

Benzene Adsorption and Dehydrogenation on Pt/ZnO(0001)–O Model Catalysts

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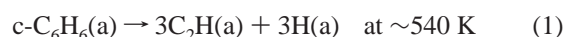
Received: August 19, 2002; In Final Form: November 27, 2002

The dehydrogenation of benzene on Pt/ZnO(0001)–O model catalysts was studied with temperature-programmed desorption (TPD) and low-energy ion scattering spectroscopy (LEIS). Vapor-deposited Pt grows as two-dimensional (2D) islands on this oxygen-terminated ZnO(0001)–O surface up to ~50% of a monolayer and as three-dimensional (3D) islands at higher coverage. The reactivity of these Pt islands is studied as a function of their thickness and coverage. Benzene desorbs molecularly at ~250 K from Pt-free ZnO(0001)–O, unless the surface is preannealed in ultrahigh vacuum, in which case some of it dehydrogenates and populates the subsurface ZnO with H (or D when using perdeuterobenzene, *c*-C₆D₆). Subsurface H (or D) reappears as H₂, HD, and D₂ gas above ~700 K in TPD, isotopically scrambled with the bulk H (D) reservoir. The ZnO defect sites active in benzene decomposition are passivated by annealing in O₂. On Pt islands, most of the adsorbed benzene dehydrogenates in TPD, giving a broad H₂ peak at ~560 K with a shoulder extending to ~750 K. This is attributed to the stepwise conversion of adsorbed benzene to graphitic C, as occurs at the same temperatures on bulk Pt surfaces. Some of the H abstracted by Pt diffuses into the ZnO bulk and reappears above 700 K as H₂. These H₂ peaks all appear as D₂ when using perdeuterated benzene and scramble with the subsurface H reservoir to give simultaneous HD peaks. The LEIS signal also suggests that approximately one-third of the adsorbed *c*-C₆D₆ on the Pt islands also desorbs molecularly at ~300–480 K. Benzene surface reactions and desorption do not depend strongly on island size or thickness, but its dehydrogenation probability on these islands is higher than on Pt(111) and may depend on island dimensions.

1. Introduction

The ZnO(0001)–O surface, also referred to as ZnO(000 $\bar{1}$)–O or simply ZnO(000 $\bar{1}$), terminates in a hexagonal array of oxygen anions and thus offers 3-fold oxygen anion sites common to many catalyst supports, without the complication of any cation sites (at least on a perfect surface). It is thus a very simple but interesting model catalyst support, which we apply here to study model oxide-supported Pt catalysts. As shown in ref 1, films prepared by the vapor deposition of Pt on ZnO(0001)–O follow the two-dimensional (2D) island growth mode, whereby 2D Pt islands nucleate at low coverage and grow in lateral size but not thickness until 0.5 monolayers (ML), above which the islands also grow thicker (i.e., as three-dimensional (3D) Pt islands). On these Pt/ZnO(0001)–O model catalysts, one can easily test size effects by, for example, increasing the lateral size of the 2D islands (by increasing coverage from 0.05 to 0.5 ML) or the thickness of Pt islands from 1 atomic layer to >5 (by increasing the coverage from 0.5 to 6 ML).

Benzene is the simplest aromatic hydrocarbon, so its adsorption and reactions on real and model catalyst surfaces have been studied extensively. The adsorption and dehydrogenation of benzene have been studied on a variety of Pt single crystal surfaces.^{2–11} Benzene adsorbs molecularly on Pt(111) at 100 K parallel to the surface.^{2,7–9,11} The multilayer desorbs at ~195 K, and the ML desorbs in the temperature range of 300–550 K.² At low coverages (<0.3 ML), all of the adsorbed benzene dehydrogenates on Pt(111) through a series of dehydrogenation steps.^{2,3}



The H(a) product of these reactions desorbs immediately as H₂(g), giving rise to temperature-programmed desorption (TPD) peaks at ~540 K (reaction 1) and a broad peak from 570 to 810 K (reaction 2). When using perdeuterated benzene, the D₂ peak appears ~20 K higher in temperature than the H₂ peak at 540 K, due to the primary kinetic isotope effect on C–H vs C–D cleavage in the adsorbed benzene.² After the adsorbed benzene is completely dehydrogenated, graphitic carbon, C(a), is left on the surface. This contributes to “coking” or self-poisoning of the reaction.^{2,12} When benzene is dosed on Pt(111) to a full ML coverage, about 55% of it dehydrogenates during TPD and the rest desorbs.² Because the rate constant for dehydrogenation of perdeuterobenzene is ~3.3-fold slower than for normal benzene,² only ~20% of a ML of perdeuterobenzene dehydrogenates during TPD. Similar dehydrogenation processes of adsorbed benzene on other faces of Pt give rise to H₂ TPD peaks at ~400–470 K from Pt(100), Pt(110)–(1 × 2) and steps on Pt(111); 540–550 K peak from Pt(110) and Pt(100), and 600–800 K peak from Pt(110) and Pt(100).^{2–5}

In a separate study,¹ we addressed the dehydrogenation of cyclohexane on model Pt/ZnO(0001)–O catalysts, testing the effects of island dimensions on the Pt reactivity. Because benzene is also produced as an intermediate in the reactions of cyclohexane on Pt,^{12–20} it is important to first understand its behavior on these model catalysts in order to intelligently interpret the more complex results for cyclohexane presented in that related study.

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Here, we examine the dehydrogenation of benzene on Pt/ZnO(0001)-O model catalysts using TPD and low-energy ion scattering spectroscopy (LEIS) as a detailed function of Pt coverage, which controls the Pt islands' average lateral size and thickness. The reactions of benzene on the clean and stoichiometric ZnO(0001)-O surface and on a slightly reduced form of this surface are also studied.

Benzene adsorption has been studied on the (0001)-Zn and nonpolar (10-10) faces of ZnO,^{21,22} where it was found that benzene adsorbs molecularly parallel to the surface. To our knowledge, there are no prior studies of benzene on ZnO(0001)-O or on well-defined Pt particles on ZnO or other oxide single crystals. However, the interaction of ethylene has been studied on 3 ML Pt films on ZnO(0001)-Zn with high-resolution electron energy loss spectroscopy.²³ These films were highly stepped with many low coordination sites, allowing for much more stabilization of the π -bonded species to temperatures 200 K higher than on close-packed Pt(111), where the di- σ -bonded species predominates above 40 K.²³ This π -bonded ethylene is considered to be the primary intermediate in ethylene hydrogenation.²⁴ Ethylene dehydrogenation during TPD on Pd/Al₂O₃ model catalysts was shown to be particle size-dependent with an increase in dehydrogenation extent as particle size increases from 30 to 1000 atoms, whereas supported Rh and Ir particles did not dehydrogenate ethylene.²⁴ Infrared spectroscopy showed that high-area Pt/Al₂O₃ catalysts adsorb benzene as a π -bonded species at 485 K, with its decomposition and desorption complete by 650 K.²⁵

2. Experimental Section

The experiments were performed in the same apparatus following the same procedures as described in ref 1. All X-ray photoelectron spectra (XPS) reported here used Al K α radiation (1486.6 eV). All LEIS spectra were taken using He⁺ ions from an LK Technologies ion gun, with a primary ion energy of 700 eV, a scattering angle of 135°, and a He pressure of 4×10^{-7} Torr as read by the ion gauge (giving an ion current of ~ 20 nA/cm²). The detection angle was normal to the surface in both XPS and LEIS unless otherwise stated. The heating rate was ~ 5 K/s in TPD and ~ 1 K/s in TP-LEIS.

The ZnO(0001)-O crystal preparation, mounting, and temperature control/monitoring was described in ref 1. Sample temperatures were monitored with a thermocouple attached directly to the edge of the ZnO using a high-temperature ultrahigh vacuum (UHV) alumina-based ceramic adhesive (Aremco). Routine cleaning consisted of sputtering with 700 eV Ar⁺ ions followed by annealing at 900–950 K for 20 min in UHV and then 5 min in 1×10^{-8} Torr O₂, followed by cooling in this O₂. This resulted in a good $p(1 \times 1)$ LEED pattern and clean surfaces as shown with LEIS and XPS. The Pt vapor flux was measured with a quartz crystal microbalance. The resulting Pt coverages were confirmed by XPS intensity ratios and compared to those reported with this same apparatus in ref 1.

The benzene purity was 99.9+% (Sigma-Aldrich). The perdeuterated benzene contained 99.6 atom % D (Sigma-Aldrich). All benzene exposures used a directed doser, as described previously.¹ Experiments to check the enhancement factor of the doser over backfilling the chamber with cyclohexane showed that the enhancement factor was ~ 6 . This factor was used in reporting all benzene exposures below but should only be considered accurate to within a factor of 2. In reading and reporting pressures here, the ion gauge reading was used

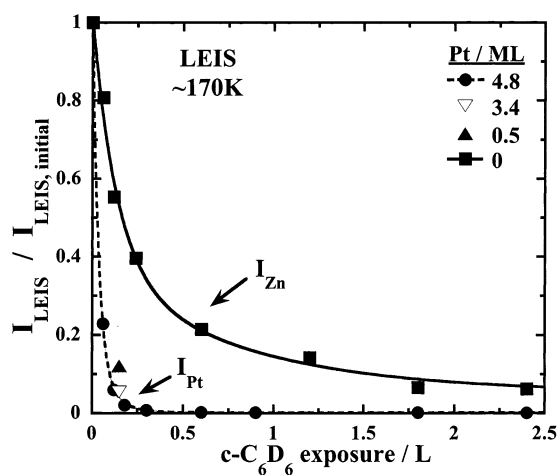


Figure 1. Attenuation of the integrated Zn or Pt LEIS peak intensity (I_{Zn} or I_{Pt}), relative to its starting value ($I_{LEIS, initial}$), shown as a function of increasing exposure of benzene to Pt-free or Pt-predosed ZnO(0001)-O at 170 K. The exposures are in Langmuirs ($1 \text{ L} = 10^{-6}$ Torr sec, corrected for the enhancement factor of the directed doser relative to background dosing). The LEIS signal was collected using 700 eV He⁺ ions with an incident angle $\sim 45^\circ$ from normal and normal detection.

directly without correction for the sensitivity factor of benzene relative to N₂.

3. Results and Discussion

3.1. Benzene Adsorption on ZnO(0001)-O. Figure 1 shows the attenuation of the normalized Zn He⁺ LEIS peak intensity with increasing exposure of benzene to Pt-free ZnO(0001)-O at ~ 170 K. The substrate Zn and O signals decrease to a saturation attenuation of 90% by an exposure of ~ 2 L ($1 \text{ L} = 10^{-6}$ Torr sec), and the He⁺ intensity below ~ 220 eV, which we attribute to C, increases. (Exposures have been corrected for the doser enhancement factor.) This saturation coverage gave a C(1s)/Zn(2p_{3/2})⁰ XPS intensity ratio of 0.0036. (The superscript "0" here refers to the signal from the clean, Pt-free ZnO surface.) In a quantitative XPS study of cyclohexane adsorption on ZnO(0001)-O, 1.0 ML of cyclohexane ($\sim 3 \times 10^{14}$ cyclohexanes/cm²) gave a C(1s)/Zn(2p_{3/2})⁰ XPS ratio of 0.0048.¹ The C/Zn ratio seen here for benzene is 25% smaller than that for cyclohexane, indicating that the benzene ML packing density is 25% smaller or $\sim 2 \times 10^{14}$ benzenes/cm². This is not surprising since on Pt(111), the packing density of the benzene ML, 2.4×10^{14} /cm²,² is also 25% less than the packing density of the cyclohexane ML.¹² This density is slightly less than the maximum packing density one can achieve for benzene molecules in a single plane without overlapping the van der Waals radii for their H atoms, 2.8×10^{14} /cm².²

When ~ 0.12 L of benzene is dosed at ~ 180 K on ZnO(0001)-O, it desorbs in a broad peak centered around 250 K in TPD (top spectrum, Figure 2). Assuming a prefactor of 10^{13} s^{-1} , this peak temperature corresponds to an activation energy for desorption of ~ 63 kJ/mol.²⁶ Assuming no activation barrier to adsorption, this is also approximately the heat of adsorption. Peak temperatures of 200 and 240 K were reported for benzene on TiO₂(110) terraces and steps, respectively.²⁷ There was also a broad peak with the same cracking pattern as benzene, which desorbs between 300 and 600 K in TPD and gives rise to the increase in background by 340 K seen in Figure 2. Control experiments similar to those outlined in ref 1 and LEIS proved that this broad peak is due to desorption of physisorbed benzene from some parts of the sample holder or transfer rod, which also warm slightly during sample heating. Large run-to-run

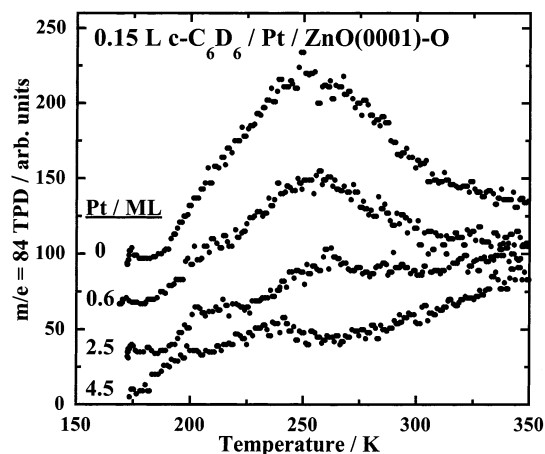


Figure 2. TPD spectra showing molecular desorption of benzene after ~ 0.15 L of perdeuterated benzene was dosed at ~ 180 K on Pt/ZnO(0001)-O, as a function of increasing Pt precoverage.

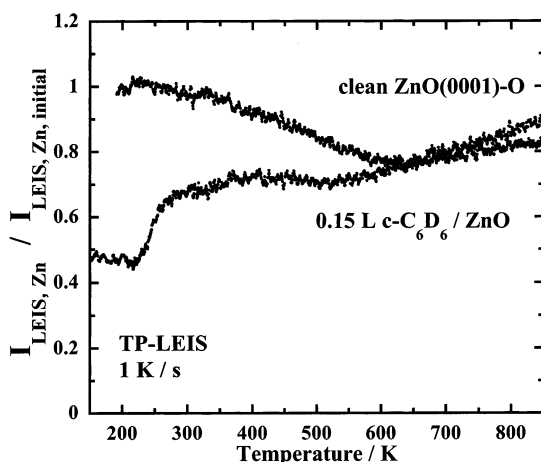


Figure 3. Variation in the Zn LEIS peak intensity, normalized to its starting value, with temperature (time) as the clean or benzene-dosed ZnO(0001)-O is heated at ~ 1 K/s.

variations in the intensity of this background peak prevented us from being able to see any possible small molecular desorption peaks for benzene from the ZnO(0001)-O or Pt/ZnO(0001)-O surfaces in this 300–600 K range.

Temperature-programmed LEIS (TP-LEIS) experiments were performed by continuously monitoring one element's LEIS peak maximum intensity while heating the surface at a rate of ~ 1 K/s. The Zn LEIS peak intensity from clean (benzene-free) ZnO(0001)-O, when monitored in this way from 160 to 850 K, first decreased by $\sim 22\%$ to a minimum at ~ 600 K and then returned to $\sim 86\%$ of its initial value (Figure 3). This suggests some temperature-dependent structural (or electronic) change in the clean surface, which we do not yet understand. If the surface is dosed with 0.15 L benzene at 160 K, the Zn LEIS peak intensity is attenuated by $\sim 50\%$ (as in Figure 1), but after it is heated to 330 K, it is restored to nearly its clean surface value. The C LEIS intensity is also removed, and the C(1s) peak returns to baseline, consistent with a model where the predominant pathway for the adsorbed benzene is to desorb molecularly below 330 K. The desorption rate (i.e., the rate of recovery of Zn LEIS intensity) maximizes at ~ 240 K in TP-LEIS, as shown in Figure 3, consistent with the TPD peak maximum of ~ 250 K (Figure 2) at a higher heating rate (~ 5 K/s). There appears to be some ion beam damage to the benzene adlayer during TP-LEIS since the Zn intensity does not recover completely to the value of the benzene-free ZnO at 330 K when

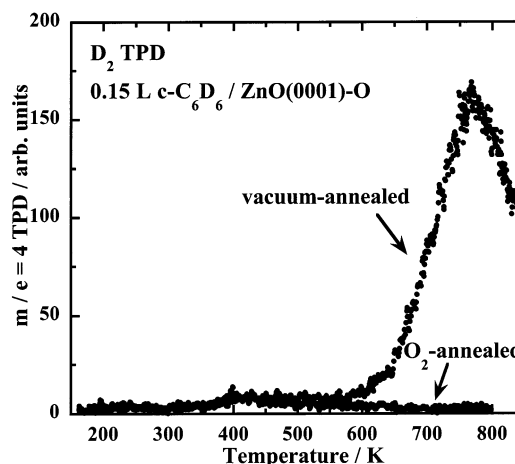


Figure 4. TPD spectra following the D_2 ($m/e = 4$) signal after ~ 0.15 L of perdeuterated benzene was dosed at ~ 180 K to clean ZnO(0001)-O prepared either by finally annealing in O_2 gas as usual or by annealing instead in UHV. The intense peak at ~ 760 K, observed only after annealing without O_2 , is attributed to the evolution of subsurface D(H) populated by benzene dissociation at oxygen vacancies. A similar peak was seen at $m/e = 3$ (HD).

continuously monitoring the signal in this way, whereas it recovered much closer to the clean ZnO value when the ion beam was left off until the temperature reached 330 K in a control TP-LEIS experiment.

When the ZnO(0001)-O surface was prepared by annealing only in UHV at 900–950 K (without the usual final anneal in 1×10^{-8} Torr O_2 for 5 min) before dosing benzene at 180 K, evolution of H_2 was seen above 700 K in TPD, which we attribute to subsurface H populated during TPD by dissociating benzene. When this same experiment was done with perdeuterobenzene, intense TPD peaks for D_2 and HD were instead seen above 700 K, as shown in Figure 4 for D_2 . (The HD line shape was almost the same.) The HD: D_2 intensity ratio in this peak ($\sim 1:1 \pm 50\%$) was much higher than expected based on the isotopic purity used (99.6 atom % D) and depended on sample history (recent use of isotopes), suggesting scrambling with the bulk H (D) reservoir in the ZnO. Similar H_2 /HD/ D_2 peaks at 700–800 K were seen after dosing HCOOD to this ZnO face and attributed to the release of subsurface H (or D) states populated upon the decomposition of the organic molecule at surface defects.²⁸ We offer that same explanation here for benzene. The Pt-dosed Zn-terminated (0001) face of this ZnO crystal also showed this same high-temperature H_2 TPD peak for subsurface H produced by methanol decomposition.²⁹ The intensities of these peaks were greatly reduced when the ZnO was preannealed instead in O_2 (1×10^{-8} Torr) as shown. The oxygen anneal apparently passivates these defects (at least for benzene decomposition), which suggests that they are oxygen vacancies.

In summary, we propose that when this ZnO surface is annealed without O_2 , it has far more oxygen vacancies, which give rise to benzene decomposition products (including subsurface H) in subsequent benzene adsorption/TPD. Except for Figure 4, all of the data presented here were acquired using a final anneal at 900–950 in 1×10^{-8} Torr O_2 when preparing the ZnO surface, to eliminate this defect-related decomposition pathway.

This difference between annealing with and without O_2 , which gives such obvious differences in the hydrogen TPD spectrum after dosing benzene, did not produce any obvious differences in the XPS or LEIS spectra of the ZnO surface, within their signal-to-noise ratios.

There is currently controversy concerning the structure of this O face of ZnO.^{30–32} On the basis of a critical review of the literature and our own observations of differences in angle-resolved LEIS spectra between the O and the Zn terminate faces,³³ we believe the surface that we study here is close to the structure expected for the ideal bulk-terminated O face but with many bilayer steps and relatively narrow terrace widths (broad LEED spots). This is also consistent with the well-known chemical reactivity difference between these two faces, whereby the Zn face is much more reactive toward organic molecules³⁴ and water^{35,36} than is this O face.

3.2. Benzene Adsorption and Dehydrogenation on 2D and 3D Pt Islands and Pt Films on ZnO(0001)-O. As reported elsewhere,¹ Pt grows as 2D islands on this ZnO(0001)-O surface up to a coverage of ~ 0.5 ML. One Pt ML is defined as 1.505×10^{15} atom/cm², the packing density of the Pt(111) surface plane, corresponding to 2.25 Å thickness. This corresponds to ~ 1.36 Pt atoms for each oxygen surface atom or ZnO(0001)-O unit cell (which has 1.1×10^{15} O atoms/cm²). Above 0.5 ML, the Pt islands thicken (i.e., become 3D) and spread until, at 4 ML, nearly 100% of the surface is covered with Pt.¹

Perdeuterated benzene was used in the figures presented here in order to minimize problems with the background H₂ signal. However, experiments with natural isotopic benzene (i.e., predominately c-C₆H₆) gave similar results with the exception that the only isotopes seen in TPD were H₂ since these experiments were done before buildup of any D in the ZnO bulk.

Dosing benzene onto the Pt-predosed surfaces at ~ 170 K attenuates the normalized Pt LEIS peak area ~ 4 -fold faster than the normalized Zn peak of the Pt-free ZnO, as shown in Figure 1 for several Pt coverages from the range of 2D Pt islands up to a continuous multilayer Pt film. This shows that benzene adsorbs faster (i.e., with a 4-fold higher initial sticking probability) on Pt islands and Pt films than on clean ZnO. Oxide-supported metal particles often show higher adsorption rates due to gas molecules that strike the oxide surface and physisorb there, then diffuse to a nearby metal particle and stick on that metal particle.^{37,38} If this capture zone model was operative here, the attenuation of the Pt LEIS signal with benzene exposure would be faster for Pt islands at low Pt coverage than for a continuous, multilayer Pt film. However, the Pt LEIS signal for Pt islands decreased with hydrocarbon exposure (Figure 1) only as fast as it did for a continuous Pt film, at least within the scatter in the data. Perhaps if lower exposures had been studied, we might have seen evidence for this effect.

The C LEIS intensity grows to approximately the same size on the multilayer Pt film as on the Pt-free ZnO surface, when normalized to the starting (Pt-free) Zn LEIS signal. This shows that the saturation coverage of benzene on the Pt multilayer is similar to that on clean ZnO(0001)-O, consistent with the XPS results above which indicated similar saturation coverages on Pt(111) and ZnO(0001)-O. The similar relative attenuation of the Pt LEIS signal at benzene saturation on the Pt islands (Figure 1) suggests that the local benzene coverage on Pt islands is the same as well.

A series of TPD experiments to probe benzene desorption and dehydrogenation was performed as follows. First, Pt was vapor-deposited onto clean ZnO(0001)-O at ~ 300 K. Then, the sample was cooled to ~ 180 K, and XPS was taken while cooling to confirm the Pt coverage (by comparison to XPS results reported in ref 1). Next, the sample was briefly flashed to ~ 600 K to desorb any background gases such as H₂ and CO and quickly recooled. Then, ~ 0.15 L of perdeuterobenzene

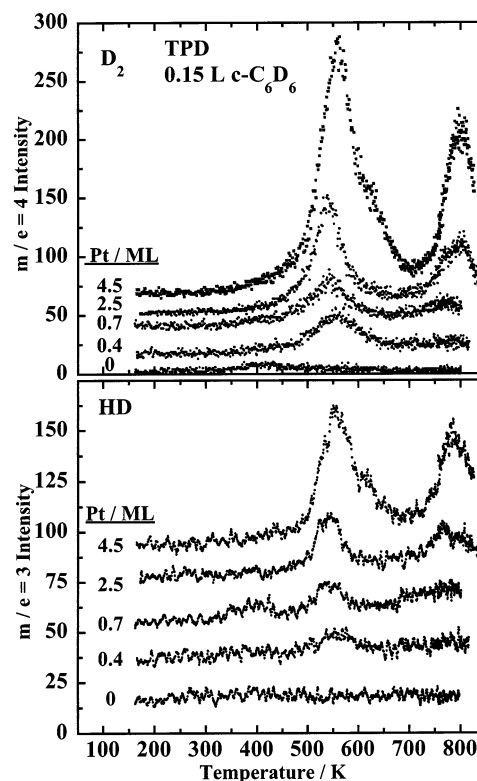


Figure 5. TPD spectra from the same types of experiments as in Figure 2, showing instead the evolution of D₂ (top panel) and HD (bottom panel) after dosing ~ 0.15 L of perdeuterated benzene at ~ 180 K onto Pt/ZnO(0001)-O. The Pt was predeposited on the clean ZnO surface at 300 K and preflashed to ~ 600 K before benzene exposure.

(c-C₆D₆) was dosed as the sample cooled at ~ 180 K. This exposure produces $\sim 40\%$ of a ML of benzene on clean ZnO(0001)-O but a much higher coverage on the Pt islands (nearly a full ML), as shown by the attenuation of the Zn and Pt LEIS peaks in Figure 1. A TPD was performed immediately after pump down (i.e., as soon as the mass spectrometer showed that the benzene pressure was insignificant). Before another experiment, the surface was sputtered (to remove C and Pt), annealed in a vacuum, and then oxygenated to order the ZnO and remove oxygen vacancies, and finally dosed with fresh Pt. The results are presented in Figures 2 and 5.

Typical results for the molecular desorption of perdeuterated benzene as a function of Pt coverage are shown in Figure 2. This shows the signal at $m/e = 84$, the most intense fragment in the cracking pattern of c-C₆D₆. The broad peak at ~ 250 K from the Pt-free surface loses intensity with predosed Pt, with a height above background roughly proportional to $(1 - \theta_{\text{LEIS}})$, where θ_{LEIS} is the fraction of the surface covered by Pt islands as measured by the Pt LEIS signal (relative to its saturation level). Molecular benzene desorption from bulklike Pt sites should be seen at ~ 340 – 530 K,^{2,20} if it occurs. While a benzene signal was seen in this temperature range, it was difficult to distinguish molecular desorption of benzene on the sample surface from the intense background peak at 330–600 K arising from benzene desorption from the sample manipulator (see above), due to large run-to-run variation in this background peak's intensity. Evidence for molecular benzene desorption between 300 and 500 K from Pt sites from TP-LEIS is presented below.

Figure 5 shows typical TPD of the corresponding dehydrogenation products, D₂ ($m/e = 4$) and HD ($m/e = 3$). On the Pt-free surface (bottom), no significant desorption of D₂ or HD

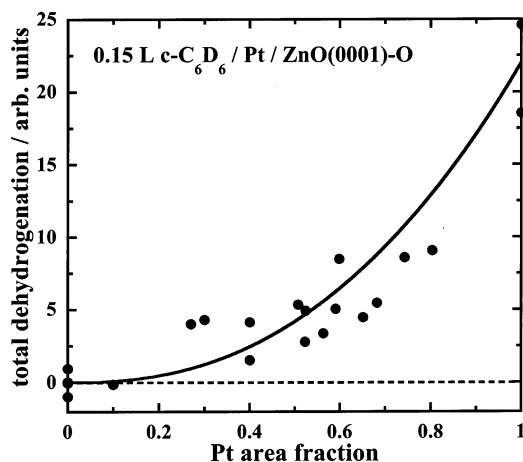


Figure 6. Variation in the total amount of dehydrogenation products seen in TPD after a 0.15 L dose of perdeuterated benzene at 180 K, estimated from the sum of the integrated $m/e = 4$ (D_2) plus $m/e = 3$ (HD) TPD peak areas (from experiments such as Figures 2 and 5) plotted as a function of the fraction of the surface covered by Pt islands. This Pt area fraction was measured by the Pt LEIS intensity (before the benzene dose) relative to that from a continuous Pt multilayer film.

is seen. When Pt is present on the surface, an intense TPD peak is seen for both D_2 and HD at ~ 560 K, which is accompanied by low- and high-temperature shoulders extending from 420 to 500 K and ~ 600 to >750 K, respectively, as well as a smaller peak at ~ 800 K. The amount of desorbing H_2 was very small and so not discussed further here.

The small D_2 and HD peaks at ~ 800 K are attributed to D and H removal from the near surface bulk of the ZnO crystal, based on prior reports of such a peak on ZnO crystals whenever dehydrogenation occurs either on the ZnO surface or on Cu or Pt particles on ZnO^{28,29,39,40} (see also above). Thus, some of the D(a) product from dehydrogenation of benzene on these Pt islands diffuses into the ZnO bulk and scrambles with bulk H. The other D_2 and HD TPD peaks seen from benzene on these Pt islands are attributed to a combination of the same dehydrogenation processes, which give rise to the 400–470, 540–560, and 600–800 K H_2 TPD peaks seen in TPD after adsorbing $c\text{-}C_6H_6$ dehydrogenation on Pt single crystal surfaces: the ~ 400 –470 K peak from Pt(100), Pt(110)–(1 \times 2) and steps on Pt(111); the 540–550 K peak from Pt(111), Pt(110), and Pt(100); and the 600–800 K peak from Pt(111), Pt(110), and Pt(100).^{2–5} Note that the dominant H_2 peak seen from benzene on Pt(111) at 540 K is shifted to 560 K for the D_2 peak from perdeuterated benzene,² so a ~ 20 K correction should be applied when comparing D to H abstraction in these examples.

The HD: D_2 intensity ratios in the peaks in Figures 5 and 6 are much higher than expected for the isotopic purity of the $c\text{-}C_6D_6$ used (99.6 atom % D). We attribute this to the kinetically allowed movement of H and D between the Pt island surfaces and the near surface bulk of the ZnO at these temperatures. In the 420–700 K range, the net (D + H) movement is into the bulk, whereas by 750 K it is dominantly outward. Similar isotopic scrambling between the surface H and the subsurface H was also seen at about this temperature during labeled formate decomposition on Cu particles on ZnO(0001)–O.²⁸

As the Pt coverage increases, all of these peaks increase in size to saturation. The total amount of dehydrogenation, estimated from the total integrated areas of all D_2 peaks plus 50% of the areas of the HD peaks, is plotted in Figure 6 vs Pt area fraction. This increases faster than linearly with Pt area, especially above 0.5 ML when the islands start to be thicker than a single Pt atom (i.e., when they are 3D). (Below 0.5 ML,

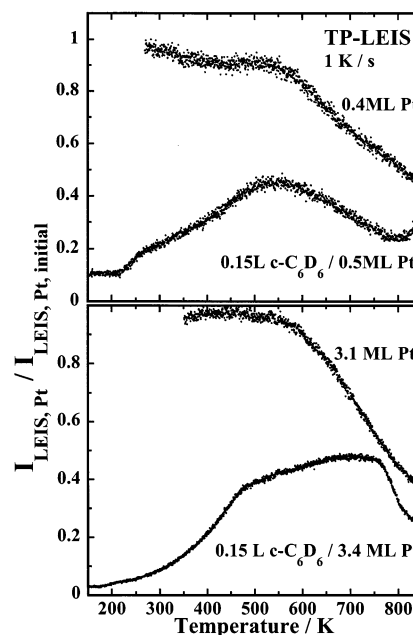


Figure 7. Variation in the Pt LEIS peak intensity, normalized to its starting value, with temperature (time) as the benzene-free or benzene-dosed Pt/ZnO(0001)–O is heated at ~ 1 K/s, for two different Pt precoverages giving 2D Pt islands (top) and a 3D film (bottom).

they are mainly 2D islands.¹) This faster increase may occur because of a true increase in probability for dehydrogenation of adsorbed benzene or due to a decreasing probability for loss of D into the bulk of ZnO as the islands on which they are produced get thicker. This loss into the bulk is obviously competing with the associative desorption process, which gives rise to the observed D_2 and HD intensities. Previous studies showed that the surface H product of H abstraction from adsorbed metal islands on ZnO(0001) has a higher probability to disappear into the bulk of the ZnO during TPD when the metal coverage is lower (i.e., when the metal islands are thinner/smaller).^{28,29,39,40}

Before the above TPD studies with $c\text{-}C_6D_6$, we performed similar TPD studies with unlabeled benzene ($c\text{-}C_6H_6$). Qualitatively similar behavior to Figures 2 and 5 was observed but with H_2 as the only dehydrogenation product.

We performed TP-LEIS experiments by continuously monitoring the Pt LEIS peak maximum intensity while heating the Pt/ZnO(0001)–O surface. The results for both the benzene-free and the benzene-dosed surfaces are shown in Figure 7, for two Pt precoverages: ~ 0.45 ML Pt, where the Pt is mainly in the form of 2D islands initially, and ~ 3.2 ML Pt, where it is a nearly continuous multilayer film. In both cases, the Pt LEIS signal is stable in the absence of benzene until ~ 550 K, where it starts to decrease due to Pt particle sintering (i.e., individual Pt island thickening, Ostwald ripening, or Pt particle diffusion/coalescence).

Similar results for surfaces with nearly the same Pt coverage but after a 0.15 L dose of perdeuterated benzene are also shown in Figure 7. This benzene attenuates the Pt LEIS signal by $\sim 90\%$ in both cases, indicating near ML coverage on the Pt islands or film. About 30–40% of the Pt LEIS signal is recovered between ~ 300 and ~ 480 K, which we attribute to some molecular desorption of benzene from the Pt sites, since no dehydrogenation of the benzene occurs until above ~ 480 K (see above). Assuming that there is no associated change in the neutralization probability of He ions scattered from Pt atoms, the magnitude

of this signal change suggests that 30–40% of this perdeuterated benzene ML desorbs molecularly and ~60–70% dehydrogenates, independent of the Pt island thickness. On Pt(111), ~55% of a ML of normal benzene dehydrogenates during TPD, with the rest desorbing molecularly.² Because the rate constant for benzene dehydrogenation on Pt(111) is ~3.3-fold slower with perdeuterobenzene,² ~20% of a ML of perdeuterobenzene should dehydrogenate during TPD on Pt(111). The much larger extent of dehydrogenation seen on the Pt/ZnO samples suggests that these Pt islands are more reactive for benzene dehydrogenation than Pt(111). The same result was found for cyclohexane¹ and methanol.²⁹ The similar, large extent of dehydrogenation seen from all Pt coverages on ZnO suggests that dehydrogenation proceeds on all of these Pt islands to the maximum extent allowed by surface site availability for the decomposition products. In the top panel of Figure 7 for the benzene-dosed surface, there is also a small increase in the Pt signal at ~250 K, which is possibly due to desorption of some background impurity (e.g., water) from that surface. No such increase was seen for two similar TP-LEIS experiments done at 0.8 ML Pt, where the signal was otherwise intermediate between the two Pt coverages shown in Figure 7.

The Pt LEIS signal remains relatively constant between 500 and 600–700 K (Figure 7), despite the large amount of D desorption (Figure 5). The signal is still well below the benzene-free value, since the adsorbed product(s) of benzene dehydrogenation still mask the Pt surface. The decrease in Pt signal above 600 or 700 K may be due to sintering of the Pt islands as seen without the benzene dose but complicated by other processes (e.g., more dehydrogenation and surface carbon graphitization).

4. Conclusions

Perdeuterated benzene adsorbs and thermally desorbs molecularly at ~250 K from ZnO(0001)-O. It adsorbs with high probability on 2D and 2D Pt islands supported on this surface. Benzene-*d*₆ dehydrogenates upon heating with 3- or 4-fold higher probability than on Pt(111) but with similar chemistry. The resulting D₂ TPD peak temperatures (~560 and 600–700 K) are similar to those seen on low index Pt single crystal surfaces. The overall dehydrogenation probability for a 0.15 L dose of perdeuterobenzene (which gives ~0.9 ML benzene on the Pt islands) is nearly the maximum amount allowed by site requirements for all coverages of Pt. This suggests that the dehydrogenation probability is so high that it is limited more by site availability than by any inherent differences in reactivity with Pt island size, which may still exist. For all island sizes, the Pt sites are much more reactive than sites on Pt(111). The D product of dehydrogenation rapidly scrambles with dissolved H in the ZnO bulk, giving rise to strong HD intensity as well. When the Pt islands are 2D, there is a competition between associative desorption of D₂ and loss of D into the ZnO bulk. When the Pt islands are 3D, there is a decreasing probability of D loss into the ZnO bulk and a subsequent increase in prompt D₂ desorption.

Acknowledgment. We acknowledge the Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, for support of this work. L.T.N. thanks the University of Washington, Center for Nanotechnology, for an NSF-IGERT graduate research fellowship.

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