Particle Size Effects in the Acetylene Cyclotrimerization on Planar Model Al_2O_3 Thin Film Supported Pd Clusters

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The low-temperature cyclotrimerization of acetylene to benzene on alumina thin film supported Pd particles of controlled size has been studied by temperature-programmed desorption. The reactively formed benzene is observed to desorb in three distinctly separate features with kinetics resembling those observed for acetylene cyclotrimerization on Pd single crystals. An enhanced activity for low-temperature benzene desorption is observed for the larger Pd particles, consistent with single-crystal results that reveal that the Pd(111) surface favors low-temperature desorption of the reactively formed benzene relative to more open surfaces. Additionally, a pronounced drop-off in benzene production is observed for the smallest particles studied, suggestive of an ensemble size requirement for the reaction.

1. Introduction

The cyclotrimerization of acetylene to benzene on low-index single-crystal Pd surfaces has received considerable attention since its discovery by Tysoe et al.[1,2] and Sesselmann et al.[3] This reaction has been shown to be a structure sensitive reaction with the Pd(111) facet being the most active.[4,5] In a temperature-programmed desorption (TPD) experiment, benzene evolution resulting from low-temperature ($<$200 K) adsorption of C_2H_2 on Pd(111) occurs in a low-temperature feature at ∼250 K and a high-temperature feature at ∼500 K. An additional intermediate feature is present for Pd(100) just below 400 K. In one case, a similar desorption feature at ∼400 K has been reported for Pd(111).[6] It is generally agreed that the high-temperature desorption feature arises from benzene lying flat on the surface, while the low-temperature desorption feature results from reactively formed benzene on an initially crowded surface that forces the benzene molecules into a weaker binding configuration with the molecular plane tilted with respect to the surface. The origin of the intermediate desorption feature at ∼400 K has alternately been explained as desorption from a close-packed flat-bonded layer of benzene[7] or from adsorption sites at defect sites.[8]

The mechanism of benzene formation is not completely understood, but is believed to involve the consecutive addition of acetylene molecules without C−C bond scission as inferred from isotopic labeling experiments.[9] A pentadiene metallocycle (PdC_4H_4) has been proposed as an intermediate species;[10,11] this model is further supported by the observation of small amounts of furan[12] and thiophene[13] reactively formed from C_2H_2 on Pd(111) in the presence of oxygen and sulfur, respectively. The adsorption of acetylene and its thermal evolution have also been studied by vibrational spectroscopies, and CCH, CCH_2 CCH_3, and CH surface species have been detected.[14−17] Acetylene adsorbs in the 3-fold hollow site on the Pd(111) surface,[17,18] and the conversion to benzene from this flat-lying acetylene species proceeds at temperatures as low as 140 K.[6] There exists a critical threshold acetylene coverage of 0.33 ML (monolayers) for benzene formation to occur,[2,19] and this threshold can be reduced by inert spectator molecules.[19]

It has been suggested that a critical ensemble size is required for acetylene trimerization to benzene; this possibility has been addressed using Au/Pd(111) and Pd/Au(111) surface alloys and Au/Pd colloid particles.[20−22] In this work, it has been argued that an ensemble of seven Pd atoms or six Pd atoms with a central Au atom is required for benzene formation. Additionally, it was also concluded that a Pd ensemble involving a Au atom is more effective than a pure Pd ensemble, possibly by reducing decomposition as opposed to desorption of the reactively formed benzene. This ensemble model has also been applied to rationalize experimental results for cyclotrimerization of acetylene on Pd(111) with coadsorbed oxygen.[23]

Finally, the cyclotrimerization of acetylene has been studied at elevated pressures on Pd single crystals and supported Pd particles, and it has been demonstrated that the reaction can be operated as a genuine catalytic process.[5,24]

The morphology of Pd planar model catalysts has previously been addressed by scanning tunneling microscopy (STM), transmission electron microscopy (TEM), and infrared reflection adsorption spectroscopic (IRAS) studies of adsorbed CO.[25,26] The number density and size distribution of these Pd particles obtained from vapor deposition onto thin film oxide substrates can be controlled by the amount of Pd deposited and subsequent annealing. The IRAS results for adsorbed CO exhibit absorption features indicating that the particles are primarily comprised of (111) and (100) facets with a higher proportion of edge/defect sites for the smaller particles.

Due to the structure sensitivity of the acetylene cyclotrimerization, it is expected that the reaction will be sensitive to the Pd particle size. The results reported here do in fact unambiguously reveal a pronounced particle size effect.

2. Experimental Section

The experiments were carried out in a stainless steel ultrahigh-vacuum chamber with a base pressure less than 10−9 Torr. The apparatus was equipped with Auger electron spectroscopy (AES), a quadrupole mass spectrometer (QMS) for TPD, and IRAS.

The alumina thin films were grown on a Mo(110) substrate initially cleaned by several cycles of oxidation and electron beam heating to above 2000 K. Cleanliness was verified by AES. The alumina films were prepared by evaporating aluminum onto the Mo(110) in 2.5×10^{-6} Torr ambient oxygen at 900 K with a subsequent annealing to 1200 K. The thickness of the films (∼30 Å) was estimated from the deposition time and the ratio of the Al^{3+}(∼54 eV) to the Mo(∼180 eV) AES signals.[27]

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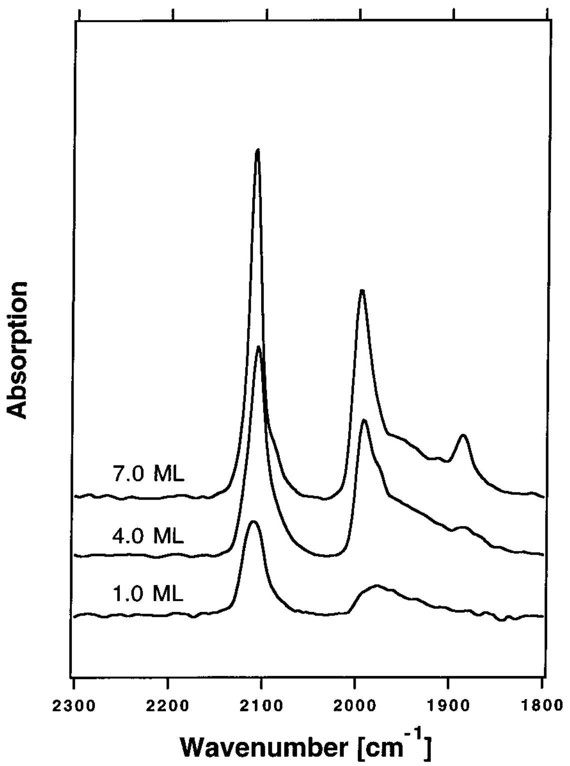

Figure 1. IRA spectra of CO chemisorbed on alumina thin film supported Pd particles corresponding to deposition of 1, 4, and 7 ML of Pd. All spectra are obtained at 110 K in 1.5×10^{-6} Torr CO.

The Pd particles were deposited by vapor deposition of Pd onto the alumina film at 500 K at a rate of 0.6 ML/min, followed by annealing to 800 K. This preparation method has been used in studies of Pd planar model catalysts; the particle sizes here have been estimated from the TEM and STM images and particle size distributions reported previously.[25,26] Deposition of 1, 2, 4, and 10 ML of Pd results in particles with average diameters of approximately 20−25, 40−50, 70−80, and 100−120 Å, respectively.

Calibration of the Pd evaporation rate was accomplished by several TPD experiments following deposition of Pd onto the bare Mo(110) sample. The monolayer equivalent referred to in this paper according to this calibration is 1 ML = 1.43×10^{15} cm^{-2}. The acetylene (Matheson 99.6%) was passed through a charcoal trap at room temperature and stored in a glass bulb prior to use. A TPD experiment was carried out by initially growing a fresh alumina film and then cooling the sample and manipulator to 90 K prior to evaporation of Pd. Seventy langmuirs of acetylene was then adsorbed at 150 K onto the Pd particles; after 20 min a TPD was recorded with a heating rate of 5 K/s.

3. Results and Discussion

The Pd particles were characterized using IRAS of chemisorbed CO. Figure 1 shows IRA spectra of CO adsorbed onto three different particle sizes corresponding to Pd depositions of 1, 4, and 7 ML onto the alumina film. The spectra were all obtained in a background of 1.5×10^{-6} Torr CO at 110 K. Three sharp absorption features at 2108, 1995, and 1886 cm^{-1}, are resolved for the particles resulting from 7 ML of Pd, with the latter two superimposed on a broader band stretching from 2000 cm^{-1} downward. As the Pd loading is decreased, all bands attenuate in intensity; for 1 ML of Pd the bands at 1886 and 1995 cm^{-1} are no longer visible and only the band at 2108 cm^{-1} and the broad band in the 2000−1900 cm^{-1} region remain. The vibrational spectra of adsorbed CO on the thin film alumina supported Pd particles shown in Figure 1 are consistent with those previously reported for this system,[25,26] displaying bands associated with CO adsorbed on Pd(111) and Pd(100). Of special interest is the feature at 1886 cm^{-1}, indicative of CO bound in the 3-fold hollow site of the ⟨111⟩ facet. The intensity of this band is clearly increasing with increasing Pd particle size, consistent with previous work[25] and with expectations based purely on thermodynamic considerations, with the larger particles exhibiting a higher incidence of ⟨111⟩ faceting.

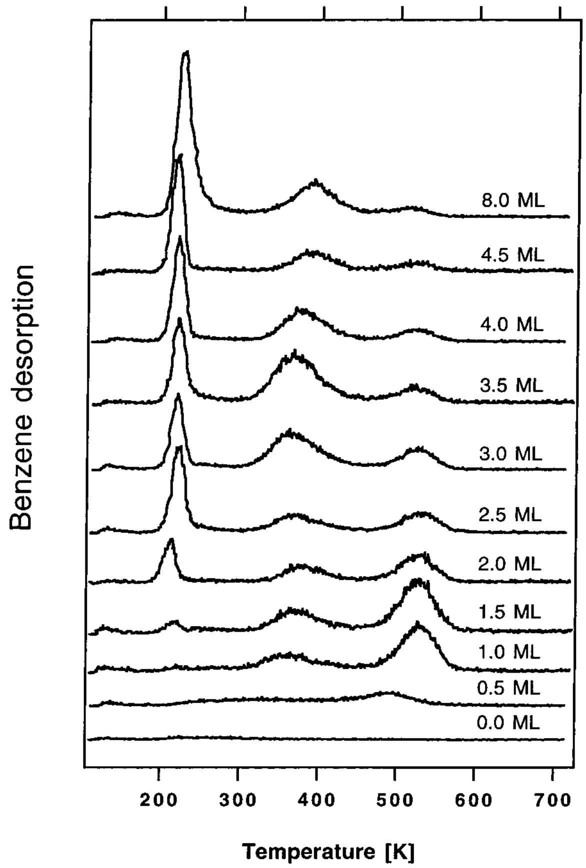

Figure 2. Desorption of benzene ($m/e = 78$) following a 70 langmuir acetylene exposure at 150 K for various Pd loadings as indicated.

Benzene TPD results for the supported particles are very similar to the analogous low-index single-crystal results. Figure 2 illustrates that three distinct desorption features are apparent across a range of Pd loadings in planar model supported Pd/Al_2O_3/Mo(110) catalysts; a low-temperature feature at 270 K, an intermediate feature at 370 K, and a high-temperature peak at 530 K. Comparisons of the TPD results reveal distinct particle size effects. For the smallest particles (∼15−20 Å d_{av}), most of the benzene desorption occurs above 500 K, with very little low-temperature benzene evolution. As the particle size is increased, the high-temperature peak begins to attenuate, while the desorption peak at 230 K increases in intensity. For Pd loadings ≥4 ML (average particle size ≥50 Å), the low temperature desorption pathway is clearly favored. This will be discussed in detail below.

Several other interesting observations can be made for this data set. First of all, a substantial decrease in benzene production is observed between the 1.0 and 0.5 ML Pd coverages; the TPD peak area decreases by about a factor of 4 going from the higher to the lower Pd coverage, even though the Pd surface area is decreasing by just under a factor of 2. This marked drop-off in activity at the extreme lower end of the particle size range studied (average particle diameter ∼15

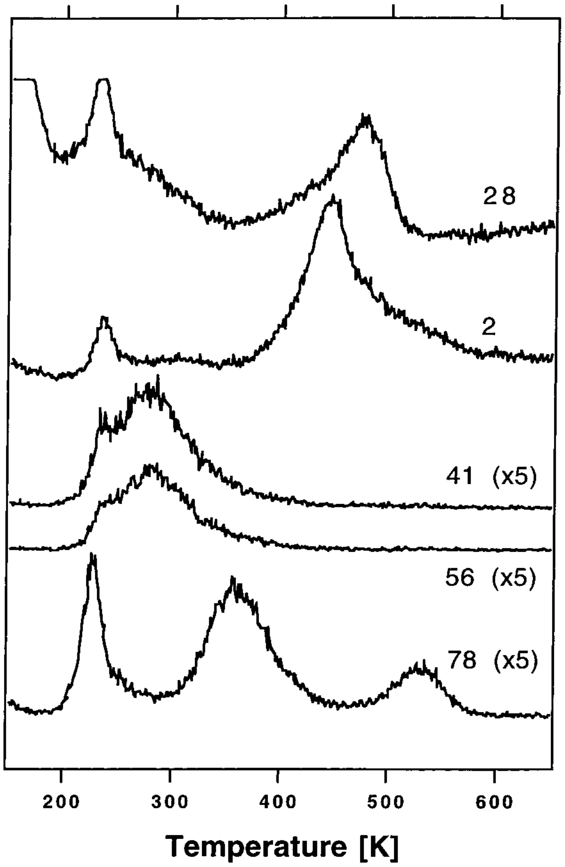

Figure 3. Mass fragments *m/e* = 2, 28, 41, 56, and 78 detected in TPD following a 70 langmuir acetylene exposure at 150 K on particles corresponding to 3 ML of Pd (~50 Å).

Å, with a significant fraction of even smaller particles in the lower wing of the distribution) suggests the manifestation of the anticipated ensemble effect.

Another point of interest involves the desorption peak at 370 K; the presence of this feature on the supported particles suggests that it is probably related to benzene adsorbed at defect sites. In fact, this feature is suppressed to a greater degree than the other desorption maxima upon iterative reaction runs, consistent with having preferential buildup of inactive carbon on reactive defects, as discussed in more detail below. That surface decomposition is one (or one group) of the reaction pathways available for the benzene formed at low temperatures is demonstrated by the evolution of smaller hydrocarbons between 230 and 320 K observed for every Pd loading studied; this is illustrated by the TPD spectra for the *m/e* = 41 and 56 fragments shown in Figure 3. These species also yielded fragments at *m/e* = 55, 43, 42, 40, and 39. The total desorption yield associated with this feature was essentially constant with Pd loading above 1 ML of Pd. Figure 3 also shows the desorption of hydrogen (*m/e* = 2) between the low-temperature benzene and the smaller hydrocarbon desorption. Simultaneous with this hydrogen desorption, a fragment at *m/e* = 28 is also seen which cannot be attributed to CO, since no *m/e* = 12 fragment was associated with this peak. Both CO and H_2 desorb at higher temperatures in rather broad features.

This interpretation is further supported by the effect of sequential reactions on the intensity of the 370 K benzene peak. In Figure 4, the TPD of benzene following a second adsorption of acetylene onto Pd particles with an average diameter of ~50 Å (3 ML of Pd) clearly reveals that the 370 K benzene feature is strongly suppressed in a subsequent TPD run. Again, this is is suggestive that carbon deposited by decomposition in the initial TPD experiment preferentially chemisorbs at edges and defects, leading to suppression of benzene interacting with these sites in subsequent runs and thus to the attenuation of the desorption feature at 370 K. The total yield of benzene is not significantly affected in the TPD following the second adsorption of acetylene (Figure 4b), but the distinct desorption features of (a) are broadened in (b). The low-temperature and the high-temperature desorption features are still resolved and slightly shifted in peak temperature, whereas the intermediate feature around 370 K is strongly suppressed. Also (not shown), the evolution of other hydrocarbons in the temperature range 230–320 K is completely absent in the second TPD.

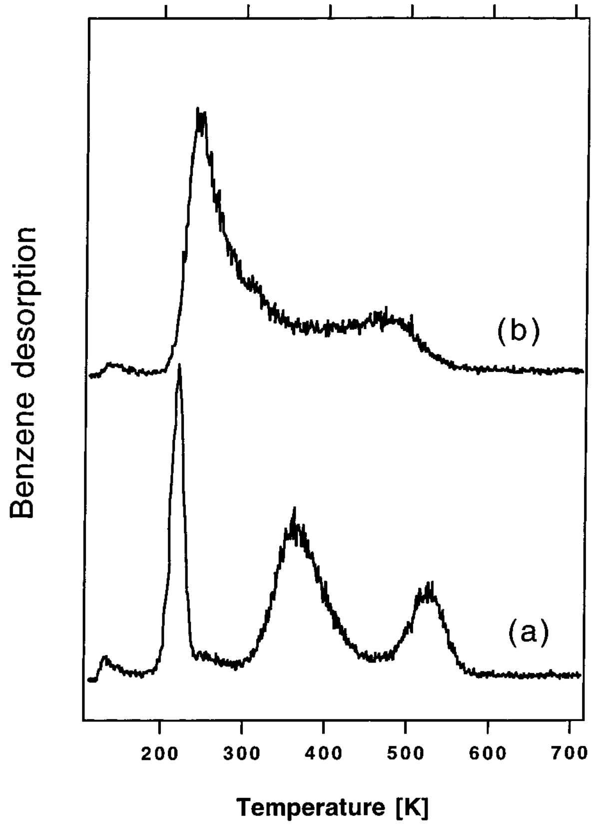

Figure 4. Benzene (*m/e* = 78) desorption following (a) initial and (b) repeated adsorption of 70 langmuirs of C_2H_2 at 150 K on Pd particles (~50 Å).

Intuitively then, if the feature at 370 K is in fact related to benzene adsorbed at defect sites, one might expect to see the ratio of this feature to the other desorption features in the TPD traces increase with decreasing particle size. The behavior actually observed, however, is quite different. A relatively small contribution from the 370 K peak compared to the high-temperature peak is observed for the smallest particles. The ratio increases as the contribution from the high-temperature peak diminishes with increasing particle size up to a Pd coverage of ~3.5 ML, where a maximum is reached. Above this coverage, the ratio starts to decline again as the low-temperature peak gains in intensity, and the 370 K peak attenuates. Apparently, then, the relative contribution from this feature is only partly influenced by the density of surface defects. Perhaps both of the explanations advanced to explain this feature for single crystals (discussed above) are valid, and there is a convolution of the two effects. Alternatively, perhaps the smaller particles favor the decomposition reaction at the lower temperature, deactivating the defect sites for benzene adsorption. This is an interesting issue that warrants further study.

Returning to the observation that the larger particles favor the low-temperature reaction pathway, there are a couple of ways to interpret this. Assuming regular polyhedra comprised exclusively of ⟨111⟩ and ⟨100⟩ facets, the ratio of the former to the latter increases with increasing particle size. Single-crystal TPD studies of Pd(111) and (100) have revealed a similar enhancement for the low-temperature desorption on the (111) surface.[5] Therefore, this effect may well be related to the ratio of ⟨111⟩ facets on the surface. An alternate explanation invokes the enhanced curvature of the smaller particles that precludes the degree of compression in the benzene overlayer that results in the tilted, weakly bound configuration.

These results may also have implications for reaction activity under equilibrium conditions. The reactively formed benzene in the tilted configuration in the compressed overlayer has several reaction pathways available to it, including desorption, decomposition, and transition to the strongly flat bound species. While a definitive enhancement for benzene evolution was not observed for the larger particles in the TPD experiments, the data suggest an activity dependence nonetheless. Generally, one would expect an enhanced propensity for low-temperature desorption to likewise enhance the rate of benzene formation in a reaction equilibrium situation. Single-crystal studies by Somorjai et al. that point to benzene desorption as the rate-determining step lend further support to this viewpoint. For Pd single crystals at atmospheric pressures under batch reaction conditions, the (111) surface is more reactive than the (100) surface if corrections are made for site blocking by inactive carbon.[5] In fact, Lambert et al. have shown that larger Pd particles in conventional supported catalysts are more active.[24]

In this interpretation then, the lower activities for the smaller particles is not due to a critical size ensemble effect (except for the extremely small particles exhibiting the dramatic intensity drop-off), but rather to the enhanced curvatures and absence of large, ⟨111⟩ terraces. These characteristics preclude the formation of the ordered compressed overlayer of reactively formed benzene weakly bound in the tilted configuration and favor the more strongly adsorbed flat bonded benzene. Also, the smaller particles with their higher densities of defects may favor the low-temperature decomposition reaction, as suggested by the attenuation of the benzene peak at 370 K associated with defects.

While these low-temperature adsorption, low-pressure experiments reveal interesting particle size effects, it is difficult (and perhaps dangerous) to attempt to extrapolate these results to the high-pressure, high-temperature situation in a conclusive way. Changes in surface coverages of reactants and poisons can have profound effects on reaction mechanisms, as shown by single-crystal work (Somorjai et al.[5]). Ideally, these experiments must be expanded to include high-temperature, high-pressure reaction kinetics. Nevertheless, these results provide yet another example of the excellent utility and scope associated with these unique model catalysts for investigation of heterogeneous catalytic processes.

4. Conclusion

The cyclotrimerization of acetylene to benzene on alumina thin film supported Pd particles exhibits a particle size effect. For small particles, benzene evolution is only observed from a high-temperature state (∼520 K), whereas larger particles desorb benzene in a high- (∼520 K) and a low-temperature (∼220 K) state, as observed on Pd single crystals. The results are consistent with the (111) facet being the most efficient for trimerization, resulting in an enhanced activity for larger particles. A pronounced drop-off in benzene yield is observed beneath a critically small particle size, suggestive of an ensemble size requirement for the reaction.

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References and Notes

(1) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *J. Chem. Soc., Commun.* **1983**, 623.

(2) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *Surf. Sci.* **1983**, *135*, 128.

(3) Sesselmann, W. S.; Woratschek, B.; Ertl, G.; Kuppers, J.; Haberland, H. *Surf. Sci.* **1983**, *130*, 245.

(4) Gentle, T. M.; Muetterties, E. L. *J. Phys. Chem.* **1983**, *87*, 2469.

(5) Rucker, T. G.; Logan, M. A.; Gentle, T. M.; Mutterties, E. L.; Somorjai, G. A. *J. Phys. Chem.* **1986**, *90*, 2703.

(6) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *J. Phys. Chem.* **1986**, *90*, 3188.

(7) Tysoe, W. T.; Ormerod, R. M.; Lambert, R. M.; Zgralich, G.; Ramirez-Cuesta, A. *J. Phys. Chem.* **1993**, *97*, 3365.

(8) Ormerod, R. M.; Baddeley, C. J.; Lambert, R. M. *Surf. Sci.* **1991**, *259*, L709.

(9) Patterson, C. H.; Lambert, R. M. *J. Phys. Chem.* **1988**, *92*, 1266.

(10) Patterson, C. H.; Mundenar, J. M.; Timbrell, P. Y.; Gellman, A. J.; Lambert, R. M. *Surf. Sci.* **1989**, *208*, 93.

(11) Pacchioni, G.; Lambert, R. M. *Surf. Sci.* **1994**, *304*, 208.

(12) Ormerod, R. M.; Lambert, R. M. *Catal. Lett.* **1990**, *6*, 121.

(13) Gellman, A. J. *Langmuir* **1991**, *7*, 827.

(14) Gates, J. A.; Kesmodel, L. L. *Surf. Sci.* **1982**, *124*, 68.

(15) Kesmodel, L. L.; Waddill, G. D.; Gates, J. A. *Surf. Sci.* **1984**, *138*, 464.

(16) Marchon, B. *Surf. Sci.* **1985**, *162*, 382.

(17) Gates, J. A.; Kesmodel, L. L. *J. Chem. Phys.* **1982**, *76*, 4281.

(18) Hoffmann, H.; Zaera, F.; Ormerod, R. M.; Lambert, R. M.; Yao, J. M.; Saldin, D. K.; Wang, L. P.; Bennett, D. W. Tysoe, W. T. *Surf. Sci.* **1992**, *268*, 1.

(19) Ormerod, R. M.; Lambert, R. M. *Surf. Sci. Lett.* **1990**, L20.

(20) Baddeley, C. J.; Tikhov, M.; Hardacre, C.; Lomas, J. R.; Lambert, R. M. *J. Chem. Phys.* **1996**, *100*, 2189.

(21) Lee, A. F.; Baddeley, C. J.; Hardacre, C.; Ormerod, R. M.; Lambert, R. M. *J. Phys. Chem.* **1995**, *99*, 6096.

(22) Baddeley, C. J.; Ormerod, R. M.; Stephenson, A. W.; Lambert, R. M. *J. Chem. Phys.* **1995**, *99*, 5146.

(23) Ormerod, R. M.; Lambert, R. M. *J. Phys. Chem.* **1992**, *96*, 8111.

(24) Ormerod, R. M.; Lambert, R. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1421.

(25) Rainer, D. R.; Wu, M.-C.; Mahon, D. I.; Goodman, D. W. *J. Vac. Sci. Technol. A* **1996**, *14* (3), 1526.

(26) Rainer, D. R.; Xu, C.; Goodman, D. W. *J. Mol. Catal. A* **1997**, *119*, 307.

(27) Wu, M.-C.; Goodman, D. W. *J. Phys. Chem.* **1994**, *98*, 9874.