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# High-temperature desorption of benzene from zirconium surfaces

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## Abstract

We report on the interaction of benzene with zirconium (0001) surfaces. Following adsorption at 150 or 170 K benzene desorbs near 715 K at exposures above one Langmuir. The high desorption temperature of benzene is indicative of the complicated kinetics that zirconium surfaces exhibit. For lower exposures benzene dissociates during heating and an increase of the oxygen content at the surface is detected. We propose that hydrogen from the dissociated layer(s) attracts subsurface oxygen and that an exchange of adsorbed carbon with this oxygen takes place.

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## 1. Introduction

Various molecules dissociate on zirconium surfaces even for adsorption at much below room temperature [1]. This low-temperature cracking of adsorbed species is often accompanied by diffusion of atomic fragments into the subsurface regions. This diffusion and its influence on zirconium surface chemistry are not fully understood with respect to the interaction of organic compounds with zirconium surfaces. While of fundamental interest, understanding the adsorption and dissociation of hydrocarbons on zirconium-based materials is of applied interest as well. For example, some organic compounds cause stress corrosion cracking of zirconium but it is not clear how this relates to the presence of water and halides in solution [2].

Zirconium surfaces exhibit complicated kinetics in the presence of carbon-free species such as ammonia [3,4], nitric oxide [5], oxygen [6] and water [1,7]. However, very few studies of the interaction of carbon-containing species with zirconium surfaces under ultrahigh vacuum (UHV)

conditions have been reported [8–12]. The interaction of carbon-free molecules with Zr(0001) surface showed strong dependence of desorption peak temperature on adsorption temperatures [1]. On the other hand, observations concerning the exposure of zirconium to methanol [12] reveal different desorption kinetics than those of carbon-free species and suggest that carbon might play a key role in determining the resulting kinetic pathways. Here, our motivation is to explore the role of carbon further, by using benzene as a class of molecules (aromatics) that has not been studied on Zr(0001).

## 2. Experimental methods

Detailed descriptions of the UHV system used in this study have been given previously [5,13]. The substrate is a Zr(0001) single crystal in the form of cylindrical disc. The thickness of the crystal is 1 mm and the radius is 3 mm. The crystal is polished on one side to 30 nm with uncertainty in orientation of less than 1°. Two tantalum wires and two thermocouples (type-E) are spot-welded to the sample. The tantalum wires provide dc heating whereas the thermocouples constitute part of a temperature-controlled feedback

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loop. A copper braid attached to a liquid-nitrogen cold finger is used for cooling the sample.

In order to clean the sample surface several sputtering cycles with  $\text{Ar}^+$  ( $2 \text{ keV}$ ,  $2 \mu\text{A cm}^{-2}$ ) bombardment, followed by annealing to  $860 \text{ K}$ , are carried out. The cleanliness of the sample is monitored by Auger electron spectroscopy (AES) and a sharp ( $1 \times 1$ ) low energy electron diffraction (LEED) pattern characteristic of the clean Zr(0001) surface. Major contaminants of zirconium surfaces (C, O, and S) are kept at their clean surface levels prior to experiments,  $\text{C(KLL)}/\text{Zr(MNN)} \sim 0.21$ ,  $\text{O(KLL)}/\text{Zr(MNN)} \sim 0.15$  and  $[\text{Zr(MNV)} + \text{S(LMM)}]/\text{Zr(MNN)} \sim 0.91$ , consistent with what we previously reported [4]. We verify that the oxygen AES signal is at most just above the signal-to-noise limit before conducting the experiments presented here. We intentionally avoid annealing to higher temperatures, which would diminish the surface O and C content further. However, this would cause sulfur segregation to the surface, which has a stronger effect on chemisorption than C or O.

Experiments are performed at a base pressure of about  $3 \times 10^{-10} \text{ Torr}$ . Exposures are performed by backfilling the chamber and are expressed in Langmuir ( $1 \text{ L} = 10^{-6} \text{ Torr s}$ ) units without correction for ion-gauge sensitivity. After introducing benzene ( $\text{C}_6\text{H}_6$ , Fisher, purity  $>99.0\%$ ) into a glass bulb the dissolved gases are removed by several freeze-pump-thaw cycles. During backfilling the purity is monitored by a quadrupole mass spectrometer (QMS). For monitoring the mass-to-charge ratios in temperature programmed desorption (TPD) experiments the QMS and the sample are positioned in line-of-sight geometry.

The heating rate during TPD and stepwise-annealing AES, LEED, and secondary electron emission crystal current (SEEC) experiments is  $1.8 \text{ K/s}$ . All measurements, however, are taken after the sample is cooled back down to  $150 \text{ K}$ . For SEEC data an ammeter is connected in series between the sample and ground, and measurements are taken prior to each AES scan. Exposure of the sample to the AES beam ( $3 \text{ keV}$ ,  $15 \mu\text{A cm}^{-2}$ ) causes the sample temperature to rise about  $7 \text{ K}$ , and no change in temperature is observed when the LEED ( $60 \text{ eV}$ ,  $2 \mu\text{A cm}^{-2}$ ) electron beam is used.

### 3. Results and discussion

Fig. 1 shows benzene ( $78 \text{ amu}$ ) desorption spectra from Zr(0001) surfaces following  $150 \text{ K}$  adsorption. For exposures up to  $1.1 \text{ L}$  no desorption peak is present. This dissociation of benzene on Zr(0001) for low exposures is a direct consequence of the reactive nature of zirconium. For exposures of  $2.1 \text{ L}$  and higher, desorption peak features are well defined and desorption occurs near  $715 \text{ K}$ . The increase in benzene desorption yield is rapid in the  $1\text{--}3 \text{ L}$  range. It has been shown by others that benzene dissociates on

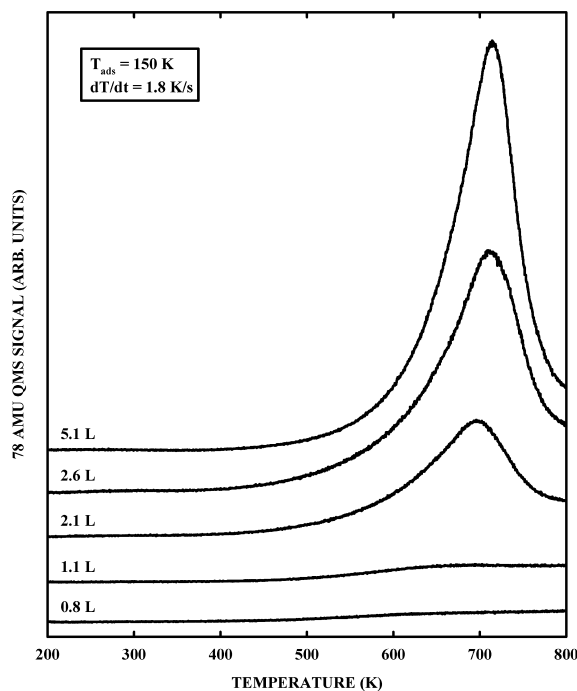


Fig. 1.  $\text{C}_6\text{H}_6^+$  ( $78 \text{ amu}$ ) TPD spectra following  $150 \text{ K}$   $\text{C}_6\text{H}_6$  adsorption on Zr(0001) surfaces. Benzene and its cracking fragments are the only species detected.

Re(0001) at room temperature for low coverage [14,15]. There are also similarities between our results and those reported for platinum [16], where for lower exposures benzene mainly dissociates whereas at higher exposures it mainly desorbs. However, this  $715 \text{ K}$  desorption temperature that we observe is unexpectedly high and to our knowledge is the highest reported desorption temperature for benzene from any transition metal surface.

Adsorption of benzene at  $170 \text{ K}$  also results in a  $715 \text{ K}$  desorption temperature (not shown). Integrated peak areas again increase with exposure but with less benzene desorption as compared to the  $150 \text{ K}$  adsorption case. These data are shown in Fig. 2. The difference in yield at the two adsorption temperatures is significant at higher exposures. This is consistent with what we observed for the interaction of methanol with Zr(0001) [12]. Reduced benzene desorption, as compared to that at  $150 \text{ K}$ , may be explained by a lower sticking coefficient at the higher adsorption temperature. We cannot, however, rule out the formation of condensed molecular ice at these adsorption temperatures. What is most important is that the change in adsorption temperature does not change the desorption temperature as observed for carbon-free molecules on Zr(0001) [1].

Our current model to explain these observations is that the first benzene layer(s) dissociate, yielding no thermal desorption products and participating in surface-subsurface exchange. Subsequent benzene molecules adsorb on a

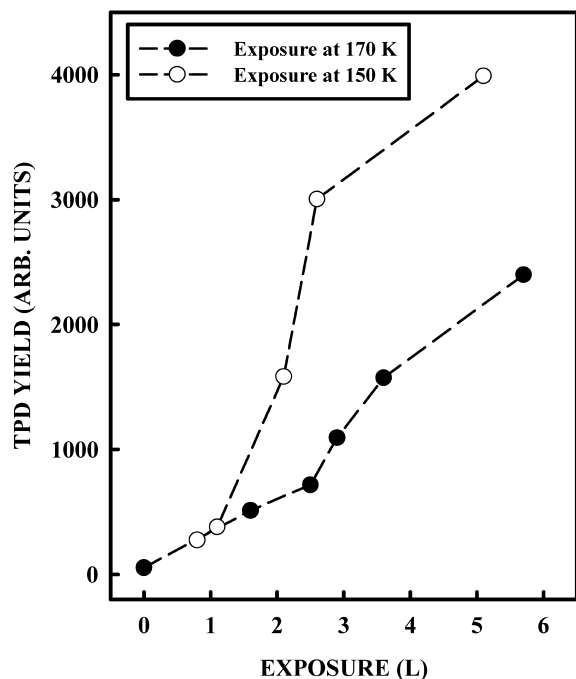


Fig. 2. Integrated TPD yields of benzene vs. exposure for two different adsorption temperatures.

carbon-modified Zr surface with reduced propensity for benzene decomposition, as observed on molybdenum [17]. However, this carbon-modified zirconium surface still has a strong affinity for benzene, resulting in a rapidly increasing benzene uptake vs. exposure. Since we only detect significant amounts of benzene and its cracking fragments in TPD, we conclude that the C–C bonds remain intact at these higher exposures. Otherwise we would expect to see other hydrocarbon species in TPD. Since we detect no  $H_2$  in TPD experiments, hydrogen liberated from dissociated benzene most likely remains in the near surface region.

Fig. 3 shows derivative mode Auger electron spectra of cleaned Zr(0001), after exposure to 1.7 L of  $C_6H_6$ , and after annealing to 860 K. The presence of carbon on the surface, prior to exposure, is a consequence of the high affinity of zirconium for carbon and a relatively high carbon AES cross section. On the other hand, the oxygen Auger signal is at the edge of the detection limit. It is possible to reduce the amount of carbon in the near-surface region by increasing the annealing temperature, but this causes unwanted sulfur segregation to the surface.

Note how exposure of Zr(0001) to 1.7 L of  $C_6H_6$  does not seem to affect the C(KLL) Auger signal whereas an increase in the O(KLL) signal is evident. However, the main zirconium features (Zr(MNV) and Zr(MNN)) are attenuated by benzene adsorption. Therefore, by looking at the Auger peak-to-peak height (APPH) ratios we determine that both C(KLL)/Zr(MNN) and O(KLL)/Zr(MNN) ratios increase upon exposure. The relative increase in oxygen signal is

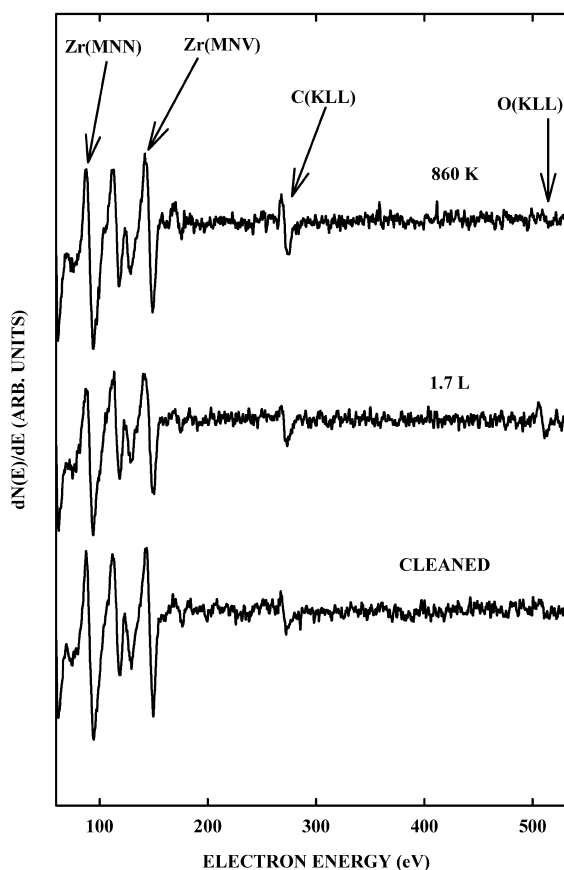


Fig. 3. Derivative mode Auger electron spectra taken at 150 K of cleaned Zr(0001), after exposure to 1.7 L of  $C_6H_6$ , and after annealing to 860 K. Note that oxygen returns to its initial value after annealing, but carbon does not.

even larger than that of carbon. From these AES data we propose that at low exposures benzene dissociates and the liberated C replaces O from the subsurface region. Since no hydrogen desorption is detected in TPD we propose that hydrogen plays a role in attracting oxygen to the surface as observed by others [18].

For exposures of 2 L and higher, where the desorption peak is notable in TPD, the carbon AES signal becomes more pronounced compared to that of oxygen. Note that in a study of CO adsorption on polycrystalline zirconium, ion scattering spectroscopy revealed oxygen, not carbon, in the topmost layer even after exposure to 2500 L of CO [10]. In the same study, AES revealed the presence of carbon beneath the oxygen. We propose that a similar effect occurs between solid-solution phase oxygen and carbon liberated from benzene at low exposures. The C–O exchange mechanism is expected to saturate after adsorption of the first layer or two of carbon, consistent with our data.

Although we do not have conclusive proof that our qualitative model is correct, this is a reasonable explanation for what we observe.

The stepwise-annealing behavior of carbon and oxygen differ substantially. The spectra in Fig. 3 clearly show that the carbon AES signal does not decrease after annealing to higher temperatures. From various studies it is known that both carbon and oxygen diffuse into the bulk of zirconium at higher temperatures. Oxygen, however, diffuses faster than carbon [8]. The annealing temperature that we use is not high enough to cause significant carbon diffusion into the bulk and we still observe carbon after annealing. The SEECC measurements (not shown) are consistent with what we observe in AES.

LEED experiments (not shown) are performed at 150 K after stepwise annealing and for exposures in the 1–6 L range. No ordered layers of benzene on Zr(0001) are observed. However, LEED images become more diffuse after adsorption. It is interesting to note that after adsorption of C<sub>2</sub>H<sub>4</sub> on Zr(0001) [11] it was found that carbon forms two different ordered (1 × 1)-C structures. This might be the case in our experiments for C<sub>6</sub>H<sub>6</sub>/Zr(0001) as well, but we cannot perform LEED intensity analysis to verify the presence of (1 × 1) superstructures.

There are possible alternative explanations for our observations. Even under UHV conditions, Zr can getter oxygen-containing species from the background gas (CO, water, etc.). Backfilling of the UHV system is not the best method to study such a complicated materials system in detail, and we are currently employing a newly constructed capillary-array gas doser to the problem of benzene adsorption/desorption on zirconium. There is a need in our future work to investigate the influence of oxygen on benzene adsorption/desorption behavior in a systematic way. Since hydrogen is not liberated during benzene TPD experiments, we are presently left with a mass-balance question as well. However, it is known that O and H interact strongly with one another on and within Zr. Thus there are potentially several processes occurring simultaneously in the reactive C<sub>6</sub>H<sub>6</sub>/Zr(0001) system in the presence of subsurface oxygen that we will investigate in future work.

#### 4. Summary

We have provided evidence that benzene adsorption on Zr(0001) is dissociative at low coverages, and that subsurface oxygen is attracted to the surface by the hydrogen and is replaced by adsorbed carbon. In these cases, essentially no species are detected in thermal desorption experiments, and the surface retains carbon after annealing. At greater

exposures benzene desorption is detected at unexpectedly high temperature. We find that the desorption temperature is not affected by the adsorption temperature, unlike what has been observed for carbon-free molecules on Zr(0001).

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