Mechanism of Diethyl Ether Formation on Ag(110) and Its Dependence on Coadsorbed Oxygen Species

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The reactions of adlayers consisting of ethyl ligands, ethoxide groups, and oxygen atoms on Ag(110) were investigated using temperature-programmed desorption and high-resolution electron energy-loss spectroscopy. Iodoethane adsorbs dissociatively at 150 K to produce surface-bound ethyl ligands. These species react to form butane, which desorbs at 221 K, diethyl ether (236 K), ethylene (245 K), water (258 K), acetaldehyde (268 K), and ethanol (268 K). To determine the mechanism of formation of diethyl ether (the most abundant product), several surface mixtures of ethyl and ethoxide species were prepared by adsorption of different coverages of oxygen, iodoethane, and ethanol. While ethyl groups and ethoxides did couple to form diethyl ether in some cases, this reaction occurred only in the presence of additional coadsorbed oxygen atoms on the surface. The kinetics of diethyl ether formation are identical for the two reaction channels investigated: ethyl−ethyl−oxygen coupling and ethyl−ethoxide coupling. Therefore, formation of diethyl ether from two ethyl ligands and an oxygen atom appears to involve the sequential reaction of these species to first form an ethoxide, followed by coupling of the ethoxide with an ethyl group in the presence of additional oxygen atoms. This pathway was confirmed by experiments in which ^{13}C-labeled ethoxides and unlabeled ethyl groups were deposited on the surface in the presence of oxygen; the product ethers contained either zero or one labeled ligands. The requirement of coadsorbed oxygen atoms for ether synthesis by alkyl−alkoxide coupling is reminiscent of the need for subsurface oxygen in the silver-catalyzed formation of ethylene oxide (a cyclic ether) from ethylene.

Introduction

Understanding the reactions of alkyl groups with oxygen-covered metal surfaces is of importance, since these adsorbates have been postulated to play a key role in heterogeneous partial oxidation of hydrocarbons.[1,2] In surface-science studies, adsorbed alkyl ligands can be formed on a number of transition-metal surfaces via dissociation of the corresponding alkyl iodide.[3−5] In a previous report, we demonstrated that ethyl groups formed by this process (C−I bond dissociation of ICH$_2$-CH$_3$) can react with oxygen atoms on Ag(110) to form diethyl ether.[6] Since this is the first system where an alkyl ether has been formed from the reaction of an iodoalkane with oxygen on a metal single-crystal surface, determination of the reactive intermediates and the mechanism of diethyl ether synthesis is of particular interest.

The data presented here and in our previous report demonstrate that ethyl, ethoxide, and oxygen species coexist on the surface during the reaction of iodoethane on oxygen-dosed Ag-(110).[6] Therefore, diethyl ether must be derived from reactions of these surface intermediates. Reactions of iodoalkanes on O/Rh(111)[7−9] and O/Ni(100)[10] lead only to alkoxide decomposition and dehydrogenation products. Although ethoxides undergo bimolecular coupling reactions to form diethyl ether on TiO$_2$,[11,12] these reactions do not occur on Ag surfaces. On

Ag(110), ethoxides decompose via β-hydride elimination to form acetaldehyde, others scavenge the hydrogen released by this reaction, forming ethanol.[13,14] Thus, the possible routes for formation of diethyl ether on Ag(110) from ethyl groups and oxygen are either (1) concerted addition of two ethyl ligands to an oxygen atom or (2) initial formation of an ethoxide (from an ethyl group and an oxygen atom) followed by ethyl−ethoxide coupling to form the ether.

In the present study we investigated the mechanism of diethyl ether formation on Ag(110) by preparing several surface mixtures of ethyl and ethoxide species. The characteristic reactions of the adlayers were determined using TPD. Coupling of ethyl and ethoxide species to form diethyl ether was observed; however, this reaction occurred only in the presence of excess surface oxygen atoms. These results show that diethyl ether formation from two ethyl groups and an oxygen atom involves the sequential addition of the ethyl groups to oxygen to first form an ethoxide and then the ether.

Experimental Section

All experiments were performed in one of two ultrahigh vacuum (UHV) chambers. The chamber used for temperature-programmed desorption (TPD) experiments was evacuated to a base pressure of 1×10^{-10} Torr by a combination of ion and diffusion pumps and has been described previously.[15] This system was equipped with four-grid optics for LEED and AES

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experiments, a sputter ion gun for sample cleaning, and a UTI 100C quadrupole mass spectrometer for TPD experiments. Identification of the products desorbed in TPD experiments was carried out by deconvolution of the contributions of mass fragments from each product. The mass spectrometer fragmentation pattern for each product was determined experimentally, by admission of the pure component into the vacuum system.

HREELS (high-resolution electron energy-loss spectroscopy) experiments were conducted in a separate UHV chamber, which was evacuated to 1×10^{-10} Torr by a combination of turbomolecular and ion pumps; that system has been described previously.[16] The chamber was equipped with an LK Technologies ELS 3000 spectrometer for collecting HREEL spectra. All spectra were collected in the specular direction with the electron beam incident 60° from the surface normal. The HREELS experiments were conducted at an electron beam energy of 3 eV and a full width at half-maximum (fwhm) resolution of 24−30 cm^{-1} for the elastically scattered beam. The HREELS chamber also had LEED and AES capabilities.

The silver single crystal was aligned to the (110) orientation using the Laue method and mechanically polished using standard metallographic techniques. The surface orientation was verified using LEED. In both systems, the Ag(110) sample was supported by a tantalum foil backing plate which was spot welded to two tantalum wires. Resistive heating of the sample was achieved by passing current through the tantalum support wires. The crystal temperature was monitored with a chromel−alumel thermocouple. Carbon and sulfur impurities were removed from the fresh crystal surface by cycles of argon-ion bombardment followed by annealing at 1000 K. Any residual carbon remaining on the surface was desorbed in the form of CO_2 by successive cycles of oxygen exposure and TPD. Surface cleanliness was verified using oxygen TPD and HREELS. Iodoethane (Aldrich, 99%) and ^{13}C-ethanol (Isotec, 99%) were purified by repeated freeze−pump−thaw cycles and stored in glass tubes, which were covered to protect these reagents from light.

The absolute yields of the TPD products were determined in the following manner. First, the TPD peak areas for all of the products were corrected for mass spectrometer sensitivities, as described by Ko et al.,[17] so that the spectra for all products could be compared quantitatively. To obtain a standard reference, a Ag(110) surface covered with 0.33 ML (monolayers) of oxygen atoms was verified, by LEED, to give the corresponding (3×1) diffraction pattern. (One monolayer is defined as the number of silver atoms located in the troughs of the ideal Ag(110) surface, 8.4×10^{14} Ag atoms/cm^2.) The area obtained by integration of the oxygen desorption spectrum, corrected for mass spectrometer sensitivity, was then used to convert the corrected areas of the other desorbing products to absolute yields, in units of monolayers.

Results

In a previous report we showed that iodoethane adsorbs dissociatively on oxygen-covered Ag(110) to form surface ethyl ligands.[6] Those species reacted to form butane (221 K), diethyl ether (236 K), ethylene (245 K), water (258 K), acetaldehyde (268 K), and ethanol (268 K), which evolved from the Ag-(110) surface at the indicated temperatures. The HREEL spectra indicated that a fraction of the ethyl groups reacted with oxygen atoms to form ethoxides and that ethyl and ethoxide species coexisted on the surface. The formation of butane and ethylene (plus water) were attributed to the coupling and oxidative dehydrogenation of ethyl groups, respectively. The acetaldehyde and ethanol which evolved at 268 K were attributed to the
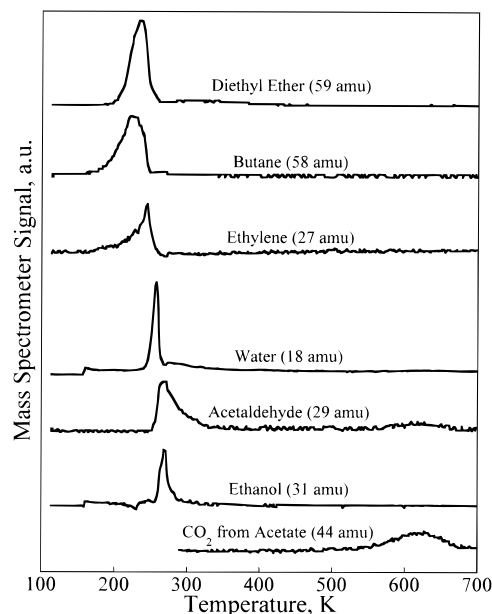

Figure 1. Corrected TPD spectra for the products formed by reacting 0.58 ML of iodoethane on a Ag(110) surface precovered with 0.33 ML of oxygen atoms. Correction involves subtraction of the contributions from fragmentation of overlapping products. Thus, the spectrum shown for each mass corresponds only to the contribution from the product designated in each case.

reactions of surface ethoxide species. While our earlier report detailed the products formed from ethyl groups and oxygen on Ag(110), the focus of this report is on the mechanism of product formation, in particular the sequential vs concerted nature of ether formation from surface alkyls.

Temperature-Programmed Desorption of Iodoethane on Oxygen-Covered Ag(110). Figure 1 shows temperature-programmed desorption spectra for 0.58 ML of ethyl groups reacted with 0.33 ML of oxygen atoms adsorbed on Ag(110). The principal reaction channel involved coupling of two ethyl groups with an oxygen atom to form diethyl ether, which desorbed at 236 K. Additional oxygenates, including ethanol and acetaldehyde, were observed to desorb at 268 K; both the temperature and products of this reaction correspond to the decomposition of adsorbed ethoxides.[13] The HREELS results shown below support the identification of the intermediate which decomposes at this temperature as an ethoxide. The small CO_2 peak at 627 K results from the decomposition of surface acetate intermediates formed by the reaction of product acetaldehyde with excess surface oxygen.[18] No CO_2 was observed from the direct combustion of surface ethyl groups under these conditions. However, the formation of ethylene at 245 K likely involves an oxygen-assisted dehydrogenation pathway since ethylene is not formed in the reaction of ethyl groups on the clean surface.[6] In addition to these oxygenate products, substantial quantities of butane were produced at 221 K. Butane has previously been shown to form by coupling of two ethyl species on clean Ag-(110)[6] and Ag(111)[19] surfaces. This reaction pathway is analogous to the decomposition of ethyl−Ag complexes in solution, which also yields butane.[20] Finally, although some of the product desorption curves in Figure 1 exhibit overlapping temperature ranges, they are not coincident. However, all of the products desorbed can be attributed to the reactions of two surface intermediates, ethyl and ethoxide, as shown by the HREELS results below.

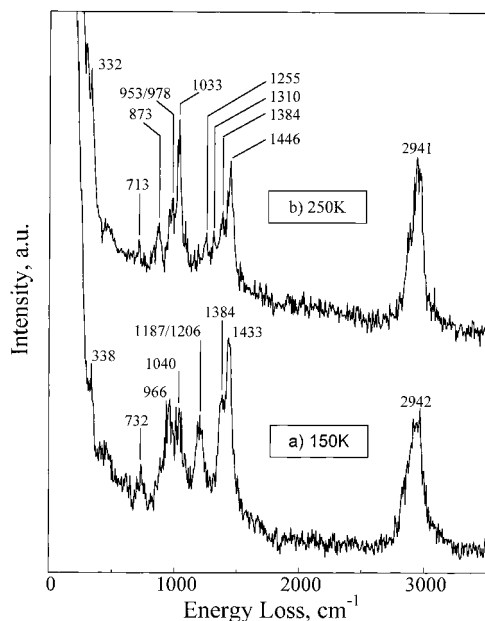**High-Resolution Electron Energy Loss Spectroscopy of Iodoethane on O/Ag(110).** Figure 2 shows the vibrational

Figure 2. HREEL spectra obtained at (a) 150 and (b) 250 K[25] after exposing a 0.33 ML oxygen-covered Ag(110) surface to 1 L of iodoethane at 150 K. The vibrational spectra represent (a) adsorbed ethyl species and (b) ethyl−ethoxide surface mixture.

spectra obtained following a 1 L exposure of iodoethane on a Ag(110) surface precovered with 0.33 ML of adsorbed oxygen atoms at 150 K. The mode assignments for the HREEL spectra are summarized in Table 1 along with the corresponding mode assignments for ethyl and ethoxide species bound to clean Ag-(110). Spectrum 2a was collected at 150 K and is characteristic of adsorbed ethyl species. The absence of the C−I stretch at 510 cm^{-1} [7,21] and the presence of the Ag−C stretch at 338 cm^{-1} [22−24] both demonstrate that, at these exposures, all of the iodoethane molecules dissociate upon adsorption to form surface-bound ethyl ligands. (The very weak feature at ca. 440 cm^{-1} is not assigned. It was not observed when iodoethane was adsorbed on a clean surface but did sharpen when the ethyl−oxygen adlayer was heated to form ethoxides, as shown below.) The weak feature at 732 cm^{-1} and the intense feature at 966 cm^{-1} in Spectrum 2a represent the CH$_2$ and CH$_3$ rocking modes, respectively, of ethyl ligands. The C−C stretching mode is observed at 1040 cm^{-1}. The loss located at 1187/1204 cm^{-1} is identified as a CH$_2$ wagging mode. The doublet at 1384 and 1433 cm^{-1} represents symmetric and asymmetric deformation modes of the CH$_3$ group, respectively. The feature at 2942 cm^{-1} corresponds to the C−H stretching mode.

Spectrum 2b is characteristic of the species present after annealing the ethyl−oxygen adlayer to 250 K.[25] Annealing the surface induced several changes in the vibrational spectrum as follows: (1) the mode at 1033 cm^{-1} intensified and became the dominant feature and (2) a new loss appeared at 873 cm^{-1}, which was not present in Spectrum 2a. The 1033 and 873 cm^{-1} losses can be attributed to the C−C and C−O stretching modes of an ethoxide, respectively. These assignments are supported by previous HREELS results[26] and the TPD observations noted above. However, ethoxide species alone cannot account for all of the vibrational features in Spectrum 2b; additional features, characteristic of ethyl groups, are also present. The losses attributed to ethyl groups include the Ag−C stretch at 332 cm^{-1} and the CH$_3$ rocking mode observed at 953/978 cm^{-1}. In addition, the relative intensities of the 1384 and 1446 cm^{-1} modes are inconsistent with their assignment to ethoxides alone. Thus, Spectrum 2b is characteristic of a mixture of ethoxide

and ethyl species; the ethoxides were formed by the addition of an ethyl group to an oxygen atom. Individual assignments of the vibrational features to ethyl and ethoxide species are summarized in Table 1.

Temperature-Programmed Desorption of Ethyl/Ethoxide Mixtures on Ag(110). The results presented above demonstrate that ethyl, ethoxide, and atomic oxygen species are all present on the Ag(110) surface during the course of the TPD experiment. However, the role of these various intermediates in the formation of oxygenates from iodoethane and oxygen on Ag(110) is not clear. The TPD experiments described below were performed in order to investigate the role, if any, of ethoxides in diethyl ether formation reactions. The results are divided into three sections based upon the formation sequence of ethyl and ethoxide ligands.

A. Oxygen + Saturation Ethanol Exposure + Iodoethane. The reaction of an adsorbed layer consisting of ethoxide and ethyl species on the Ag(110) surface was investigated using temperature-programmed desorption. The ethoxide−ethyl adlayer studied in this experiment was prepared as follows. First, the Ag surface was covered with 0.33 ML of oxygen atoms at 300 K. This oxygen coverage was verified using LEED and resulted in a (3 × 1) diffraction pattern. The oxygen-dosed surface was cooled to 110 K and exposed to a dose of ethanol sufficient to completely titrate preadsorbed oxygen from the surface upon flashing the sample to 240 K. This dose is referred to as a "saturation" dose below. Surface oxygen atoms act as Brønsted bases and remove the hydroxyl protons of the alcohol molecules. The products of this reaction are surface-bound ethoxides and water molecules; the latter immediately desorb from the surface.[13] Exposure of the oxygen-covered surface to ethanol, followed by annealing to 240 K, resulted in complete removal of the oxygen atoms initially adsorbed on the surface. Iodoethane was then dissociatively adsorbed onto the ethoxide-covered Ag(110) surface at 110 K to form the ethoxide−ethyl reaction mixture.

Figure 3 illustrates the TPD results from this adsorbed layer. The products formed in this reaction are separated into three categories: (1) ethyl products, (2) ethyl−ethoxide products, and (3) ethoxide products. Since there are no oxygen atoms present on the surface at the start of the temperature ramp, any diethyl ether formed must result from ethyl−ethoxide coupling reactions. However, as shown by the desorption trace for $m/e = 59$, there is no diethyl ether formed during the TPD experiment; the ethyl ligands and ethoxides produced by the adsorption sequence above do not couple. The small $m/e = 59$ signal detected near 220 K is associated with butane desorption at that temperature. The ethyl groups react independently of the ethoxides and couple to form butane at 218 K as they do on the clean Ag(110) surface;[6] no other products were associated with reaction of ethyl species. Likewise, the ethoxides react via their normal decomposition pathway at 280 K to form acetaldehyde and ethanol.[13] In addition to the results presented in Figure 3, a similar experiment was carried out in which the initial ethoxide layer was formed from 0.13 ML of oxygen atoms, rather than 0.33 ML. This experiment was performed in order to determine if diethyl ether could be formed from an adsorbed layer with a different ethyl:ethoxide ratio. However, no diethyl ether was formed in that reaction either; only butane and ethoxide decomposition products were observed. These results would seem to indicate that ethyl and ethoxide ligands do not couple to form diethyl ether on Ag(110). However, before drawing any conclusions, two other methods for producing ethyl−ethoxide surface mixtures are considered.

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TABLE 1: Vibrational Modes of Ethyl and Ethoxide Groups Adsorbed on Ag(110) (cm^{-1})

ethyl mode	ethyl/Ag(110)	ethyl/O−Ag(110)		ethyl−ethoxide/Ag(110)		ethoxide/Ag(110)	ethoxide mode
ν(Ag−C)	332	338	←	332			
				443	→	443	b(C−C−O)
ρ(CH$_2$)	738	732	←	713			
				873	→	880	ν(C−C)
ρ(CH$_3$)	960	966	←	953/978			
ν(C−C)	1046	1040	←	1033	→	1052	ν(C−O)
ω(CH$_2$)	1187	1187/1206		n.r.			
tw(CH$_2$)	1224	n.r.	←	1255			
				1310	→	1298	ω(CH$_2$)
δ_s(CH$_3$)	1366	1384	←	1384	→	1372	δ(CH$_2$), δ(CH$_3$)
δ_a(CH$_3$) χ(CH$_2$)	1427	1433	←	1446	→	1446	δ(CH$_2$), δ(CH$_3$)
ν(C−H)	2916	2942	←	2941	→	2922	ν(C−H)

^{a} ν = stretch, ρ = rock, ω = wag, tw = twist, δ_s = symmetric deformation, δ_a = asymmetric deformation, χ = scissor, b = bend. Note: The ethyl mode assignments are for the spectra collected after dosing iodoethane on the clean and oxygen-covered Ag(110) surfaces. The ethoxide mode assignments are for the spectrum collected after reacting ethanol with oxygen-covered Ag(110).
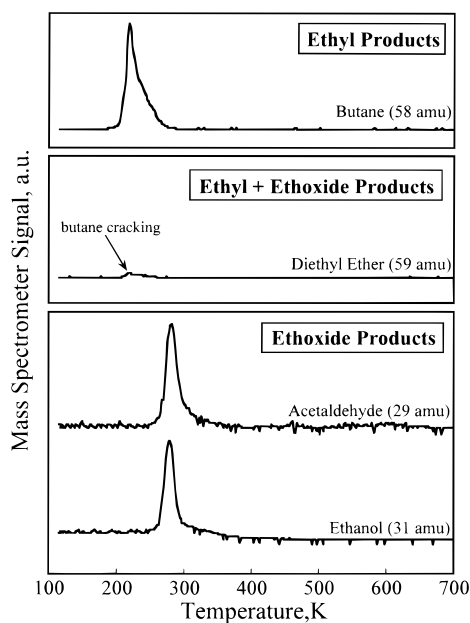

Figure 3. TPD spectra for the products formed from a mixture of ethoxide and ethyl. The oxygen-covered Ag(110) surface was exposed to a saturation dose of ethanol, resulting in an ethoxide-covered surface. Iodoethane was then dissociatively adsorbed on that surface to yield the ethyl−ethoxide mixture. The absence of diethyl ether in the spectra indicates that ethyl groups do not couple with ethoxides under these conditions.

Figure 4. TPD spectra for the products formed from a mixture of ethoxide and ethyl. First, the ethyl layer was formed by dissociatively adsorbing iodoethane. Next, a fraction of the ethyl groups was titrated from the surface by exposing them to ethanol; the net result was a mixture of ethyl and ethoxide. The absence of diethyl ether in the spectra indicates that ethyl groups do not couple with ethoxides under these conditions.

B. Iodoethane + Ethanol. As in the previous section, the reaction of an adsorbed layer consisting of ethoxide and ethyl species on Ag(110) was investigated using temperature-programmed desorption. However, a different process for forming the adlayer was employed in this experiment and is described below. Barteau et al.[27] have previously demonstrated that the relative acidity scale of Brønsted acids on Ag(110) correlates well with the acidity hierarchy observed in the gas phase, according to the reaction BH(g) + B′(a) ↔ B′H(g) + B(a). In these reactions, adsorbed bases, B′(a), can be titrated from the surface using a stronger Brønsted acid, BH(g); the conjugate base, B(a), remains adsorbed on the surface. The values of $\Delta H°_{acid}$ for ethanol and ethane in the gas phase are 376.1 and 404.0 kcal/mol, respectively.[28] Therefore, one might expect that ethanol molecules could displace ethyl groups adsorbed on Ag(110) to form surface-bound ethoxides and gaseous ethane. This strategy was followed to form a mixture of ethyl and ethoxide ligands on the Ag(110) surface. Iodoethane was dissociatively adsorbed onto the clean Ag(110) surface at
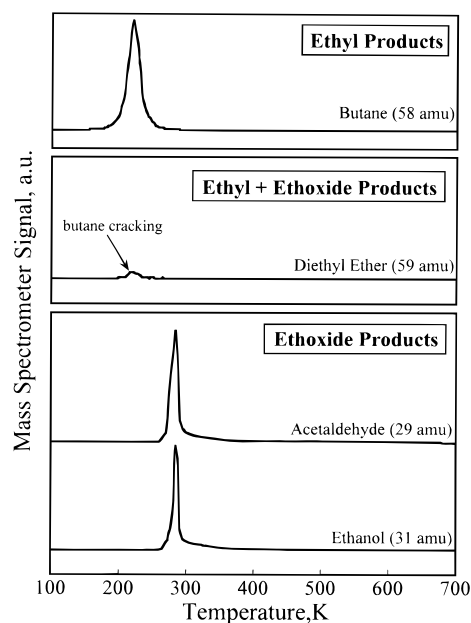
110 K to form surface ethyl ligands. The sample was flashed to 200 K to ensure that all of the iodoethane molecules were dissociated or desorbed. The ethyl-covered Ag(110) surface was then cooled to 110 K and exposed to ethanol to create a mixture of ethyl and ethoxide via the acid−base pathways described above. The relative ratios of ethyl:ethoxide in the reacting adlayer could be varied by changing the ethanol exposure during the titration reaction.

Desorption spectra observed for this ethyl−ethoxide mixture are shown in Figure 4. Once again, since this reaction mixture is devoid of oxygen, any diethyl ether formed must result from ethyl−ethoxide coupling. However, as in the previous example, no diethyl ether was formed during the TPD experiment. All of the ethyl groups coupled to form butane at 219 K, while the ethoxides decomposed at 283 K to give acetaldehyde and ethanol.

C. Oxygen + Subsaturation ^{13}C-Ethanol + Iodoethane. Finally, a reaction mixture was formed which consisted not only of ethyl and ethoxide ligands, but also adsorbed oxygen atoms.
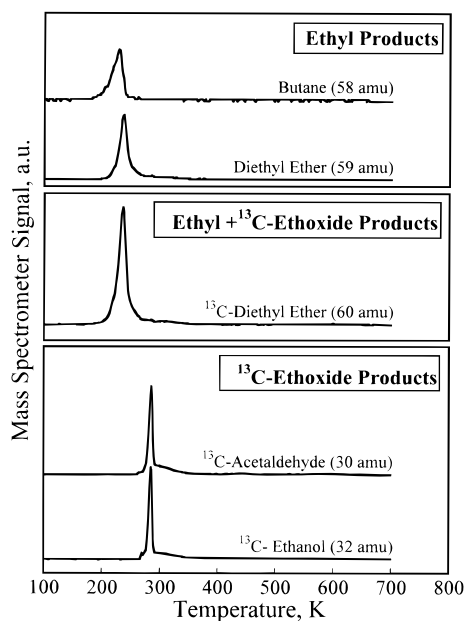
Figure 5. TPD spectra for the products formed from a mixture of ^{13}C-ethoxide, ethyl, and oxygen. The oxygen-covered Ag(110) surface was exposed to a subsaturation dose of ^{13}C-ethanol, resulting in a mixture of ^{13}C-ethoxide groups and oxygen atoms. Iodoethane was then dissociatively adsorbed on that surface to yield the ethyl$-^{13}$C-ethoxide$-$oxygen mixture. The formation of ^{13}C-diethyl ether indicates that ethyl groups couple with ethoxides in the presence of coadsorbed oxygen atoms.

This adsorbed layer was formed by a method similar to that used in part A of this section. The surface was first covered with 0.33 ML of adsorbed oxygen atoms at 300 K. After the sample was cooled to 110 K, the surface was exposed to a dose of ^{13}C-ethanol (CH$_3$^{13}CH$_2$OH) insufficient to completely titrate surface oxygen and flashed to 240 K to produce ethoxides. The resulting adlayer consisted of a mixture of ethoxides and oxygen atoms. Iodoethane was then dissociatively adsorbed onto this surface to give the ethyl$-$ethoxide$-$oxygen reaction mixture. The addition of oxygen to the reaction mixture in this experiment created a new reaction pathway not present in the previous two mixtures, coupling of two ethyl groups with an oxygen atom to form diethyl ether. To distinguish between diethyl ether formed via ethoxide$-$ethyl coupling and ethyl$-$ethyl$-$oxygen coupling, the ethoxides formed in this experiment were labeled with ^{13}C; any ether containing ^{13}C must be derived from ethoxides.

The desorption curves for the various products are shown in Figure 5. Again, the products formed in this reaction are separated into three categories: (1) ethyl products, (2) ethyl$-$^{13}C-ethoxide products, and (3) ^{13}C-ethoxide products. The ethyl-derived products included butane at 227 K and unlabeled diethyl ether at 236 K. The ^{13}C-ethoxide decomposition products, ^{13}C-acetaldehyde and ^{13}C-ethanol, were evolved at 285 K. However, the key result from this experiment is that ^{13}C-ethoxide and ethyl couple to form ^{13}C-diethyl ether at 236 K. This result is shown by the desorption trace for $m/e = 60$, which corresponds to the fragment of ^{13}C-diethyl ether (CH$_3$CH$_2$O^{13}CH$_2$CH$_3$) which has lost a methyl group (either CH$_3$CH$_2$O^{13}CH$_2-$ or $-$CH$_2$O^{13}CH$_2$-CH$_3$). This result is further supported by the desorption trace for the parent mass fragment of ^{13}C-diethyl ether, $m/e = 75$, which is not shown here. Of additional importance is the fact that diethyl ether and ^{13}C-diethyl ether evolve with identical peak shapes and desorption temperatures, 236 K. This fact indicates that both products are formed via a common rate-determining step, which suggests that formation of diethyl ether from two ethyl groups and an oxygen atom involves initial

formation of an ethoxide followed by ethyl$-$ethoxide coupling. This result and the role of oxygen in these experiments are addressed below.

Discussion

Here and in a previous report[6] we have shown that iodoethane reacts on oxygen-dosed Ag(110) to form a variety of hydrocarbon and oxygenate products. As demonstrated in Figure 1, those products include diethyl ether, butane, ethylene, water, acetaldehyde, ethanol, and acetate decomposition products. In addition, the HREELS results shown in Figure 2a demonstrate that these products are formed by the initial dissociation of iodoethane to form surface-bound ethyl ligands. The question of interest then is the mechanism by which adsorbed ethyl and oxygen species react to form the various products observed. Butane likely evolves via coupling of two ethyl groups, as it does on the clean Ag(110)[6] and Ag(111)[19] surfaces. The formation of ethylene from surface ethyl groups occurs in the presence of adsorbed oxygen atoms but not on the clean surface; thus, this reaction likely involves hydrogen abstraction by surface oxygen.[6] Water was also observed as a side product of this reaction. Acetaldehyde and ethanol evolve at 268 K and are the products of ethoxide decomposition; acetaldehyde can react further with oxygen atoms to form surface acetate species, which decompose at 627 K. Figure 2b supports the identification of the 268 K intermediate as an ethoxide, obviously formed from addition of an ethyl group to an oxygen atom.

Diethyl ether is the only product whose formation requires further investigation since there are two possible pathways for its formation: (1) concerted addition of two ethyl groups to an oxygen atom or (2) sequential addition of two ethyl groups to an oxygen atom. The second mechanism involves initial formation of an ethoxide followed by coupling of that species with an ethyl group to form diethyl ether. Although both pathways are possible, the second reaction channel seems more plausible since it involves consecutive bimolecular reactions rather than a single termolecular reaction. To test the plausibility of ethyl$-$ethoxide coupling to form diethyl ether, several mixtures of ethyl, ethoxide, and oxygen were investigated on the Ag(110) surface using TPD, as described above. Figure 5 clearly demonstrates that under the proper reaction conditions ethyl groups and ethoxides couple to form diethyl ether. Furthermore, the peak shape and desorption peak temperature for diethyl ether formation via ethyl$-$ethoxide coupling are identical to those for diethyl ether formed from ethyl groups and oxygen. This fact is demonstrated by the coincident $m/e = 59$ and 60 TPD traces in Figure 5 and indicates that both reaction channels involve a common rate-determining step. That is, the formation of diethyl ether from ethyl groups and oxygen on Ag(110) involves addition of an ethyl group to an oxygen atom to form the ethoxide, followed by ethyl$-$ethoxide coupling to form diethyl ether. The rate-limiting step for this process is the ethyl$-$ethoxide coupling step. These results also indicate that two ethoxides do not couple together to form diethyl ether, since none of the product ether was observed to have multiple ^{13}C labels.

Coupling of ethyl groups with ethoxides to form diethyl ether has not been observed previously on a metal surface under UHV conditions. The reactions of iodoalkanes on O/Rh(111)[7−9] and O/Ni(100)[10] lead to alkoxide formation, but no evidence has been reported that alkoxides can react with alkyl ligands to form ethers on those surfaces. However, in solution metal alkoxides react with primary alkyl halides to yield ethers via an S$_N$2 reaction; i.e., the Williamson ether synthesis.[29] The alkoxide

species participating in the Williamson reaction are typically formed by reaction of an alcohol with a strong base such as sodium hydride. The metal alkoxide is then reacted with the alkyl halide to give the corresponding ether. An important variation of the Williamson synthesis involves the use of silver oxide, Ag_2O, as base, rather than NaH. In this reaction it has been suggested that the free alcohol reacts directly with the alkyl halide to form the ether; there is no need to preform the metal alkoxide salt.[29] The similarities between this homogeneous reaction and our heterogeneous reaction are noteworthy. Although the surface reaction cannot formally be categorized as S_N2, the overall reaction scheme is the same in both cases: an alcohol (ROH) and an alkyl halide (R′X) react with Ag_2O or oxygen-covered Ag(110) to form the corresponding ether (ROR′).

The formation of ethers from reactions between alkyl species and oxygen on Ag(110) might be expected considering silver's standing as a unique metal catalyst for the industrial epoxidation of olefins[30,31] and diolefins.[32,33] Of particular interest is the fact that diethyl ether formation involves sequential, not concerted, formation of the C−O bonds. This observation may suggest that ethylene oxide synthesis, from ethylene and oxygen over silver catalysts, involves sequential addition of the oxygen atom to each carbon of ethylene rather than direct reaction between the ethylenic π-orbitals and adsorbed oxygen. This assertion is supported by the fact that epoxidation of ethylene by oxygen-covered silver surfaces is not stereoselective. Epoxidation of either *cis*- or *trans*-1,2-dideuterioethylene yields a mixture of the *cis*- and *trans*-d_2 epoxides which is nearly equilibrated.[34,35] In addition, no intra- or intermolecular hydrogen−deuterium transfer was observed in those studies. Such experiments demonstrate that considerable rotation about the C−C bond can occur in the course of this reaction and are inconsistent with the concerted addition of oxygen to ethylene. Stepwise formation of the two C−O bonds would, at some point along the reaction coordinate, produce an asymmetric species. This intermediate has been depicted both as an $\eta^1(O)$ radical[36] or cation[37] and as an oxametallacycle intermediate[38] which is bound to the surface by one Ag−C bond and one Ag−O bond. The metallacycle structure is favored by a number of arguments, from the implausibility of stable structures that would maintain reactive radical functions apart from the reactive surface to the fact that ethylene is initially π-bonded to the surface,[39] and minimization of the number of bond-making and breaking processes involved in oxygen addition would retain at least one carbon attached to the surface. We have recently isolated and spectroscopically characterized an oxametallacycle on Ag(110).[40,41] Although ethylene oxide was not a product in the decomposition of that species, the oxametallacycle vibrational modes calculated using density functional theory (DFT) included a possible reaction coordinate for ring closure to give the epoxide. Small changes in the reaction conditions may influence the selectivity of oxametallacycle reactions to give ethylene oxide, especially since we have shown here that coadsorbed oxygen atoms are necessary for ethyl−ethoxide coupling on Ag(110). Ring closure of an oxametallacycle ($-OCH_2CH_2-$) can be thought of as an analogous intramolecular coupling of alkoxide and alkyl functions.

In the present study and our previous report[6] we have investigated a variety of reaction mixtures containing ethyl, ethoxide, and oxygen species on the Ag(110) surface. Table 2 summarizes the products evolved from TPD experiments for the different combinations of these adsorbates on Ag(110). The key point is that while ethyl ligands and ethoxides can couple

TABLE 2: Effect of Ethyl−Ethoxide Adsorption Sequence on Surface Intermediates and Final Products Formed on Ag(110)[a]

adsorption sequence	adsorbed species	ether formed?
$O_2 + C_2H_5I$	$C_2H_5 + C_2H_5O + O$	yes
C_2H_5I	C_2H_5	no
C_2H_5OH	----	no
$O_2 + C_2H_5OH$	C_2H_5O	no
$O_2 + C_2H_5OH$ (saturation) $+ C_2H_5I$	$C_2H_5 + C_2H_5O$	no
$C_2H_5I + C_2H_5OH$	$C_2H_5 + C_2H_5O$	no
$O_2 + C_2H_5OH$ (subsaturation) $+ C_2H_5I$	$C_2H_5 + C_2H_5O + O$	yes

[a] Excess surface oxygen is required for diethyl ether formation from ethyl−ethoxide.

to form diethyl ether on Ag(110), that reaction only occurs in the presence of coadsorbed oxygen atoms, even though oxygen itself is not necessarily consumed in that reaction. Likewise, the original experiments of Wachs and Madix[13] (reproduced in our laboratory), in which ethanol was reacted with ^{18}O, showed no evidence for exchange of oxygen atoms between the surface and adsorbed ethoxides. The function of "spectator" oxygen (oxygen neither consumed nor exchanged during reaction) in Ag-catalyzed reactions is not well understood, however, the requirement of such species has a variety of precedents. For example, Jørgensen and Larsen[42] have found that Ag_2O in combination with iodosylbenzene can mediate the epoxidation of alkenes. Isotope-labeling experiments involving ^{18}O-labeled iodosylbenzene have demonstrated that it, rather than the Ag-complexed oxygen, acts as the oxygen donor in those experiments. Even though the oxygen in the epoxide is derived from iodosylbenzene, it is Ag_2O, rather than Ag, which is used as the catalyst. Likewise, Ag_2O is used in the Williamson ether synthesis described above, although the oxygen in the product ether is derived from the starting alcohol. Perhaps the best example of the requirement of oxygen species which do not participate directly in the catalytic reaction is in the heterogeneously catalyzed epoxidation of ethylene by silver. It has long been known that the presence of subsurface oxygen is required for this reaction to occur.[43] Although subsurface oxygen has been shown to exchange with surface atomic oxygen,[44] which then reacts with ethylene[45−47] to form ethylene oxide and combustion products, its involvement in the epoxidation reaction is more complicated than simple exchange and has been explained by both electronic and geometrical arguments, noted below.

To address the effects of oxygen on the ethyl−ethoxide coupling reactions observed in this study, we first need to consider the changes which occur in the Ag(110) surface structure upon oxygen adsorption. The oxygen-free Ag(110) surface has a ridge and trough structure as shown in Figure 6a. The ridge Ag atoms, represented as the large gray circles, constitute the outermost monolayer of Ag atoms. Adsorption of oxygen onto the Ag(110) surface induces a reconstruction of the simple ridge and trough structure. Similar reconstructions have been observed to form (2×1) oxygen islands on Cu(110).[48−50] Scanning tunneling microscopy (STM) studies for the O/Ag(110) system have demonstrated the formation of long $-Ag-O-$ chains parallel to the [001] direction.[51−53] Additional STM studies have investigated the growth of these linear chains and concluded that they are the result of an added-row rather than missing-row structure.[54] This structure is depicted in Figure 6b for the $(3 \times 1)-O/Ag(110)$ example. Here, the black circles represent the added-row Ag atoms associated with the surface reconstruction. The small white circles are the oxygen atoms
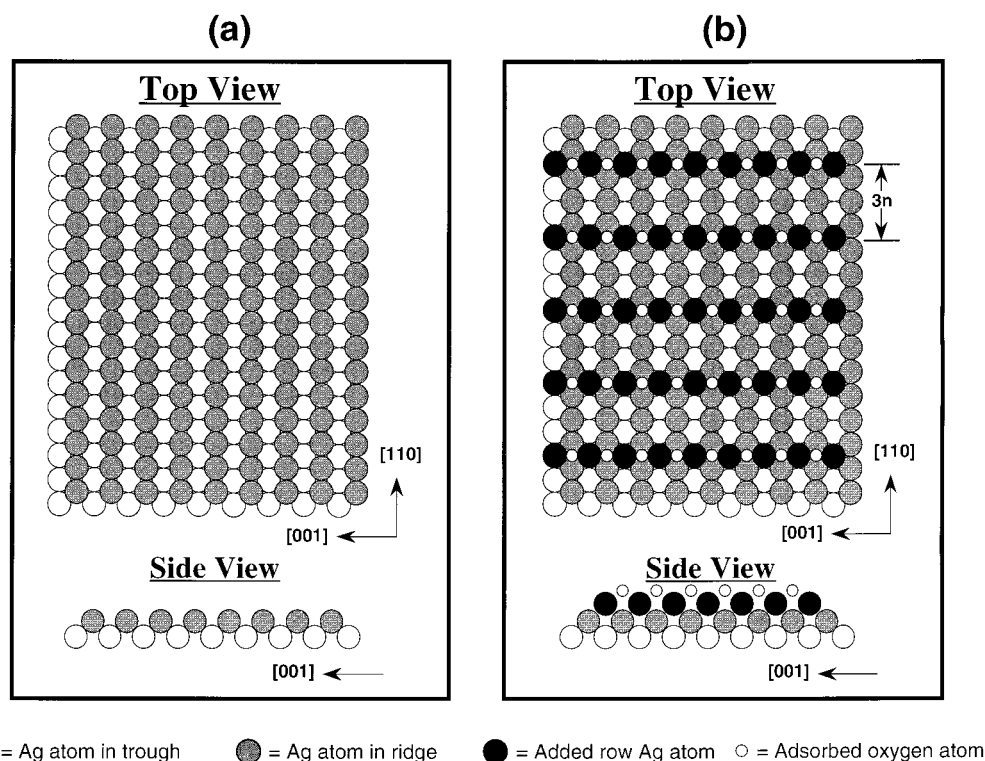
(a)

Top View

[110]

[001]

Side View

[001]

(b)

Top View

3n

[110]

[001]

Side View

[001]

○ = Ag atom in trough   ◉ = Ag atom in ridge   ● = Added row Ag atom   ○ = Adsorbed oxygen atom

Figure 6. Top and side view of (a) the clean Ag(110) surface and (b) the added-row structure for the $(3 \times 1)-O/Ag(110)$ surface.

which are positioned above the added Ag atoms in long-bridge sites.[55] The large gray circles are the surface Ag atoms remaining intact from the terrace of the clean Ag(110) surface.

Since the added-row structure is associated with surface oxygen atoms (which are a prerequisite for ethyl−ethoxide coupling), the presence or absence of this structure may influence the ethyl−ethoxide coupling reactions. Bowker et al.[56,57] have shown that methanol reacts with oxygen at the ends of the −Cu−O− chains to form methoxy on Cu(110). The methoxy is bound to the Cu terrace (not the added Cu atom) and is free to migrate within the regions not covered by oxygen islands. The Cu atom exposed at the end of the −Cu−O− chain by reaction then diffuses away from the active site to expose another oxygen atom. Thus, an oxygen-dosed Cu(110) surface which is partially reacted with methanol has been shown (by STM) to consist of phase-separated oxygen islands with methoxy units located between the oxygen islands. By analogy, an oxygen-dosed Ag(110) surface which is partially reacted with ethanol might be expected to consist of −Ag−O− chains with ethoxide species occupying the clean surface region between the added rows. The −Ag−O− added rows remaining on the surface may provide sites for iodoethane adsorption and dissociation. It is clear that prior to ether formation on such a surface, ethyl ligands are located near the added −Ag−O− rows since diethyl ether is formed by both ethyl−ethyl−oxygen and ethyl−[13]C-ethoxide coupling reactions. One possibility is that some ethyl groups are adsorbed at the added-row Ag sites and can react with the adjacent ethoxide species. STM investigations of this system may help to elucidate any geometrical influences of the added-row structure in ethyl−ethoxide coupling reactions. At this point, however, caution should be exercised in making analogies between Ag(110) and Cu(110) since a recent study suggests that some species interact at different reactive sites on these oxygen-covered surfaces;[58] electronic influences of coadsorbed oxygen should also be considered.

The ability of coadsorbed oxygen atoms to facilitate ethyl−ethoxide coupling may be related to alterations in the electronic properties of the surface due to the presence of oxygen. For example, surface oxygen atoms on Ag(110) have been shown to increase the heat of adsorption and sticking probability of various molecules, including ethylene[59] and ethylene oxide.[60] This effect is presumably due to the creation of electron-deficient silver atoms or Lewis acid sites. In addition, the electronic effects of subsurface oxygen in ethylene epoxidation over silver surfaces have been the subject of a large number of reports in recent years[43,61−71] and may be related to the current phenomenon. In those studies, the influence of subsurface oxygen has mostly been attributed to its ability to withdraw electron density from the silver surface. This creates (1) $Ag^{\delta+}$ sites for ethylene adsorption and (2) surface oxygen species which are more "covalent"[68] or "electrophilic"[64] in nature and therefore tend to react with ethylene to form ethylene oxide. Also, theoretical results suggest that subsurface oxygen may reduce the bond energy between silver and adsorbed oxygen, thereby facilitating the epoxidation reaction.[62] The presence of coadsorbed oxygen atoms in the present study may have similar effects on the ethyl−ethoxide coupling reactions. That is, adsorbed oxygen atoms may alter the bond strengths or the character of the bonds between ethyl or ethoxide and the silver surface in such a way as to promote the coupling reactions. Although the exact role of coadsorbed oxygen is not clear in this study, it is clear that it is necessary for diethyl ether formation from ethyl and ethoxide. It remains to be seen whether other electronegative adsorbates can likewise promote this reaction.

Conclusions

Iodoethane adsorbs dissociatively on the oxygen-dosed Ag-(110) surface to form ethyl ligands. A fraction of the ethyl ligands formed on the surface react with oxygen atoms to form surface ethoxide intermediates. Diethyl ether is the predominant oxygenate product evolved from the surface in these reactions. Separate TPD experiments with ethoxide−ethyl mixtures dem-

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onstrate that these species can couple to form diethyl ether with kinetics identical to those of the ether formation reaction noted above. However, the ethyl−ethoxide reaction occurs only in the presence of additional coadsorbed oxygen atoms. These experiments demonstrate that formation of diethyl ether from the ethyl−oxygen reaction on Ag(110) occurs via sequential addition of ethyl groups to form first the ethoxide and then the ether.

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