and Pd-(111).^{18,19,23} In all cases, the C-O bond is retained, yielding acetone and CO in conjunction with H₂. The C-O bond of 2-propanol is similarly retained on Rh(111) and Pt(111), on which CO and H₂ are formed.^{21,49} In contrast, C-O bond cleavage is promoted on Mo(110);^{16,17} the greater Mo-oxygen bond strength (133.9 ± 5 kcal/mol)^{24,26} provides a greater thermodynamic driving force for C-O bond cleavage.

The proposed mechanism for 2-propanol reaction (Figure 7) is consistent with all of our data. The O-H bond of 2-propanol is cleaved below 250 K on the Co overlayer, affording 2-propoxide, based on X-ray photoelectron and infrared reflection absorption studies. There is also competing molecular desorption at 210 K for high 2-propanol exposures. 2-Propoxide has also been identified on other surfaces investigated, including Mo(110),¹⁶ Rh(111)⁵⁰ and Pd(111).⁴⁹ On Co-covered Mo(110), selective β C-H bond cleavage is the rate-limiting step for acetone formation, as shown by selective isotopic labeling experiments. A similar mechanism is operative for acetone formation from 2-propanol on O-covered Rh(111) and is attributed to the lower homolytic C-H bond energy due to electron withdrawal by the neighboring oxygen atom.²¹ The weaker C–H bonds β to the metal center also lead to preferential β C–H bond breaking in other alkoxides bound to both surfaces and metal clusters, provided that the C-O bond remains intact.17,19,51-60

Nonselective dehydrogenation and C-C bond scission, yielding CO, competes with acetone elimination. Although the detailed mechanistic steps are not identified by our experiments, our infrared data show that adsorbed CO is formed by 375 K, and acetone evolution is complete at this temperature. The CO remains on the surface until approximately 425 K. There is also some C-O bond dissociation competing with acetone and CO production, based on the detection of residual carbon and oxygen following temperature-programmed reaction to 375 K using X-ray photoelectron spectroscopy. The residual carbon is partly a by-product of CO production, but the oxygen must be due to competing C-O bond dissociation. Carbon monoxide is known to dissociate on stepped CO surfaces, polycrystalline Co,⁶¹⁻⁶³ and Co overlayers on Mo(110),⁵ W(110), and W(100).⁶ In contrast, no CO dissociates on Co(0001).^{37,64,65} These results suggest that the C-O dissociation might occur on defects in the Co overlayer and that the dissociation proceeds, at least in part, via adsorbed CO.

Co overlayers on Mo(110) show predominantly an additive rather than synergistic effect in the reactions of 2-propanol since the product distributions are mainly due to independent reaction on the two metals. Because 2-propanol forms different products on the Co overlayer (acetone and CO) and the Mo(110) surface (propene and propane), the contributions of the two metals can be easily distinguished. The smooth increase in the yields of products with intact C–O bonds is consistent with an independent and simultaneous decrease in C–O bond cleavage products (Figure 2). Notably, there are no significant differences in the reactivity of 2-propanol as the overlayer changes from a pseudomorphic to the close-packed structure in the Co coverage range 1.0-1.5 ML.

The only evidence for a reactivity different than those of the two constituent metals is the evolution of β_2 -propene at 455 K (Figure 3). The β_2 state cannot be attributed to pure Co sites even though it persists up to 1.5 ML of Co, since it decreases with increasing Co coverage above 0.5 ML. Neither is it due to pure Mo, since there is not a β_2 feature in the temperatureprogrammed reaction spectrum of 2-propanol on Mo(110). Furthermore, β_2 -propene production is greatest in the range 0.25-0.5 ML of Co, a coverage at which the population of mixed Co-Mo sites is at a maximum. For example, the yield of β_1 -propene, which is associated with the Mo(110) surface, is virtually zero at the highest Co coverage (1.5 ML). The yield of β_2 -propene is ~5% that of the β_1 -propene signal from clean Mo(110). At 0.5 ML, the β_1 and β_2 propene peak heights are nearly the same, although the total yield of propene is reduced to approximately half that on Mo(110). As the Co coverage is increased, β_1 production decreases more rapidly than β_2 , suggesting that the β_2 -propene is related to the presence of Co.

The persistence of propene production at coverages above 1 ML of Co is explained in terms of accessibility of 2-propanol to the Mo atoms. At a Co coverage of 1 ML, the β_2 -propene production is $\sim 15\%$ of the total propene production on Mo-(110) itself, and the packing density of this pseudomorphic layer is $\sim 23\%$ lower than for bulk Co.⁶⁶ As the Co coverage is increased, the packing density is also increased to nearly that of Co(0001) for coverages above 1.3 ML. The β_2 -propene production is lower on the more densely packed Co overlayers with relative yields of 6% and 4% compared to Mo(110) for reaction on 1.5 and 2.5 ML of Co, respectively. We tentatively attribute the small amount of propene production on the densely packed Co films to defects in the overlayer that render mixed Co-Mo sites accessible to the 2-propanol. This assertion is supported by the splitting in the C-O stretch in 2-proposide on 1 ML of Co, which suggests that the Co overlayers are heterogeneous. Furthermore, the dependence of the propene evolution yields and peak shapes on degree of order in the Co overlayers is consistent with our proposal that β_2 -propene formation is related to defect sites.

The lack of a significant synergistic effect in the reactions of 2-propanol on Co-covered Mo(110) is different from previous work on other bimetallic systems, but similar to our previous study of methanethiol on the same Co overlayers.¹⁵ Although X-ray photoelectron studies of bimetallic surfaces indicate that the overlayer metal is electronically perturbed,⁶⁷ 2-propanol reaction on Co-covered Mo(110) is apparently not sensitive to these electronic effects. Theoretical modeling is necessary to fully address this point by specifically determining the types of orbital interactions that are important in bonding and reactivity of 2-propanol. The chemistry of 2-propanol is not sensitive to the lattice spacing of the Co overlayer. Previous studies of other metal overlayers deposited on metal substrates have shown that molecules like CO, H₂, NO, and ethylene have desorption characteristics on the monolayer films that are different than on the bulk metals.^{4,6-10,68,69} It is interesting to note that the molecules for which a sensitivity to surface structure has been reported have π bonds. These results suggest that the degree of chemical sensitivity to the surface geometric structure depends strongly on the reactant bound to the surface. However, the degree of synergy might also depend on the nature of the two metals involved as well as on the geometric structure of the surface. Recent studies of methanethiol on Ni overlayers supported on W(100) indicate a high degree of sensitivity to the geometric structure.⁷⁰ Hence, more open faces of the supporting metal may lead to a larger perturbation in the chemical properties.

Conclusions

2-Propanol reaction on the Co overlayers occurs through a 2-propoxide intermediate. Acetone and CO are evolved from reaction of 2-propanol on Co, while propene and propane are evolved from reaction on Mo. The β_2 propene peak in the temperature-programmed reaction data may be from a mixed Co–Mo site. Acetone is formed via selective β C–H bond scission, and decomposition to CO is a competing process. Aggregation of the Co overlayer is not induced by 2-propoxide below 500 K and therefore should not influence the chemistry of 2-propanol.

Acknowledgment. We gratefully acknowledge the support of this work by the U.S. Department of Energy, Office of Basic Energy Sciences, Grant DE-FG02-84-ER13289.

References and Notes

(1) Sachtler, W. M. H.; Ichikawa, M. J. Phys. Chem. 1986, 90, 4752–4758.

- (2) Brown, N. F.; Barteau, M. A. Langmuir 1992, 8, 862-869.
- (3) Harris, S.; Chianelli, R. R. J. Catal. 1986, 98, 17-31.

(4) Neiman, D. L.; Koel, B. E. Mater. Res. Soc. Symp. Proc. 1987, 83, 143-153.

(5) He, J.; Goodman, D. W. Surf. Sci. 1991, 245, 29-40.

(6) Johnson, B. G.; Berlowitz, P. J.; Goodman, D. W. Surf. Sci. 1989, 217, 13–37.

(7) Heitzinger, J. M.; Gebhard, S. C.; Koel, B. E. Surf. Sci. 1992, 275, 209–222.

(8) Berlowitz, P. J.; Goodman, D. W. *Langmuir* **1988**, *4*, 1091–1095.

(9) Heitzinger, J. M.; Gebhard, S. C.; Koel, B. E. Chem. Phys. Lett. 1992, 200, 65–70.

(10) Heitzinger, J. M.; Gebhard, S. C.; Koel, B. E. J. Phys. Chem. 1993, 97, 5327–5332.

(11) Tikhov, M.; Bauer, E. Surf. Sci. 1990, 232, 73-91.

(12) He, J.; Kuhn, W. K.; Goodman, D. W. J. Am. Chem. Soc. 1991, 113, 6416-6419.

(13) Kuhn, W. K.; He, J.-W.; Goodman, D. W. J. Phys. Chem. 1994, 98, 264–269.

(14) Chen, D. A.; Friend, C. M. Surf. Sci., in press.

(15) Chen, D. A.; Friend, C. M.; Xu, H. Langmuir 1996, 12, 1528-1534.

(16) Uvdal, P.; Wiegand, B. C.; Serafin, J. G.; Friend, C. M. J. Chem. Phys. **1992**, 97, 8727–8735.

(17) Wiegand, B. C.; Uvdal, P. E.; Serafin, J. G.; Friend, C. M. J. Am. Chem. Soc. **1991**, 113, 6686-6687.

- (18) Johnson, S. W.; Madix, R. J. Surf. Sci. 1982, 115, 61-78.
- (19) Davis, J. L.; Barteau, M. A. Surf. Sci. 1987, 187, 387-406.

(20) Wiegand, B. C.; Uvdal, P.; Serafin, J. G.; Friend, C. M. J. Phys. Chem. 1992, 96, 5063-5069.

- (21) Xu, X.; Friend, C. M. Surf. Sci. 1992, 260, 14-22.
- (22) Benziger, J. B.; Madix, R. J. J. Catal. 1980, 65, 36-48.
- (23) Sault, A. G.; Madix, R. J. J. Phys. Chem. 1988, 92, 6025-6028.

(24) Bond strengths are reported for diatomic molecules in the gas phase.(25) The reactivity of bulk Co has not been studied, but it is expected

to behave similarly to Rh, Ni, and Fe, which are its neighbors in the periodic table. The reactions of alcohols of these surfaces result in products with intact C–O bonds. 18,21,22

(26) CRC Handbook of Chemistry and Physics; CRC Press: Boca Raton, FL, 1989.

(27) A monolayer of Co corresponds to the same number of atoms as in the underlying Mo(110) surface.

(28) Xu, X.; Friend, C. M. J. Am. Chem. Soc. 1991, 113, 6779–6785.
(29) Roberts, J. T.; Friend, C. M. J. Am. Chem. Soc. 1986, 108, 7204–7210.

(30) Weldon, M. K.; Uvdal, P.; Friend, C. M.; Serafin, J. G. J. Chem. Phys. 1995, 103, 5075.

(31) Weldon, M. K.; Friend, C. M. Surf. Sci. 1994, 310, 95-102.

(32) Liu, A. C.; Friend, C. M. Rev. Sci. Instrum. 1986, 57, 1519-1522.

(33) We did not observed the LEED pattern associated with Co–Mo alloying that was reported by Bauer et al. for higher Co coverages.¹¹ Furthermore, the Co(2p) and Mo(3d) peaks in the X-ray photoelectron spectra did not shift in energy compared to the pure Co and Mo binding energies. Finally, the Co desorption peak shape in the temperature programmed desorption spectra for Co on Mo(110) is characteristic of first-order kinetics, which is the expected behavior for metal desorption from a metal substrate. Thus, we do not observe any evidence for Co–Mo alloying, which is consistent with the results reported by Goodman et al.⁵

(34) The heating was not exactly linear but was highly reproducible. It was 7.8-13.1 K/s for temperatures between 250 and 500 K.

(35) Isobutane is ruled out as a product of 2-propanol reaction on Cocovered Mo(110) based on studies of $(CD_3)_2CHOH$ on 1 ML of Co. There was no 49 amu signal, which is the major cracking fragment of isobutane d_6 in the reaction of $(CD_3)_2CHOH$. Similarly, no 50 amu signal above 200 K was observed in the reaction of $(CD_3)_2CDOD$, which would result from isobutane- d_7 .

(36) The mass spectrometer signals were corrected for mass fragmentation of the various other products by using measured ion ratios. Acetone is the only source of 58 amu signal, and its contribution to the 43 amu signal is derived from the measured 43:58 amu of 4.44. The resulting peak area for 43 amu was entirely accounted for by propane (in the Mo(110) case). The 41 amu peak, which was used to monitor propene, was then corrected for the contribution from acetone (41:58 amu = 0.18) and from propane (41:43 amu = 0.66). The 29 amu signal was corrected for propene fragmentation (29:41 amu = 0.01) and acetone fragmentation (29:58 amu = 0.20). The 28 amu signal was used to monitor CO production, after subtracting the rising base line due to background CO. Corrections for propane (28:29 amu = 0.68), propene (28:41 amu = 0.025), and acetone (28:58 amu = 0.76) were subsequently made.

(37) Bridge, M. E.; Comrie, C. M.; Lambert, R. M. Surf. Sci. 1995, 67, 393-404.

(38) The reaction of $(CD_3)_2$ CHOH does not yield propene- d_6 . The major product is probably propene- d_5 , but it is difficult to determine whether any other isotopes of propene are present because acetone- d_6 has a major cracking fragment at 46 amu, and the exact cracking pattern of propene- d_5 is not known.

(39) No propene- d_1 was produced since the product 41:42 amu ratio was 1.5, which is the same as an authentic sample of propene in our chamber. Also, the 43:58 amu ratio was 5.5, which is correct for an authentic sample of acetone. Note that deuterium incorporation may not occur simply because deuterium desorbs around 300 K, while propene is not formed until 450 K.

(40) Gelius, U.; Heden, P. F.; Hedman, J.; Lindberg, B. J.; Manne, R.; Nordberg, R.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, *2*, 70–80.

(41) The O(1s) region was difficult to integrate reliably due to a rising baseline at \sim 535 eV from the Co $L_3M_{23}M_{45}$ Auger transition at 538 eV.

(42) This calculation assumes that there are no significant changes in the morphology of the Co overlayer occur at 250 K.

(43) The 2-propoxide coverage calculated here is in agreement with previous work.¹⁶

(44) Queeney, K. T.; Arumainayagam, C. R.; Weldon, M. K.; Friend, C. M.; Blumberg, M. Q. J. Am. Chem. Soc. **1996**, *118*, 3896–3904.

Reactions of 2-Propanol on Co-Covered Mo(110)

(45) Detailed assignments of the modes of 2-propoxide require theoretical modeling due to intramolecular coupling, which changes upon perturbation of one or more modes.^{16,20} Specifically, the extensive coupling between the ν (C–O) and other modes such as the δ (CH₃) and ν_a (C–C) stretch is different for 2-propoxide- d_0 and 2-propanol- d_0 because of differences in their C–O force constants. Isotopic substitution also alters the degree of coupling by shifting the vibrational energies. Both *ab initio* calculations and experimental studies of isotopic forms of 2-propoxide on Mo(110) show that there is less intramolecular coupling in (CD₃)(CH₃)CHO– than in (CH₃)₂CHO–, (CD₃)CHO–, or (CD₃)₂CDO– on Mo(110).^{16,71}

(46) Note that the C–O stretching frequency for CO depends strongly on CO coverage.

(47) The C–O stretch for 2-propoxide- d_0 on Mo(110) shifts from 919 cm⁻¹ at saturation coverage to 903 cm⁻¹ at 75% saturation coverage; likewise, the C–O stretch for (CD₃)₂(CH₃)₂CHO– shifts from 894 to 887 cm⁻¹.

(48) For 2-propoxide- d_0 , the 1107 cm⁻¹ peak, which also has significant intensity, shifts to 1098 cm⁻¹ for a subsaturation exposure on 1 ML of Co. However, the frequencies of the other less intense modes do not change with coverage. This is expected since the extent of dipole–dipole coupling scales with the intensity of the dipole moment.

(49) Sexton, B. A.; Řendulic, K. D.; Hughes, A. E. Surf. Sci. **1995**, 121, 181–198.

(50) Bol, C. W. J. Partial Oxidation of Hydrocarbons on Rh(111). Ph.D. Thesis, Harvard University; 1995.

(51) Brainard, R. L.; Madix, R. J. Surf. Sci. 1989, 214, 396-406.

- (52) Bowker, M.; Madix, R. J. Surf. Sci. 1982, 116, 549-572.
- (53) Bowker, M.; Madix, R. J. Surf. Sci. 1980, 95, 190-206.

(54) Brainard, R. L.; Peterson, C. G.; Madix, R. J. J. Am. Chem. Soc. **1989**, 111, 4553-4561.

(55) Davis, J. L.; Barteau, M. A. Surf. Sci. 1988, 197, 123-152.

(56) Davis, J. L.; Barteau, M. A. Surf. Sci. 1990, 235, 235-248.

(57) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. J. Am. Chem. Soc. **1986**, 108, 4805–4813.

(58) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. J. Am. Chem. Soc. **1986**, 108, 5347-5349.

(59) Chisholm, M. H.; Tatz, R. J. *Organometallics* **1986**, *5*, 1590–1598.
(60) Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C.;

Tatz, R. J. Organometallics 1986, 5, 1599-1606.

(61) Papp, H. Surf. Sci. 1985, 149, 460-470.

(62) Prior, K. A.; Schwaha, K.; Lambert, R. M. Surf. Sci. 1978, 77, 193–208.

(63) Jagannathan, K.; Srinivasan, A.; Hedge, M. S.; Rao, C. N. R. Surf. Sci. 1980, 99, 309–319.

(64) Bridge, M. E.; Comrie, C. M.; Lambert, R. M. J. Catal. 1979, 58, 28-33.

(65) Papp, H. Surf. Sci. 1983, 129, 205-218.

(66) Hydrocarbon formation accounts for \sim 67% of the total reaction,¹⁷ and we are assuming that the selectivity for propene evolution on the mixed Co–Mo sites is not significantly lower.

(67) Rodriguez, J. A.; Goodman, D. W. Science 1992, 257, 897–903.
(68) Koel, B. E.; Smith, R. J.; Berlowitz, P. J. Surf. Sci. 1990, 231, 325–332.

(69) Berlowitz, P. J.; Goodman, D. W. *Surf. Sci.* **1987**, *187*, 463–480. (70) Mullins, D. R. Private communication, 1996.

(71) Uvdal, P.; MacKerell Jr., A. D.; Wiegand, B. C.; Friend, C. M. *Phys. Rev. B* **1995**, *51*, 7844–7848.

JP9621989