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An experimental study on adsorption of benzene on Co(0 0 0 1)

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Abstract

The adsorption of benzene on Co(0 0 0 1) was studied by X-ray photoelectron spectroscopy, temperature programmed desorption, low energy electron diffraction (LEED) and work function measurements. The adsorption was found to be molecular at room temperature and to saturate at a fractional coverage of 0.125 ML. With LEED a c($2\sqrt{3} \times 4$) overlayer structure was seen. Below 220 K at high exposures a p($\sqrt{7} \times \sqrt{7}$)$R19°$ LEED pattern was observed corresponding to a coverage of 0.143 ML. Temperature programmed desorption measurements stated that benzene starts to decompose around 340 K to hydrogen and a hydrocarbon fragment, most likely C_6H_5. While the hydrogen desorbed, the hydrocarbon stayed at the surface. The desorption of molecular benzene was negligible. The activation energy for the dehydrogenation was calculated to be about 102 kJ/mol. The work function of Co(0 0 0 1) decreased by 1.3 eV upon saturation with benzene. The induced dipole moment was calculated to be 1.9 Debye/molecule. © 2002 Published by Elsevier Science B.V.

Keywords: Aromatics; Cobalt; Low energy electron diffraction (LEED); Low index single crystal surfaces; Thermal desorption spectroscopy; X-ray photoelectron spectroscopy; Work function measurements

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1. Introduction

Benzene, C_6H_6, is the simplest aromatic hydrocarbon. The scientific interest in benzene originates from using benzene as a model molecule for more complicated cyclic aromatic hydrocarbons. It is known to be adsorbed easily on most transition metal surfaces [1]. Within such an adsorption system the benzene molecule acts as an electron donor. Cobalt-containing materials are commonly used in hydrocarbon catalysis, e.g. in Fischer–Tropsch catalysis.

The benzene/metal interaction has been studied on a large number of metal surfaces, e.g. Pt(1 1 1) [2–4], Pt(1 1 0) [5], Pd(1 1 1) [6], Cu(1 1 1) [7,8], Rh(1 1 1) [9], W(1 1 0) [10], WC(0 0 0 1) [11], Ni(1 1 1) [12–17], Ni(1 0 0) [16–18], Ru(0 0 0 1) [19–21], Os(0 0 0 1) [22], Ir(1 1 1) [23] and Ir(1 0 0) [24]. A good review on some of these systems can be found in [1,13]. For cobalt so far only adsorption of benzene on Co($1 0 \bar{1} 0$) [25,26] and W(1 1 0) supported Co(0 0 0 1) films [27] have been studied.

Getzlaff et al. studied benzene on supported Fe(1 1 0) and Co(0 0 0 1) films. The films were made by MBE and were uniformly magnetized. The measurements were done by ARPES. They stated a molecular adsorption of benzene with a flat adsorption geometry and a C_{3V} symmetry.

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Measurements of benzene on Co(1 0 $\bar{1}$ 0) were done by low energy electron diffraction (LEED) [25] and ARPES [26]. A p(3 × 1) LEED pattern was found which is formed by a strongly distorted partially hydrogenated cyclic C_6 intermediate. As possible candidates for this molecule C_6H_4 or C_6H_5 were suggested. The geometric structure was found to be a non-flat-lying molecule, adsorbed in an off-centre bridge site across the [1 2 $\bar{1}$ 0] rows.

In this work we have studied the adsorption of benzene on a pure Co(0 0 0 1) single crystal. This has been done to generate basic information, how aromatic molecules adsorb on the hexagonal surface of cobalt.

2. Experimental

A detailed description of the apparatus can be found in [28–30]. All measurements were performed in an UHV stainless steel chamber with a base pressure of 2×10^{-10} Torr. The chamber was pumped with an ion pump, a turbo molecular pump and an additional titanium sublimation pump to maintain the necessary UHV condition. The chamber was equipped with X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TDS) and low energy loss diffraction (LEED) systems. Additionally, the system contained an Ar^+ ion sputter gun, a quadrupole mass spectrometer, a dual anode (AlK_α and MgK_α) and a hemispherical electron energy analyzer.

A glass flask containing the liquid benzene was attached to the dosing system (separate gas inlet). The benzene was purified by several freeze–thaw cycles with subsequent pumping down.

The Co(0 0 0 1) crystal was mounted to the sample holder by 0.25 mm thick tantalum wires. These wires served also as heating current conductors for the TDS measurements. The temperatures to perform the measurements were restricted by the cooling system, which allowed sample temperatures as low as 160 K, and the phase transition temperature of cobalt at about 690 K, where the phase transition of hcp to fcc takes place.

To remove the major impurity carbon, the sample had to undergo a sputtering process, which was followed by annealing. The purity was proofed by C 1s XPS measurements and a bright hexagonal LEED pattern.

3. Results and discussion

In Fig. 1 TD spectra of hydrogen originating from adsorbed benzene at various coverages are shown. Benzene was initially adsorbed at 300 K. The heating rate was 2.6 K/s. The desorption of hydrogen starts at 340 K. At all coverages TDS yields a broad hydrogen peak with a desorption maximum at 390 K, which is followed by a tail at the high temperature side. The inset of Fig. 1 shows the uptake curve of benzene on Co(0 0 0 1) at 300 K. The uptake curve was obtained by integrating the area under the TD spectra and plotting it against the exposures. The saturation coverage was determined to be around 30 L. Additional C 1s measurements with XPS gave the same value for saturation.

In TDS measurements no desorption of hydrocarbon fractions originating from benzene

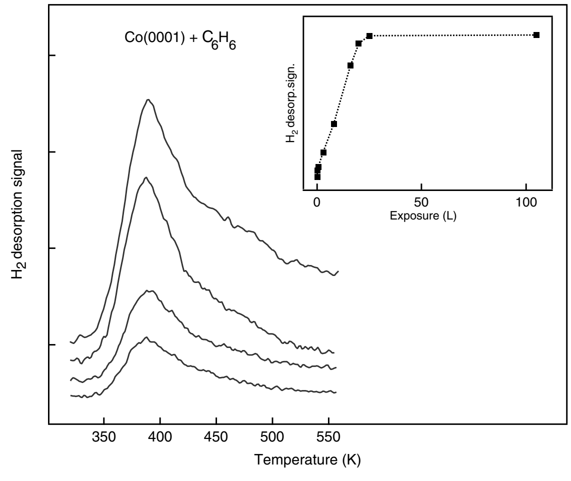

Fig. 1. Thermal desorption spectra obtained after exposing a clean Co(0 0 0 1) surface to benzene. The exposure temperature was 300 K. The exposure time was kept constant to 100 s, while the pressure was changed. The heating rate was 2.6 K/s. The coverage was varied between 4 and 25 L. The inset shows the H_2 desorption signal as a function of benzene exposure. The line is drawn to guide the eye.

molecules were registrated and the desorption of benzene (mass 78) was negligible. Only the desorption peak of hydrogen was observed. The desorption measurements indicated that benzene on Co(0 0 0 1) partially dissociates around 340 K. While hydrogen desorbed, the hydrocarbon fragments remained at the crystal surface. This agreed with the XPS results, which showed no change in the carbon coverage before and after the heating.

By knowing the coverage from the LEED experiments (see below) and comparing the H_2 desorption peak with that of D_2 on Co(0 0 0 1) [31] we could estimate that only one hydrogen per benzene molecule is desorbed. This loss suggests that with increasing temperature an intermediate, possibly C_6H_5, is formed. Such a process was already suggested for Os(0 0 0 1) [22] and Co(1 0 $\bar{1}$ 0) [25,26].

With increasing coverage there is no temperature shift visible in the desorption-peak maximum. Therefore a second order process can be ruled out and a first-order process has to be considered. The first-order behaviour of the TDS data suggests that the decomposition process might be the limiting step of the desorption. The activation energy of the decomposition was estimated to ~102 kJ/mol, assuming the pre-exponential factor to be 10^{13} s^{-1}. This value is almost the same as suggested for the dehydrogenation of benzene on Co(1 0 $\bar{1}$ 0) [26].

In Fig. 2 the observed LEED picture and pattern for benzene adsorbed around 300 K is shown. The LEED pattern was easily reproduced over a wide range of exposure from 2 L up to 30 L. At all coverages the same c($2\sqrt{3} \times 4$) LEED pattern was obtained. The c($2\sqrt{3} \times 4$) structure determines a saturation coverage of 0.125 ML. The comparison of the C 1s coverage of benzene on Co(0 0 0 1) with the known C 1s coverage of 0.33 ML of the pure Co($\sqrt{3} \times \sqrt{3}$) structure suggested a similar result of 0.12 ± 0.01 ML. Island formation might be the reason for the steady LEED picture over the wide range of exposure.

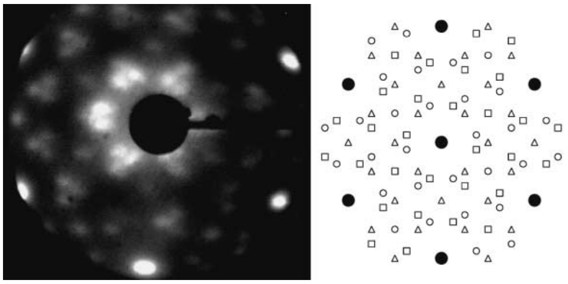

Fig. 2. Observed and schematic LEED pattern of benzene adsorbed on Co(0 0 0 1) at room temperature (66 eV): c($2\sqrt{3} \times 4$).

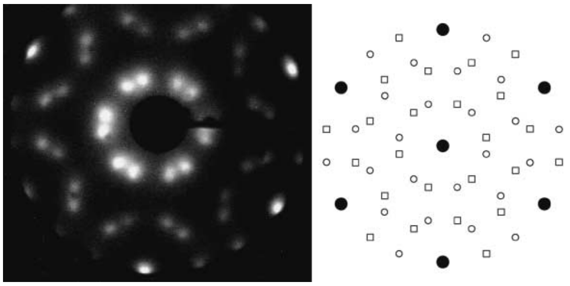

Fig. 3. Observed and schematic LEED pattern of benzene adsorbed on Co(0 0 0 1) at 220 K (62 eV): p($\sqrt{7} \times \sqrt{7}$)R19°.

At adsorption temperatures below 220 K and higher coverages a second LEED structure was visible (Fig. 3). This p($\sqrt{7} \times \sqrt{7}$)R19° structure corresponds to a higher coverage of 0.143 ML.

Both structures were also found during the adsorption of benzene on Ru(0 0 0 1) [21]. For Ru(0 0 0 1) also a third commensurate superstructure was seen at low coverages. This p($2\sqrt{3} \times 2\sqrt{3}$)R30° pattern was not producible for benzene adsorption on Co(0 0 0 1).

Fig. 4 shows the dependence of the work function of Co(0 0 0 1) on the benzene exposure at 160 K. The work function was measured by monitoring the cutoff energy of the photoelectron spectrum. At small exposures the change in the work function decreases linearly until it reaches the minimum of −1.3 eV. Using the value of 5.55 eV for the work function of clean cobalt [32], the saturation with benzene results in a work function value of 4.25 eV. By using the Helmholtz equation the dipole moment was estimated to 1.9 Debye/molecule.

The work function decreases due to the partial charge transfer from the benzene molecules to the cobalt. After reaching the minimum $\Delta\phi$ stays constant indicating that forces between the

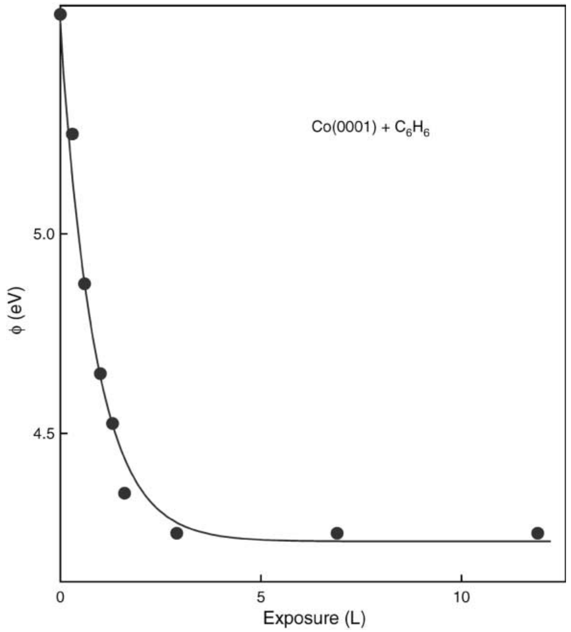

Fig. 4. Work function versus exposure of benzene on Co(0 0 0 1) at 160 K.

adsorbed molecules do not change the bonding to cobalt. The value of -1.3 eV fits well to measured work function changes of other transition metals, like -1.1 eV for Ni(1 1 1), -1.52 eV for Pt(1 1 1) and -1.82 eV for Ru(0 0 0 1) [2].

4. Summary

Benzene is adsorbed molecularly on Co(0 0 0 1) at room temperature. It forms a $c(2\sqrt{3} \times 4)$ structure. At lower temperatures (<220 K) and high doses $p(\sqrt{7} \times \sqrt{7})R19°$ was observed. During heating above 340 K benzene partially dehydrogenates to hydrogen and hydrocarbon. The hydrogen desorbs, while the hydrocarbon stays at the surface. Desorption of molecular benzene can be neglected. As a possible hydrocarbon molecule C_6H_5 was suggested. The activation energy of dehydrogenation was estimated to be around 102 kJ/mol. The work function of the benzene/Co(0 0 0 1) system is 4.25 eV, 1.3 eV lower than the work function of clean Co(0 0 0 1).

Acknowledgements

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