

Studies of the Ensemble Size Requirements for Ethylene Adsorption and Decomposition on Pt(111): Ethylene and Bismuth Coadsorption[†]

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The coadsorption of bismuth and ethylene on Pt(111) has been studied by using AES, LEED, TPD, and HREELS. These studies were carried out to determine if bismuth acts as an inert, site-blocking agent that can be used to determine ensemble size requirements of ethylene adsorption and decomposition on Pt(111). These studies show that, indeed, bismuth has no effect on the heat of adsorption of molecular ethylene, the decomposition mechanism, or the activation energy required for C-H bond breaking or subsequent elementary decomposition reactions. The vibrational frequencies of adsorbed ethylene are also independent of bismuth coverage. Preliminary modeling of the decreased adsorption and reaction of ethylene due to coadsorbed bismuth determines that an ensemble of four Pt atoms is required for adsorption and a slightly larger ensemble (possibly five or six Pt atoms) is required for decomposition.

Introduction

We have previously shown that coadsorbed potassium has large effects on the adsorption¹ and decomposition² of ethylene on Pt(111). Due to the large dipole moment associated with potassium adatoms, we have attributed many of these effects to an electronic origin. Potassium adatoms donate substantial charge to the surface Pt atoms at low coverage, altering the electron density at a given Pt atom that is involved in bonding coadsorbed molecular species. The presence of potassium adatoms at the surface also implies that not all of the Pt atoms are available for bonding or decomposing ethylene. Thus, it is unclear what role ensemble effects play in the alkali-promoted surface chemistry.

Recently, Paffett et al.³ and Campbell et al.⁴ have shown that bismuth coadsorption on Pt is a potentially useful probe of surface ensemble or site-size requirements. Bismuth's potentially unique role in these experiments is due to three factors: (1) bismuth is largely inert for chemisorption of most small molecules, notably hydrocarbons, (2) repulsive interactions lead to a laterally dispersed bismuth adlayer that is disordered (randomly distributed) at low coverages, and (3) the Pauling electronegativities of Bi (2.02) and Pt (2.28) are similar so that there are few electronic structural changes in the Pt surface layer due to bismuth adsorption. Experimental evidence supports the intuition that bismuth coadsorption does not significantly influence the chemisorption bond strength of coadsorbed small molecules, e.g., H₂ and CO.^{3,5} We extend this work here to characterize in detail the influence of coadsorbed bismuth on ethylene adsorption and decomposition on Pt(111) by using Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), temperature-programmed desorption (TPD), and high-resolution electron energy loss spectroscopy (HREELS). We will demonstrate that bismuth acts as an inert, site-blocking agent in ethylene reactions on Pt. We will also show preliminary modeling results using Monte Carlo

simulations in order to determine ensemble size requirements for ethylene adsorption and decomposition reactions.

Experimental Section

These experiments were carried out at the University of Colorado in a two-level UHV chamber¹ containing instrumentation for AES, LEED, TPD, and HREELS. Polymer grade ethylene (99.9%, SGP) was used without further purification and was dosed to the Pt(111) with a multichannel plate array doser with an effective enhancement factor of 50 over the background gas exposure. The exposures reported herein have been corrected for this doser enhancement factor and an ion gauge sensitivity factor of 2.4.⁶

The bismuth (5N purity) was deposited on the clean Pt(111) surface by means of a collimated vapor-deposition source, which has been previously described.³ To achieve the desired bismuth coverages, a multilayer was deposited on the surface and the temperature of the crystal was then increased to desorb excess bismuth until the desired coverage was obtained. No difference in the chemistry was observed for bismuth adlayers prepared in this way compared to those prepared by direct deposition of submonolayer coverages of bismuth. Bismuth TPD spectra, shown in Figure 1, were obtained in good agreement with previous work.⁷ On the basis of the observed LEED patterns, an absolute coverage of 0.56 (referred to 1 ML = 1.5 × 10¹⁵ atoms/cm², the surface Pt atom density) has been assigned to the saturated bismuth overlayer.⁷ Bismuth coverages were determined by measurement of the bismuth TPD areas in Figure 1 and by AES uptake measurements seen in the inset to Figure 1. The sharp break that occurs in the uptake plot of the Bi(101 eV)/Pt(64 eV) AES ratio versus θ_{Bi} was defined to occur at $\theta_{\text{Bi}} = 0.56$. The TPD curve that represents this point is indicated by the dashed curve (a) in Figure 1 and was also defined to represent $\theta_{\text{Bi}} = 0.56$. Further calibration

(1) Windham, R. G.; Bartram, M. E.; Koel, B. E. *J. Phys. Chem.* 1988, 92, 2862.

(2) Windham, R. G.; Koel, B. E. *J. Phys. Chem.*, to be submitted.

(3) Paffett, M. T.; Campbell, C. T.; Taylor, T. N. *J. Vac. Sci. Technol.*, A 1985, A3, 812.

(4) Campbell, C. T.; Paffett, M. T.; Voter, A. F. *J. Vac. Sci. Technol.*, A 1986, A4, 1342.

(5) Paffett, M. T.; Campbell, C. T.; Windham, R. G.; Koel, B. E. *Surf. Sci.*, in press.

(6) Summers, R. L. NASA TN-D5285, NASA, Washington D.C., June, 1969.

(7) Paffett, M. T.; Campbell, C. T.; Taylor, T. N. *J. Chem. Phys.* 1986, 85, 6176.

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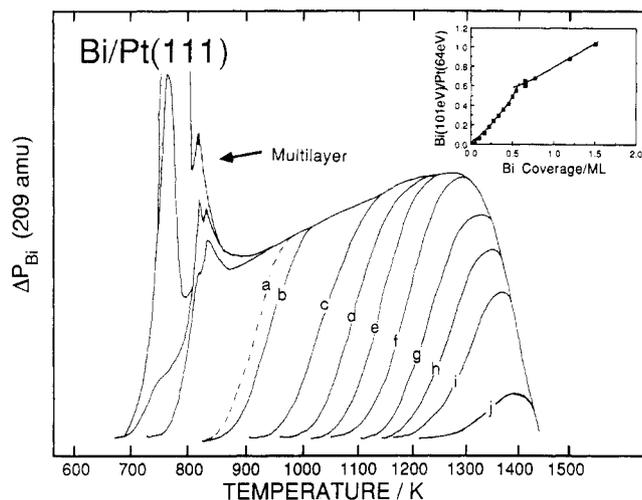


Figure 1. Temperature-programmed desorption spectra of bismuth from Pt(111) for θ_{Bi} = (a) 0.56, (b) 0.54, (c) 0.42, (d) 0.36, (e) 0.30, (f) 0.25, (g) 0.18, (h) 0.13, (i) 0.09, and (j) 0.02. The coverages were calibrated from TPD integrated areas and AES ratios (see inset). The monolayer Bi coverage, assigned to $\theta_{\text{Bi}} = 0.56$, was determined from the break in the AES ratio plot and gives the dashed TPD curve (a).

checks were provided by LEED observations. Bismuth forms several ordered overlayer structures. The surface was checked for the characteristic sharp $p(2 \times 2)$ pattern at $\theta_{\text{Bi}} = 0.25$ and the (4×4) pattern at $\theta_{\text{Bi}} = 0.56$. The Bi monolayer can be produced routinely by annealing a multilayer film to 870 K. This temperature represents a minimum in the Bi TPD trace from thick films, and TPD after annealing to 870 K gives rise to the dashed curve in Figure 1, curve a. Curve b is from a thick film annealed to 900 K, and the first multilayer curve above curve a is from a thick film which was annealed to 790 K.

The saturation coverage for ethylene is reported as an absolute coverage of $\theta_{\text{C}_2\text{H}_4} = 0.25$ (referred to 1 ML $\approx 1.5 \times 10^{15}$ atoms/cm², the surface Pt atom density) or one ethylene molecule for every four Pt atoms.^{8,9}

Results

Adsorption of Saturation Ethylene Coverages on Bismuth-Precovered Pt(111). Temperature-Programmed Desorption Studies. In Figure 2, we show C₂H₄ and H₂ TPD spectra following a 1.1-langmuir saturation ethylene exposure on bismuth-precovered Pt(111) at 100 K as a function of θ_{Bi} . The desorption traces for both 28 amu and 2 amu signals are shown on the same intensity scale. Desorption due to a low coverage of ethylene on the clean Pt crystal edges leads to a small, constant H₂ signal, with no C₂H₄ evolution. However, a small C₂H₄ desorption peak is seen at ~ 150 K that is an artifact due to ethylene desorption from the sample mount. Reversible ethylene adsorption leads to a desorption peak at 285 K with a shoulder at 260 K on the Pt(111) surface. Initially upon coadsorption with bismuth, there is a 5 K shift to lower temperatures for the low-temperature desorption state, accompanied by 3 K shift to higher temperature for the high-temperature state. The combination of these shifts is enough to allow the increased resolution of the two states over that seen on the Pt(111) surface in the absence of Bi. After these initial small shifts, no further temperature shift for either peak is observed until $\theta_{\text{Bi}} = 0.35$; where only the low-temperature state is present, there is a 5 K shift to lower temperature. The population

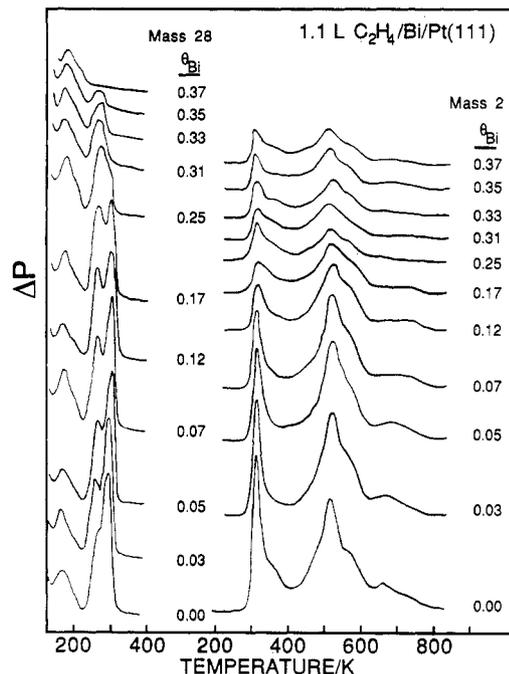


Figure 2. Temperature-programmed desorption spectra of C₂H₄ (mass 28, left panel) and H₂ (mass 2, right panel) following a 1.1-langmuir saturation exposure of ethylene to Bi-precovered Pt(111) at 100 K as a function of θ_{Bi} .

in both ethylene desorption states remains constant up to $\theta_{\text{Bi}} = 0.07$. Above this Bi coverage, the population in the high-temperature state begins to decrease while the population in the low-temperature desorption state remains constant, up to $\theta_{\text{Bi}} = 0.25$. Above $\theta_{\text{Bi}} = 0.31$, only the low-temperature state is populated. Ethylene desorption is not observed for $\theta_{\text{Bi}} \geq 0.37$, indicating that ethylene adsorption does not occur on the complete bismuth overlayer at 100 K.

Concurrently, we monitored the amount of irreversibly adsorbed ethylene as a function of θ_{Bi} by obtaining the H₂ TPD spectra. The amount of irreversibly adsorbed ethylene is proportional to the area under these H₂ TPD curves. The rich structure in the H₂ spectrum from Pt(111) for $\theta_{\text{Bi}} = 0.00$ in Figure 2 is due to the sequential decomposition of ethylene through a stable ethylidyne intermediate.¹⁰ The apparent activation energies for each sequential decomposition step can be calculated assuming a reaction rate limited unimolecular decomposition and a preexponential factor of 10^{13} s⁻¹. The H₂ peak temperature of 310 K indicates that the activation energy for forming CCH₃ is about 18 kcal mol⁻¹, and the 510 K peak indicates an activation energy of 30.4 kcal mol⁻¹ for decomposing CCH₃. The broad tail in the H₂ TPD spectra that extends to higher temperatures is due to complete dehydrogenation of the adsorbed hydrocarbon fragments to form a graphitic overlayer.

Bismuth preadsorption has little effect on the H₂ TPD spectra arising from ethylene decomposition, except to decrease the amount of decomposition that occurs upon heating in TPD. With increasing Bi coverage, the multippeak structure in the H₂ TPD line shape is almost unaltered. Importantly, the temperatures of the peak maxima are unchanged. This leads to the conclusion that both the ethylene reaction mechanism and the activation energies for the elementary decomposition steps are largely unaffected by bismuth coadsorption. Above $\theta_{\text{Bi}} = 0.25$, no

(8) Tysoe, W. T.; Zaera, F.; Davis, S. M.; Somorjai, G. A., unpublished data.

(9) Kesmodel, L. L.; DuBois, L. H.; Somorjai, G. A. *Chem. Phys. Lett.* 1978, 56, 267.

(10) Steininger, H.; Ibach, H.; Lehwald, S. *Surf. Sci.* 1982, 117, 685.

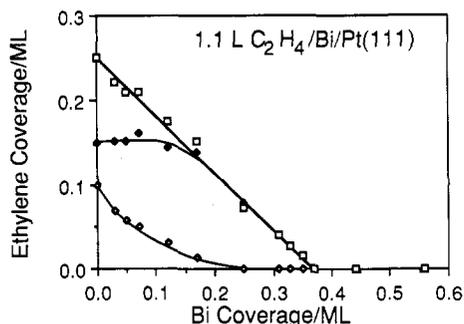


Figure 3. Plot of ethylene coverage versus bismuth coverage for the total saturation ethylene coverage (\square), the coverage of ethylene reversibly adsorbed (\blacklozenge), and the coverage of ethylene thermally decomposing during TPD, i.e., irreversibly adsorbed (\diamond).

H_2 evolution above background effects is observed, indicating that no ethylene decomposition occurs on these surfaces. The H_2 that desorbs above $\theta_{Bi} = 0.25$ in Figure 2 is due to the ethylene decomposing on clean crystal edges.

The TPD data for saturation ethylene coverages shown in Figure 2 are quantified in Figure 3. By adding the amount of reversibly and irreversibly adsorbed ethylene together, we can also obtain a plot of the total ethylene coverage as a function of θ_{Bi} . Coverages for ethylene reversibly adsorbed and ethylene decomposing were determined by normalizing TPD areas to the respective thermal desorption areas for a saturation coverage of ethylene on the clean Pt(111) surface. The area for the 28-amu signal, representing the amount of reversibly adsorbed ethylene, is normalized at saturation to a coverage of 0.15. The area for the 2-amu signal, representing the amount of ethylene decomposing, is normalized at saturation to a coverage of 0.10. These coverages assume a total saturation ethylene coverage of 0.25^{8,9} with $\sim 60\%$ desorbing molecularly and $\sim 40\%$ decomposing.^{1,11} In Figure 3, we see that bismuth linearly attenuates the saturation coverage of adsorbed ethylene on the Bi/Pt(111) surface. Initially, coadsorbing bismuth has no effect on the amount of reversibly adsorbed ethylene, while decreasing the amount of decomposition that occurs. Thus, a quick, qualitative conclusion can be made from Figure 3 that the ensemble size requirement for ethylene decomposition is slightly larger than that for ethylene adsorption. Ethylene decomposition is totally eliminated prior to ethylene adsorption at high θ_{Bi} . Initial results of modeling studies¹² performed to determine the ensemble size requirements for these two processes will be discussed later in this section.

High-Resolution Electron Energy Loss Spectroscopy Studies. Vibrational spectra are shown in Figure 4 for saturation ethylene coverages adsorbed at 100 K on the Pt(111) surface (bottom curve) and on a Pt(111) surface precovered with $\theta_{Bi} = 0.25$ (top curve). The vibrational spectra for ethylene adsorbed at 100 K on Pt(111) are in good agreement with previous studies.¹⁰ The peak at 455 cm^{-1} is due to a Pt-C₂H₄ stretching mode. The peak at 1020 cm^{-1} is due to two unresolved loss peaks: the CC stretching (ν_{CC}) mode at 1060 cm^{-1} and the CH₂ wag (δ_{w,CH_2}) mode at 980 cm^{-1} . The CH₂ scissors (δ_{s,CH_2}) mode causes the loss peak at 1420 cm^{-1} , and the symmetric CH stretching ($\nu_{s,CH}$) mode causes the loss peak at 2920 cm^{-1} . Both the $\nu_{s,CH}$ frequency, which is representative of hydrogen bonded to an sp³-hybridized carbon atom, and the near single-bond frequency of ν_{CC} indicate that ethylene adsorbed on Pt(111) is extensively rehybridized from the

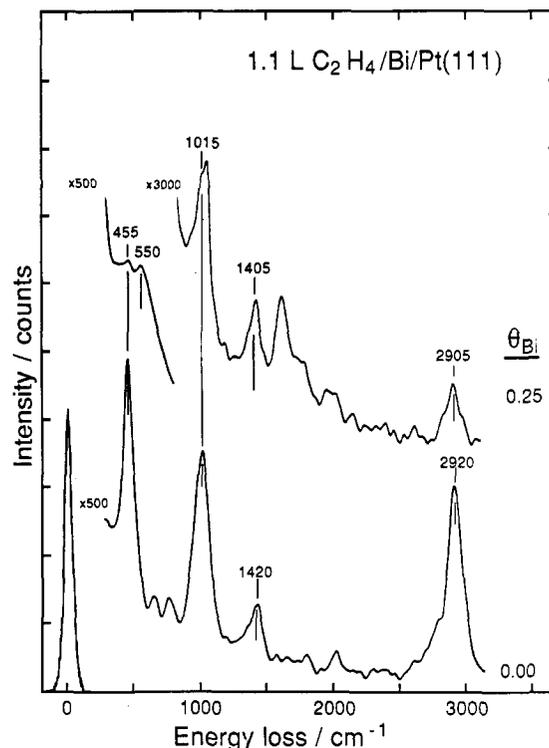


Figure 4. HREELS spectra of saturation coverages of ethylene adsorbed at 100 K on a clean Pt(111) surface and a Pt(111) surface precovered with $\theta_{Bi} = 0.25$.

gas-phase structure and is covalently bonded in a di- σ -bonding configuration to the surface.¹⁰ Figure 4 shows that there is very little perturbation of the ethylene vibrational modes upon coadsorption with Bi. The new loss peaks at 550 and 1600 cm^{-1} are attributed to the frustrated rotation and the bending mode, respectively, of a small amount of coadsorbed water. The presence of water on the surface is due to the long scan times necessary for the low coverages of ethylene at this bismuth coverage. Only very small shifts, on the order of 15 cm^{-1} , are observed for the CH modes. Both the CC stretching frequency and the Pt-C₂H₄ stretching frequency should be very sensitive to alterations in the nature of the chemisorption bond. Neither vibrational mode, however, shows a shift in frequency with increasing bismuth coverage. This is consistent with the thermal desorption data, which indicate that there is no change in the heat of adsorption of ethylene (as measured by the desorption energy) upon coadsorption with bismuth.

Importantly, HREELS spectra (not shown) were also taken to determine if bonding differences existed between the two reversible, molecular desorption states. No differences were observed in the HREELS spectra taken before and after desorption of the lower temperature ethylene desorption state, indicating no large difference in the nature of chemisorption bonding for the two states. One possible explanation for the two states is that there are two distinguishable sites for ethylene adsorption. In this case, Bi preferentially blocks the highest binding energy site at high Bi coverages.

Adsorption of Low Ethylene Coverages on Bismuth-Precovered Pt(111). Temperature-Programmed Desorption Studies. In order to better understand the ensemble requirements for ethylene adsorption and decomposition, it is important to study the two phenomena in an ethylene coverage regime where ethylene self-blocking effects are minimized. We show in Figure 5 the C₂H₄ and H₂ TPD spectra following a 0.02-langmuir

(11) Berlowitz, P.; Megiris, C.; Butt, J. B.; Kung, H. H. *Langmuir* 1985, 1, 206.

(12) Windham, R. G.; Koel, B. E.; Voter, A. F., in preparation.

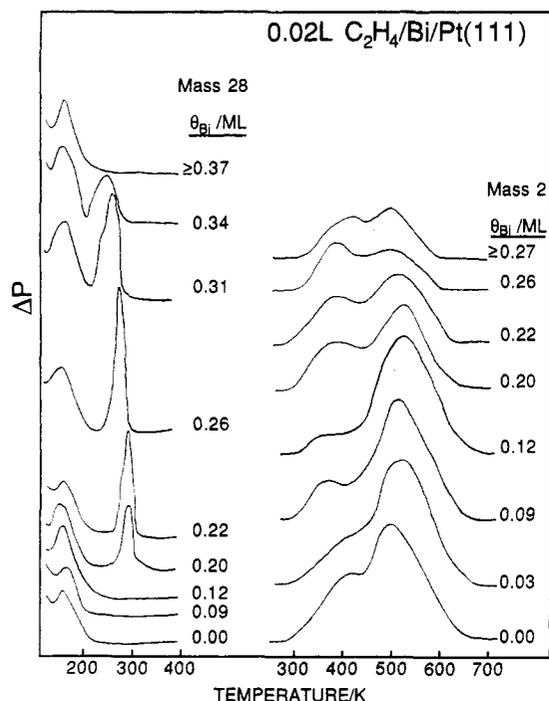


Figure 5. Temperature-programmed desorption spectra of C_2H_4 (mass 28, left panel) and H_2 (mass 2, right panel) following a 0.02-langmuir exposure of ethylene to Bi-precovered Pt(111) at 100 K as a function of θ_{Bi} . This small exposure on the Pt(111) surface gives an ethylene coverage that is $\approx 8\%$ of the saturation ethylene coverage.

ethylene exposure on bismuth-precovered Pt(111) at 100 K as a function of θ_{Bi} . The desorption traces for both the 28- and 2-amu signals are on the same intensity scale. This small exposure on the Pt(111) surface gives an ethylene coverage that is $\sim 8\%$ of the saturation ethylene coverage. At these low coverages on Pt(111), ethylene adsorption is entirely irreversible and no molecular ethylene desorption occurs, as seen in Figure 5. Preadsorption of $\theta_{Bi} = 0.20$ causes a significant increase in the amount of reversible ethylene adsorption. The peak temperature of 295 K is identical with that for ethylene desorption at low ethylene coverages from clean Pt(111). Further addition of bismuth causes an additional increase in the amount of reversibly adsorbed ethylene. The ethylene TPD peak area is increased, and the peak maximum shifts gradually to 20 K lower temperature. Preadsorption of $\theta_{Bi} = 0.31$ substantially reduces the amount of desorbed ethylene, due to a large decrease in the amount of adsorbed ethylene. A further shift in the TPD peak maximum of 30 K is seen with increasing θ_{Bi} due to population of the low-temperature ethylene desorption state, which was also observed on clean Pt(111) at high ethylene coverages. No ethylene desorption is observed for $\theta_{Bi} \geq 0.37$. As in Figure 2, the desorption peak seen at ~ 150 K is due to ethylene desorption from the sample mount.

Initially, bismuth precoverage has little effect on the amount of H_2 thermally desorbed, i.e., the amount of irreversibly adsorbed ethylene. However, at $\theta_{Bi} > 0.12$, the amount of H_2 thermally desorbing begins to decrease, concomitant with the appearance of reversibly adsorbed ethylene. Similar to the results for saturation coverage of coadsorbed ethylene, no H_2 thermal desorption is observed above $\theta_{Bi} = 0.25$. On Pt(111), the ethylene decomposition mechanism is not as clearly defined at these low ethylene coverages as it is at high coverages. However, the desorption peak representative of the first decomposition step to ethylidyne shifts to ~ 390 K due to H_2 desorp-

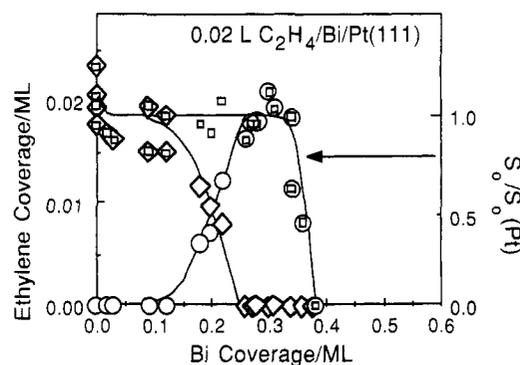


Figure 6. Plot of ethylene coverage versus bismuth coverage for the 0.02-langmuir TPD data of Figure 5, consisting of the total ethylene coverage (\square), the coverage of ethylene reversibly adsorbed (\circ), and the coverage of ethylene thermally decomposing during TPD, i.e., irreversibly adsorbed (\diamond).

tion-limited kinetics. The second and subsequent decomposition steps now occur almost simultaneously at ~ 520 K. As observed for saturation coverages of ethylene, the peak shapes and temperatures are relatively constant with increasing Bi coverage, indicating that Bi has no effect on either the decomposition mechanism or activation energies of the elementary steps. As in Figure 2, the H_2 that desorbs above $\theta_{Bi} = 0.27$ is due to ethylene decomposing on clean Pt crystal edges.

A plot of $\theta_{C_2H_4}$ for these low ethylene exposures as a function of θ_{Bi} is shown in Figure 6. Note that for this very small ethylene exposure the total ethylene coverage in this experiment represents a determination of the variation of the initial sticking coefficient of ethylene as a function of θ_{Bi} . This is indicated explicitly on the right vertical axis of Figure 6, where we show $S_0/S_0(Pt)$, where S_0 is the initial sticking coefficient of ethylene on the Bi-precovered surface and $S_0(Pt)$ is the value of the initial sticking coefficient of ethylene on Pt(111). This latter value is not known well, but we estimate it to be near unity. Our results show that S_0 is essentially independent of θ_{Bi} until $\theta_{Bi} \sim 0.35$. Higher bismuth coverages lead to a dramatic decrease in S_0 , and no ethylene adsorption is detected above $\theta_{Bi} = 0.37$. Note that this steep decrease in S_0 occurs at $\theta_{Bi} \approx 0.35$. The ethylene coverage due to this small exposure is the same as the saturation ethylene coverage that can be created by larger ethylene exposures for this amount of Bi on the surface. Above $\theta_{Bi} = 0.35$, the total chemisorbed ethylene curve in Figure 5 behaves the same as the total chemisorbed ethylene curve in Figure 3. Figure 5 also indicates the separate effects of bismuth on the amount of reversible and irreversible adsorption, in addition to the total ethylene coverage. No reversible adsorption occurs for $\theta_{Bi} \leq 0.12$, and no decomposition occurs for ethylene coadsorbed with $\theta_{Bi} \geq 0.25$.

Adsorption and Decomposition Ensemble Size Modeling Studies. At the low ethylene coverages that are plotted in Figure 6, ethylene self-blocking is minimized. This makes the adsorption data obtained more useful in modeling studies of ensemble sizes for ethylene adsorption and decomposition. The Monte Carlo simulations that were used in this study to determine the ethylene adsorption site ensemble are a modification of the simulations previously used to model adsorption site ensembles for CO, H_2 , and O_2 .⁴ The simulation has been modified to also model the ensemble site requirements for ethylene decomposition. In this decomposition simulation, bismuth is assumed to require an adsorption ensemble of three Pt atoms (a trimer of Pt atoms). For a chosen precoverage of Bi, trimers were randomly placed and oriented on the

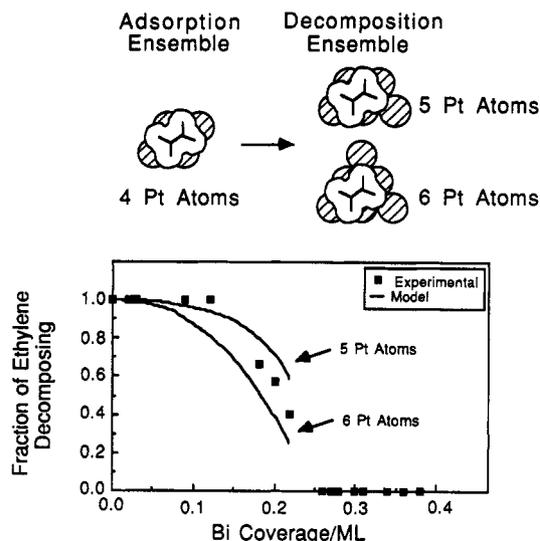


Figure 7. Plot of the fraction of chemisorbed ethylene undergoing decomposition reactions versus bismuth coverage. The experimental data from the Bi/Pt(111) surface, obtained from Figure 5, are shown as points (■). The solid lines are the simulated curves calculated for decomposition ensembles of five or six Pt atoms, as described in the text. The top panel shows pictorially the results of the simulation. A space-filling model (using van der Waals radii and gas-phase bond lengths) of chemisorbed ethylene is shown with the calculated adsorption ensemble requirement of four Pt atoms and a decomposition ensemble requirement of five or six Pt atoms. The configurations of Pt atoms are not unique.

surface until the desired θ_{Bi} was obtained. Ethylene adsorption is assumed (from modeling results) to require an adsorption ensemble of four Pt atoms. The ethylene adsorption ensembles were then randomly placed and oriented on the surface. If the ethylene adsorption ensemble did not touch any Bi masking trimers, representing allowed adsorption, it was then expanded to a larger ensemble of Pt atoms that would represent the ethylene decomposition ensemble. If the ensemble expanded without encountering a Bi trimer, it was assumed that the new, larger ensemble was available for ethylene decomposition reactions. Determining the ethylene decomposition ensemble requirement reduces to a simulation of the fraction of adsorbed ethylene that decomposes as a function of θ_{Bi} by calculating the fraction of adsorption ensembles that can be expanded to decomposition ensembles as a function of the decomposition ensemble size and the coverage of Bi.

Preliminary results of these modeling studies are briefly summarized in Figure 7. The best fit of the simulations (solid lines) to the experimental data (points) is obtained by using an ensemble size requirement of four Pt atoms for ethylene adsorption and a decomposition ensemble requirement of an additional one or two Pt atoms. This gives a total decomposition ensemble size requirement of five or six Pt atoms. The top panel of this figure shows these results pictorially. On the left, a chemisorbed ethylene molecule is shown by using a space-filling drawing in which the gas-phase ethylene bond lengths and van der Waals radii for carbon atoms and hydrogen atoms are used. This ethylene molecule is shown schematically above an adsorption ensemble of four Pt atoms. The larger decomposition ensemble of five or six Pt atoms is shown schematically on the right, underneath an ethylene molecule. The orientation of the adsorbed ethylene and the configuration of the Pt atoms are not unique. A more detailed description of the modeling studies, with several kinetic schemes and additional Monte Carlo studies for data on both low coverages and saturation coverages of ethylene, will be presented in a forthcoming publication.¹²

Discussion

Bismuth does not substantially alter the chemisorption bond strength of molecular ethylene to Pt(111). It does, however, alter the relative populations of the two desorption states of ethylene. Secondly, bismuth does not affect the decomposition reaction mechanism, nor does it affect the activation energies for the elementary steps. No ethylene adsorption was observed on the complete bismuth monolayer or thicker films. Finally, the vibrational frequencies for adsorbed ethylene are independent of bismuth coverage. On the basis of these results, we conclude that coadsorbed bismuth on Pt(111) acts essentially as an inert, site-blocking agent for ethylene adsorption and decomposition.

These results, in addition to results for H_2 and CO^{3-5} indicate that bismuth may have enormous potential for determining ensemble or site-size requirements for a variety of hydrocarbon reactions on Pt surfaces. We have exploited this fact by modeling ethylene decomposition at low ethylene coverages, where ethylene self-blocking is minimized. By choosing an adsorption ensemble size of four Pt atoms and a decomposition ensemble size of five or six Pt atoms, we have successfully modeled the fraction of ethylene decomposing using a Monte Carlo simulation.

In another laboratory, while these results were being obtained, Campbell et al.¹³⁻¹⁵ extended studies on Bi/Pt(111) surfaces to determine ensemble sizes for several cyclic hydrocarbon reactions. Other work will be required to determine if this probe will be useful on other metal surfaces as well, and we are initiating some of this work. Coadsorption of adsorbates with bismuth on Ni surfaces, for example, should also be a good probe of ensemble effects, since Bi (2.02) and Ni (1.91) have even more similar electronegativities than Bi (2.02) and Pt (2.28).

Our interest in this study was initially motivated by our desire to try to separate the site-blocking effects from the electronic effects due to coadsorbed $\text{K} + \text{C}_2\text{H}_4$ on Pt(111). Potassium coadsorption causes the formation of a weakly bound, π -bonded molecular ethylene complex, and also increases the activation energy for dehydrogenation. Neither of these effects was observed upon bismuth coadsorption with ethylene on Pt(111), and so their origins are concluded to be due to the electronic effects that potassium adatoms induce. Potassium coadsorption does cause a decrease in the coverage of di- σ -bonded ethylene and a decrease in the amount of dehydrogenation versus θ_{K} , very similar to the decreases seen on the Bi/Pt(111) surfaces versus θ_{Bi} . Thus, these effects are likely to be due to a site-blocking effect of potassium on ethylene adsorption and decomposition. A more detailed comparison of the influence of potassium and bismuth on ethylene adsorption and reaction will be presented in a forthcoming publication.¹⁶

As a final comment, we point out here that care must be taken in interpreting and modeling results for high θ_{Bi} , since the bismuth adatoms can form ordered overlayers (and thus are not randomly distributed) and also might be forced by the adsorbate to segregate into relatively dense islands. Some evidence exists in our data that this occurs at high θ_{Bi} : ethylene adsorbs at higher bismuth coverages than would be expected if the bismuth is indeed uniformly dispersed on the Pt(111) surface. From the

(13) Campbell, C. T.; Campbell, J. M.; Dalton, P. J.; Henn, F. C.; Rodriguez, J. A.; Seimanides, S. *J. Phys. Chem.*, submitted.

(14) Rodriguez, J. A.; Campbell, C. T. *J. Phys. Chem.*, submitted.

(15) Seimanides, J. M.; Campbell, J. M.; Campbell, C. T. *J. Phys. Chem.*, submitted.

(16) Windham, R. G.; Koel, B. E. *J. Phys. Chem.*, to be submitted.

space-filling model of ethylene shown in Figure 7, each ethylene molecule occupies about 21 \AA^2 on the surface. At $\theta_{\text{Bi}} = 0.33$, with a Bi radius of 1.86 \AA ,⁷ there should be no Pt ensemble available that is large enough for ethylene adsorption, even though some Pt surface remains uncovered. However, we observe ethylene adsorption until $\theta_{\text{Bi}} \geq 0.37$. This general phenomena has also been observed for larger cyclic hydrocarbons such as cyclohexane^{13,14} and benzene^{13,15} adsorbed on Bi/Pt(111) surfaces. LEED observations indicate that the bismuth adatoms are fairly mobile on the surface, even at temperatures as low as 150 K.⁷ Also, TPD shows clearly that the heat of adsorption (and, by inference, the activation energy of diffusion) is reduced as the Bi coverage is increased. The work function change with increasing bismuth coverage indicates that the bismuth adatoms, which are slightly positively charged at low coverage, depolarize and become more metallic-like at higher coverages. Thus, at higher θ_{Bi} , the Pt-Bi chemical bond and Bi-Bi lateral repulsive interactions are weakened. It is possible that the ethylene-metal interaction is strong enough to displace the bismuth adatoms laterally at high bismuth coverages, thus forcing the bismuth to segregate and leaving larger Pt ensembles available for adsorption and reaction. These effects obviously become more important with adsorbates that are more strongly chemisorbed than ethylene.

Conclusions

Coadsorbed bismuth does not substantially alter the

chemisorption bond strength of molecular ethylene to Pt(111) or affect the decomposition reaction mechanism. The activation energies for the elementary dehydrogenation steps in this mechanism are also not affected. No chemisorption is observed on complete layers of bismuth. Finally, no significant changes are observed in the vibrational frequencies of adsorbed ethylene upon coadsorption with bismuth. Thus, bismuth adatoms appear to be ideal probes for determining hydrocarbon reaction site size requirements on Pt surfaces.

Preliminary consideration of the site-blocking influence of coadsorbed bismuth indicates that an ensemble of four contiguous Pt atoms is required to chemisorb ethylene, and an ensemble of six Pt atoms is required to dehydrogenate ethylene to ethylidyne (CCH_3). A similar ensemble size requirement is also indicated for the subsequent decomposition of CCH_3 .

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Synthesis and Catalytic Activity of *N*-Oxide Surfactant Analogues of 4-(Dimethylamino)pyridine

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Surfactants of different charge types containing the 4-(*N,N*-dialkylamino)pyridine 1-oxide moiety have been synthesized and tested as catalysts for the hydrolysis of active carboxylic and phosphorus esters in the presence of cetyltrimethylammonium chloride. Their catalytic activity is compared with that of a series of simple 4-(dimethylamino)pyridine 1-oxides.

Introduction

We have previously reported¹ studies of the catalytic activity of surfactants incorporating the 4-(*N,N*-dialkylamino)pyridine moiety for the hydrolysis of fluorophosphonate and carboxylate esters. All these compounds catalyzed the hydrolysis of *p*-nitrophenyl hexanoate, but disappointingly none efficiently accelerated that of fluorophosphonate (Soman), for which hydrolysis was increased over the background by a factor of only 1.1-1.2.

In an attempt to improve the catalytic efficiency of these derivatives for the hydrolysis of fluorine-phosphorus bonds, we turned our attention to the related *N*-oxides. Recent studies have shown that, although less basic than

the corresponding pyridines, pyridine *N*-oxides are much more effective catalysts in acyl- and sulfonyl-transfer reactions.^{2,3} In particular, 4-(*N,N*-dimethylamino)pyridine 1-oxide (DMAP 1-oxide) (**2a**) was approximately 50 times more active than DMAP (**1a**) itself in the cleavage of sulfur-halogen bonds in sulfonyl halides, and the 1-(sulfonyloxy)pyridinium intermediates thus formed were 3-17 times more reactive than the 1-sulfonylpyridinium analogues toward aminolysis with arylamines.^{4,5} Thus, al-

(1) (a) Katritzky, A. R.; Duell, B. L.; Seiders, R. P.; Durst, H. D. *Langmuir* 1987, 3, 976. (b) Katritzky, A. R.; Duell, B. L.; Knier, B. L.; Durst, H. D. *Langmuir* 1988, 4, 192.

(2) Savelova, V. A.; Belousova, I. A.; Litvinenko, L. M. *J. Org. Chem. USSR (Engl. Transl.)* 1981, 17, 1333.

(3) Belousova, I. A.; Savelova, V. A.; Litvinenko, L. M.; Matvienko, V. N. *J. Org. Chem. USSR (Engl. Transl.)* 1979, 15, 1759.

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