

TPD and HREELS reinvestigation of ethylene oxide adsorption on Pt(1 1 1)

JooHo Kim^a, Haibo Zhao^a, Chameli Panja^a, Amelia Olivas^b, Bruce E. Koel^{a,*}

^a Department of Chemistry, University of Southern California, SSC 606, Los Angeles, CA 90089-0482, USA

^b CCMC-UNAM, Ensenada, B.C., UNK 22800, Mexico

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Abstract

A reinvestigation of ethylene oxide (EtO) adsorption and desorption on Pt(1 1 1) is reported using primarily TPD, AES, XPS and HREELS. EtO does not react when adsorbed on Pt(1 1 1) at 90 K and then subsequently heated under UHV conditions. Specifically, TPD results and AES measurements taken after TPD experiments place an upper limit on the extent of EtO decomposition at 0.02 ML. This work helps to correct earlier work that showed significant decomposition on this surface. HREELS identified molecular EtO adsorption at 90 K, with only small shifts in molecular vibrational frequencies from condensed phase spectra. At a coverage of less than 0.1-ML EtO, EtO is bonded oxygen-end down to the Pt(1 1 1) surface with C_{2v} symmetry, i.e., with the C_2 axis of EtO normal to the surface. By showing that the close-packed Pt(1 1 1) surface is less reactive toward the desired product of ethylene epoxidation than previously thought, these new results should be helpful in discussing differences between the chemistry of Ag and Pt catalysts for this reaction.

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1. Introduction

Ethylene oxide (EtO) is a cyclic organic molecule obtained via catalytic epoxidation of ethylene by O_2 over a promoted Ag catalyst [1,2]. In order to understand why silver shows such a high selectivity and reactivity for this important reaction, extensive catalysis studies have been carried

out, along with early surface science experiments on single crystal Ag surfaces [3–9].

One aspect of the surface science studies to understand ethylene epoxidation has been to investigate the reactivity of the EtO product at close-packed (relatively defect free) catalytic monolithic surfaces. EtO adsorbs reversibly and molecularly on Ag(1 1 0) at 110–140 K [5–8], without decomposition during thermal desorption under UHV conditions and with little evidence for ring deformation [5]. EtO is bonded via the oxygen atom to the surface at the short bridge site with the C–C bond axis parallel to the metal surface and

* Corresponding author. Tel.: +1-213-740-7036/4126; fax: +1-213-740-2701/3972.

E-mail address: koel@usc.edu (B.E. Koel).

C_{2v} symmetry. On O- and K-precovered Ag(110) surfaces, the EtO adsorption geometry was different and ring-opening reactions were reported during heating following low temperature adsorption [4,5,10]. Recent work examining adsorption and reaction of EtO on Ag(111) showed that the reaction of EtO on this surface is an activated process that requires surface temperatures approaching 250 K [11]. Adsorption at 100 K is entirely molecular, and these molecules desorb at low temperature without reacting during heating in ultrahigh-vacuum (UHV).

On other metal surfaces, EtO adsorbs and bonds on Cu(110) at 120 K very similarly to that on Ag(110) [5,12]. EtO has been reported to adsorb molecularly on Fe(100) at 140 K [6], Ni(110) at 100 K [13] and Ni(111) at 140 K [6,14] with no decomposition during heating under UHV conditions. However, there is a report of EtO decomposition at about 350 K after EtO adsorption on Ni(110) at 90 K [15]. EtO reacted on a K-precovered Ni(111) surface after adsorption at 100–140 K [14], with evidence provided by high-resolution electron energy loss spectroscopy (HREELS) for acetaldehyde as a possible intermediate [16]. In addition, EtO decomposes during heating following low temperature adsorption on Mo(110) [17], Rh(110) [18], Pd(110) [19,20], and Pd(111) [21].

Of particular interest is an early report concerning ethylene oxide adsorption on Pt(111) studied by temperature-programmed desorption (TPD) and HREELS [8]. The adsorption energy was reported to decrease slightly with coverage from 11.9 to 10.0 kcal/mol and decomposition reactions supposedly predominated over molecular desorption at low coverages [8]. H_2 , CO and residual adsorbed carbon were the ultimate decomposition products. The authors argued that a principle difference between Ag and Pt catalysts was that Pt surfaces readily dissociated EtO. This conclusion has been often cited [6,17–24], but the “common knowledge” for this chemical difference has this single surface science study as its basis.

A subsequent report of EtO adsorption on the Pt(110)-(1 \times 2) surface calls this previous result into question. EtO desorbed molecularly on the Pt(110)-(1 \times 2) surface from 140 to 230 K with

minor decomposition ($\theta_{EtO} \leq 0.02$ ML) [25]. We thought that it would be valuable to reinvestigate EtO adsorption and desorption on Pt(111) to help provide a firmer foundation for understanding the reactivity of this molecule and the extension of that insight to epoxidation and selective oxidation reactions over metal-based heterogeneous catalysts.

2. Experimental methods

Experiments were conducted in a three-level ultrahigh-vacuum (UHV) chamber with a base pressure of 2×10^{-10} Torr, as has been described previously [26]. A double-pass cylindrical mirror analyzer (CMA) was used for AES. An UTI 100C quadrupole mass spectrometer (QMS) was used for TPD studies. A LK2000 spectrometer was used for HREELS.

The Pt(111) crystal was mounted on two Ta rods that were imbedded in liquid-nitrogen cooled copper blocks at the bottom of a differentially pumped, XYZ manipulator. The temperature was measured by a chromel–alumel thermocouple spot-welded at the side of the crystal. The sample could be cooled to 90 K or resistively heated to 1200 K. The Pt(111) sample was cleaned by a standard combination of Ar^+ -ion sputtering at 5×10^{-5} Torr, O_2 treatment ($P_{O_2} = 5 \times 10^{-8}$ Torr for 5 min) at 850 K and annealing in vacuum at 1200 K. Sample cleanliness was checked with AES, and LEED was used to insure a well-ordered surface.

High purity ethylene oxide (99.5%+ purity; Aldrich Chemical Co.) was dosed onto the Pt(111) substrate via a glass microcapillary array doser connected to a leak valve. Exposure values are given in units of Langmuirs (L) as determined by the uncorrected background gas pressure in the chamber during dosing. A doser enhancement factor of 20 was utilized in the reported exposures.

TPD spectra were taken using a linear heating rate of 3 K/s with the crystal in line of sight of the QMS ionizer. A stainless steel shield with an entrance aperture of 1 cm diameter covered the ionizer region of the QMS. The crystal was placed at a distance of 1 mm in front of the aperture for TPD experiments and this effectively attenuated

background contributions to the TPD curves. Two highly transparent stainless steel screens were used—one across the end of the ionizer grid (with a bias of -55 V) and the other across the shield aperture (at ground potential) in order to stop electron emission from the QMS ionizer impinging on the substrate during TPD measurements.

HREELS spectra were recorded in a specular direction at an angle of 60° from the surface normal with an incident beam-energy of 4.5 eV. The overall energy resolution of the spectrometer was about 7 meV (56 cm^{-1}) and counting rates in the elastic peak were about 100 kHz for clean Pt(1 1 1). All spectra reported were normalized to the intensity of the elastic peak.

3. Results and discussion

3.1. TPD results

Ethylene oxide (EtO) adsorption and desorption on Pt(1 1 1) was studied by temperature-programmed desorption (TPD) mass spectrometry. After exposing the surface at 90 K to various amounts of EtO, the desorption signal of the parent molecular ion ($m/e = 44$) as well as possible fragments, reaction products, or contaminants ($m/e = 2, 16, 18, 28, 29$) were recorded simultaneously.

A series of EtO TPD spectra obtained after increasing EtO exposures on Pt(1 1 1) is given in Fig. 1. EtO desorption was monitored by the $m/e = 29$ signal which is the largest peak in the EtO mass spectrum. For low EtO exposures, a single EtO desorption peak was observed at 207 K. With increasing exposures, this peak shifted to lower temperature, with a peak temperature of 158 K when this peak was nearly saturated after an exposure of 3.0 L. The monolayer coverage of EtO was estimated to be $\theta_{\text{EtO}} = 0.25$ ML by using the C(1s) XPS peak area ratio to that for ethylene (C_2H_4) adsorption at 300 K to give ethylidyne (CCH_3) with $\theta_{\text{C}} = 0.50$ ML referenced to the Pt(1 1 1) surface atom density of 1.505×10^{15} atoms/ cm^2 defined as $\theta = 1.0$ ML [27]. After larger EtO exposures, an additional low temperature peak started growing at 120 K due to desorption

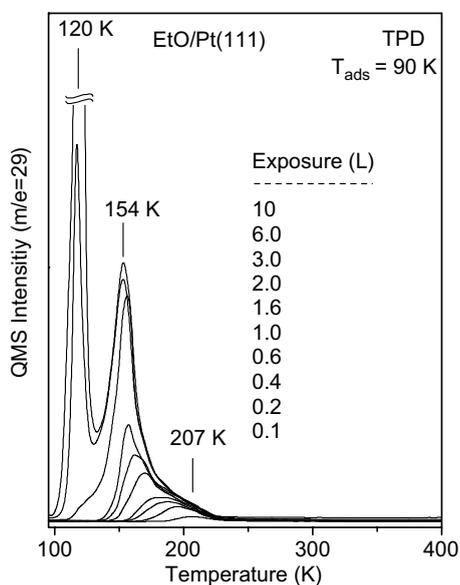


Fig. 1. EtO ($m/e = 29$) TPD spectra after ethylene oxide exposures on Pt(1 1 1) at 90 K.

from a second layer of physisorbed molecules of EtO adsorbed on top of the monolayer. The activation energy for desorption (E_d) of EtO bonded in the monolayer was estimated to be $E_d = 12.8$ – 9.3 kcal/mol as the coverage in the monolayer increased, using Redhead analysis assuming a typical preexponential factor of 10^{13} s^{-1} and first-order desorption kinetics [28].

Fig. 2 shows TPD spectra at several masses after exposing 3.0 -L EtO on Pt(1 1 1) at 90 K. The signal at 44 amu is the EtO parent peak and that at 29 amu is the largest fragment ion of EtO in the QMS corresponding to molecular desorption. There was no molecular EtO desorption above 220 K in the TPD spectra. TPD spectra at 28 amu showed a peak at 470 K and a cracking fragment peak from molecular EtO desorption at 158 K. H_2 TPD spectra at 2 amu showed a peak at 365 K and a cracking fragment peak from EtO desorption at 158 K. We believe that the high temperature CO and H_2 desorption peaks arise from coadsorbed contamination from the background gas rather than EtO decomposition. The amount of CO desorption was calculated to be 0.029 ML based on the saturation CO coverage of 0.68 ML on

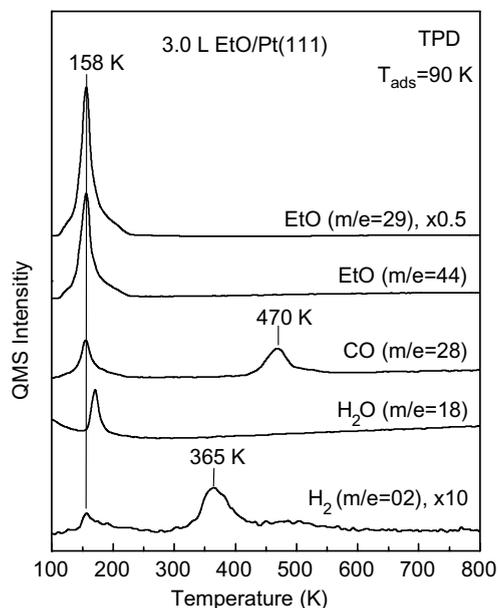


Fig. 2. TPD spectra of several gas phase products following 3.0-L EtO exposures on Pt(111) at 90 K.

clean Pt(111) at 150 K [29] and the amount of H₂ desorption was calculated to be $\theta_{\text{H}_2} = 0.038$ ML based on the saturation H_(a) coverage of 0.9 ML on clean Pt(111) at 150 K [29].

Even if these products (CO + H₂) arose from EtO dissociation, this still would correspond to only $\theta_{\text{EtO}}^{\text{dec}} = 0.03$ ML, or less than 10% of the EtO monolayer. Given a defect site concentration of a few percent typically, and the difficulties of avoiding small amounts of coadsorbed contaminants during cooling and dosing, it would appear that EtO does not dissociate under these conditions on pristine Pt(111). The TPD peak areas from Fig. 2 are plotted in Fig. 3, along with results from similar studies at many other exposures. The amounts of CO and H₂ desorption from the surface are nearly constant, independent of the amount of EtO dosed. Molecular desorption of EtO appeared even after a low exposure of 0.10 L.

We repeated these experiments on a different Pt(111) crystal in a different UHV chamber with a different source of EtO, and we found the same results. In addition, we conducted another set of experiments aimed to check if EtO reac-

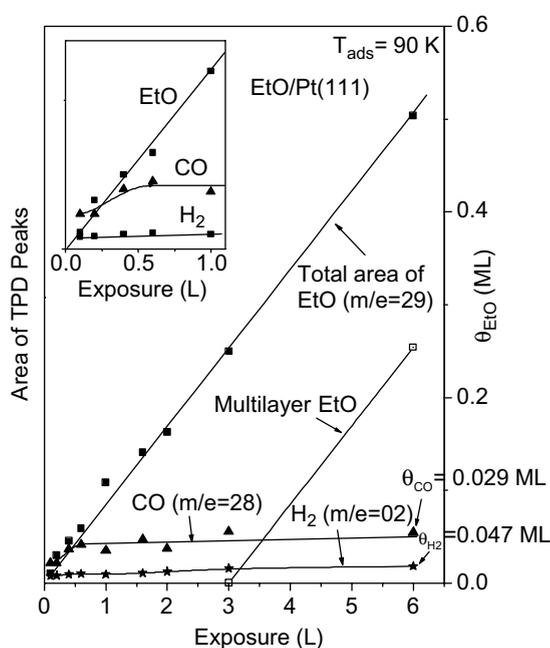


Fig. 3. Uptake curves for EtO adsorption on Pt(111) at 90 K constructed from TPD peak areas of EtO ($m/e = 29$), CO ($m/e = 28$) and H₂ ($m/e = 02$).

tion on Pt(111) was only a weakly activated process as on Ag(111). EtO exposures that produced 4-layers of EtO at 90 K were given on Pt(111) at 90, 130, and 250 K. Decomposition of less than 0.3% of one monolayer was measured in all cases. Even when an exposure that produced 40-layers of EtO at 90 K was given on Pt(111) at 250 K, decomposition less than 1% of one monolayer was measured.

3.2. HREELS

HREELS experiments were conducted after various EtO exposures on Pt(111) at 90 K (Fig. 4) and after heating a 3.3-layer film of EtO formed by a 10-L EtO exposure on Pt(111) (Fig. 5). The top curve in Fig. 4, obtained after a 10-L exposure provides reference values for molecular EtO in a solid film. The largest peaks were observed at 866, 1160, 1270, 1485, and 3070 cm^{-1} . The most intense loss peak at 866 cm^{-1} arises from the COC ring deformation mode of molecular EtO, and the loss peak at 1160 cm^{-1} is due to the CH₂ wagging

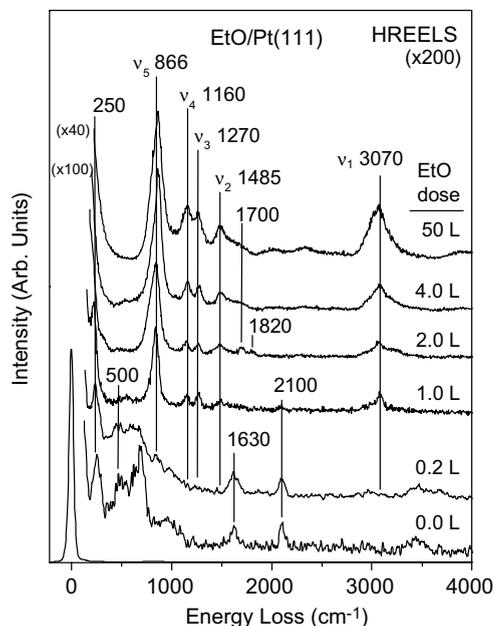


Fig. 4. HREELS spectra after EtO exposures on Pt(1 1 1) at 90 K.

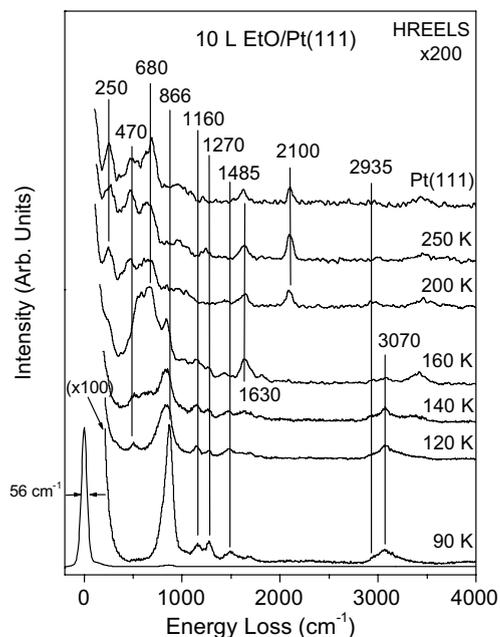


Fig. 5. HREELS spectra following a 10-L exposure of EtO on Pt(1 1 1) at 90 K and after sequentially annealing to 120, 140, 160, 200 and 250 K. All spectra were obtained after recooling to 90 K.

mode of EtO. Loss peaks at 1270, 1485, and 3070 cm^{-1} are due to the COC ring breathing mode, CH_2 scissoring mode, and CH stretching modes of molecular EtO, as assigned in Table 1.

At less than one-tenth of monolayer coverage (0.2-L EtO), a loss feature from the EtO ring deformation mode was detectable near 840 cm^{-1} , which indicates that adsorbed EtO is present in a molecular form. Other peaks at this low coverage at 680, 1630 and 3400 cm^{-1} are due to coadsorbed, contaminant H_2O , along with coadsorbed CO loss peaks at 500 cm^{-1} (Pt–CO stretching) and 2100 cm^{-1} (C=O stretching) that accumulate during the long scan time (90 min) needed to obtain the spectrum. For 1.0 and 2.0-L EtO exposures to give 1/3 and 2/3 of the monolayer coverage, the peak from the EtO ring deformation mode was red-shifted to 838 cm^{-1} , but no shift was observed for any other peaks. Small peaks at 1700 and 1820 cm^{-1} were detected in the spectrum after 2.0-L EtO exposure, and these are probably due to overtones or combination bands. The Pt–EtO stretching mode at 250 cm^{-1} appeared after 1.0-L EtO exposure on Pt(1 1 1). After this exposure, coadsorbed, contaminant CO gave a vibrational peak due to ν_{CO} at 2100 cm^{-1} . A 4.0-L EtO exposure, providing only a 1.3-layer film of EtO on the surface, resulted in a spectrum with all peaks at the same positions.

Fig. 5 shows HREELS spectra taken after a EtO multilayer film from a 10-L EtO exposure on Pt(1 1 1) at 90 K was annealed sequentially to several temperatures. All of the spectra were taken after re-cooling to 90 K. The intense ring deformation mode of EtO at 866 cm^{-1} disappeared by 200 K. This means that molecular EtO no longer exists or that the molecular plane of EtO is oriented parallel to the surface. The spectrum at 200 K and higher were similar to that obtained from clean Pt(1 1 1) (as shown in Fig. 4) in which only vibrational loss peaks due to small amounts of coadsorbed contaminant CO and H_2O that accumulated during scanning (90 min). HREELS spectra are thus consistent with conclusions from TPD that all EtO-derived species desorbed from the surface by this temperature.

Table 1
Vibrational modes of ethylene oxide

Vibrational mode		IR					HREELS					
Mode	Description	Gas phase [36]	Liquid phase [23]	Solid phase [37]	In solid Ar [38]	Au(2 1 1) [30]	Rh(1 1 1) [18]	Pd(1 1 0) [23]	Ag(1 1 0) [4]	Ag(1 1 1) ^a [11]	Pt(1 1 1) [8]	Pt(1 1 1) this work
$\nu_1(A_1)$	CH ₂ stretching	3018	3014vvs	3009, 3004	3020	2998	3050	2988	2960, 3050	3007	2955	3070
$\nu_2(A_1)$	CH ₂ scissoring	1498	1492s	1494, 1490	1496	1477	1475	1494	1475	1475	1525	1485
$\nu_3(A_1)$	Ring stretching	1270	1268vvs	1263	1273	1265, 1254	1240	1268	1250	1248	1380	1270
$\nu_4(A_1)$	CH ₂ wagging	1148	1124m	1141, 1133	1258	1140	1140	1147	1145	1130	1110	1160
$\nu_5(A_1)$	Ring deformation	877	864vs	860vvs, 855w	877	865	860	860	847	848	895	866
$\nu_6(A_2)$	CH ₂ stretching	3065		3054ms, 3048w		3048		3070				
$\nu_7(A_2)$	CH ₂ twisting	1300		1046m, 1040sh		1041						
$\nu_8(A_2)$	CH ₂ rocking	860		824w, 818ms		817		770				
$\nu_9(B_1)$	CH ₂ stretching	3006	3003	2996ms, 2986s	3010	2985, 2922		2988		3038		
$\nu_{10}(B_1)$	CH ₂ scissoring	1472	1468	1467s, 1460m	1470	1467		1434		1475		
$\nu_{11}(B_1)$	CH ₂ wagging	1151	1150	1167ms, 1164m	1154	1169		1086		1130		
$\nu_{12}(B_1)$	Ring deformation	872	864	874sh	879			935–950		787		
$\nu_{13}(B_2)$	CH ₂ stretching	3065	3072	3073w, 3066s	3071	3070		3070		2989		
$\nu_{14}(B_2)$	CH ₂ twisting	1142	1150	1158ms, 1152sh	1146	1158		1132		1130		
$\nu_{15}(B_2)$	CH ₂ rocking	821	799	794vs, 788vs	822	797		770		787		

^a We have reassigned the B₁ and B₂ modes from Ref. [11].

4. Discussion

The origin of the high selectivity and reactivity of promoted Ag catalysts for the catalytic epoxidation of ethylene by O_2 to form ethylene oxide (EtO) is still an interesting question. It is now clear that coadsorbed or preadsorbed surface or subsurface oxygen (depending on the metal) can have a tremendous influence on the reactivity of ethylene and the oxygen-containing hydrocarbon or other hydrocarbons in catalytic oxidation reactions. It has often been cited that a principle difference between Ag and Pt catalysts was that Pt surfaces readily dissociated the EtO product. This “common knowledge” seems to have a single surface science study as its basis. A study of EtO adsorption on Pt(1 1 1) by Campbell and Paffett [8] reported that EtO dissociated on the Pt(111) surface and left carbon residue as detected by AES. They also reported significant amount of H_2 , CO, and CH_4 by TPD. HREELS spectra after 1- and 30-L EtO exposures on Pt(1 1 1) at 300 K were reported and several peaks from hydrocarbon species were detected. These results are quite surprising in light of the subsequent data from Weinelt et al. [25] that showed EtO adsorbed and desorbed predominantly reversibly on Pt(110)-(1×2).

In our reinvestigation of the Pt(111) surface chemistry, carbon residue from EtO dissociation was not detected by AES after TPD experiments following less than monolayer coverages of EtO. The amounts of CO and H_2 detected in TPD following less than monolayer coverages were relatively small and nearly independent of the EtO exposure. The molecular EtO peak in TPD was eliminated by preannealing to 230 K and no other masses were detected above 230 K except H_2 and CO. TPD uptake curves showed that there was a small amount (0.02 ML) of coadsorption from the background gases, or possibly dissociation at low exposures that can easily be attributed to defects at the surface.

Table 1 gives vibrational modes and frequencies of EtO in the gas, liquid and solid phase investigated with infrared (IR) absorption spectroscopy, along with data for EtO adsorbed on several metal surfaces investigated with HREELS. The

CH stretching band at 3070 cm^{-1} is composed of four vibrational modes: $\nu_1(A_1)$, $\nu_6(A_2)$, $\nu_9(B_1)$ and $\nu_{13}(B_2)$. In infrared reflection-absorption spectroscopy (IRAS) spectra of EtO on Au(211), multiple peaks were observed at multilayer coverage: 3073 and 3061 (ν_6 and ν_{13}), 3005 and 2995 (ν_1 and ν_9), and 2915 cm^{-1} [30]. In the EtO multilayer on Au(211), molecules are sufficiently randomly oriented so that all of the possible IR active modes were observed in IRAS. The 2915-cm^{-1} band appeared only at multilayer EtO coverages on Au(211) and its origin is not clear. In HREELS spectra of EtO on Pt(111), a loss peak near this low frequency is visible from low to high coverages. This was the only peak observed in the CH stretching region for less than 10% of monolayer coverage. Even at 10% of monolayer coverage, the loss peak of the EtO-ring deformation mode at 860 cm^{-1} was observed, which establishes that EtO is adsorbed molecularly without the molecular plane parallel to the surface. We cannot determine from our data whether the adsorption geometry has the oxygen-end “up” or “down”, but we would certainly expect to have the oxygen atom coordinated to the Pt surface. Weinelt et al. [25] reported work function measurements for EtO on Pt(110)-(1×2) and concluded that the oxygen-end of EtO was down because the work function decreased as the coverage increased.

In related studies, Shekhar et al. [20,23] suggested that EtO adsorbed on Pd(110) underwent a ring-opening reaction above 200 K and ultimately produced CO and methylene species on the Pd surface. In HREELS, the intensity of the ring-deformation loss peak at 935 cm^{-1} increased after annealing to 180 K. In our studies, we did not observe this peak and only losses of coadsorbed H_2O increased after annealing to 160 and 200 K. We conclude that EtO does not undergo ring-opening on Pt(111) under these conditions.

If ring-opening reactions were to occur, methanol and acetaldehyde are likely intermediates at the surface. Methanol adsorption on Pt(111) has been investigated by many researchers. Sexton et al. [31] found that 10% of the methanol in the monolayer dissociated on Pt(111), however, this was later shown to be caused by defect sites on the Pt(111) surface [32]. A more recent study of

methanol adsorption on Pt(1 1 1) by Panja et al. [33] also found no decomposition on Pt(1 1 1). Methanol desorbed molecularly from Pt(1 1 1) in TPD with a peak at 194 K at low coverages and 183 K at monolayer coverage. Wang and Masel [34] has reported that methanol adsorbed molecularly on Pt(1 1 0)-(2 × 1) at 100 K. Some methanol decomposed to form methoxy ($\mu\text{-OCH}_3$) with heating to 125–200 K. Some surface methoxy groups recombined with hydrogen to produce methanol and some decomposed to liberate CO and hydrogen with heating to 215–275 K. There is no evidence for methanol or methoxy species in our studies of EtO on Pt(1 1 1). The other likely intermediate, acetaldehyde (CH_3CHO), adsorbs molecularly on Pt(1 1 1) at 90 K and polymerizes during TPD of multilayer films. Slightly more than one-half (56%) of adsorbed acetaldehyde in the monolayer dissociated by heating the surface to 250 K to desorb CO, H₂ and CH₄ and form carbon residue [35]. Molecular desorption of acetaldehyde occurred in two peaks at 150 and 200 K at monolayer coverage, with the high temperature peak corresponding to recombination of an acetyl ($\text{CH}_3\text{C}=\text{O}$) intermediate on the Pt(1 1 1) surface. There is no evidence for acetaldehyde or acetyl species in our studies of EtO on Pt(1 1 1).

5. Summary

TPD was used to show that ethylene oxide (EtO) adsorbs reversibly on the Pt(1 1 1) surface. EtO desorbed in a peak at 210 K which shifted to 154 K at monolayer EtO coverage, corresponding to desorption energies of $E_d = 12.8\text{--}9.3$ kcal/mol. AES did not show any carbon residues from EtO dissociation at monolayer coverage. These results extend and correct previous studies of this system that found extensive EtO dissociation on Pt(1 1 1). Our HREELS results show that EtO adsorbs molecularly even at coverages of less than 10% of a monolayer and that EtO desorbed cleanly by 250 K under UHV conditions. EtO binds to the surface in an upright configuration with C_{2v} symmetry. In discussing differences between the chemistry of Ag and Pt catalysts for ethylene epoxidation, our results and other recent surface science studies

suggest that Pt is less reactive for decomposing the EtO product of the reaction than was commonly thought in the past.

Note added in proof

One of the authors of Ref. [8] (CTC) has subsequently acknowledged to us that electron-induced chemistry due to electrons from the mass spectrometer likely influenced the results reported in that paper.

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