



Research paper

Benzene adsorption on two-dimensional silica films – Benzene on silicatene



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ABSTRACT

The kinetics of benzene adsorption on monatomic crystalline silica films (silicatene) was studied, employing temperature programmed desorption (TPD). In addition, the precursor of the silica film formation, a Mo(1 1 2)-p(1 × 3)-O missing row reconstruction, and Mo(1 1 2) were considered. Benzene adsorbed molecularly on all surfaces. Judged by the desorption temperatures, the adsorption on the Mo oxygen phase is stronger than on silica. Two binding sites were evident for the oxygen induced reconstruction, but only one for silica. Thus, the adsorption kinetics on the support and the monoatomic thin silica film were quite different. In addition, the surfaces were characterized by Auger electron spectroscopy and low energy electron diffraction (LEED).

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1. Introduction

Sparked by the discovery of graphene many inorganic two-dimensional (2D) materials were in the meanwhile synthesized [1,2]. An interesting example of a 2D crystal is silicatene which consists of a monoatomic layer of silica, SiO₂. The silicatene films were originally grown on Mo(1 1 2) supports [3–5], but more recently also other supports such as Pd(1 0 0) and Ni(1 1 1) were used [6,7]. Besides fundamental interests, applications of silicatene may include microelectronics and sensors, but also model catalysis studies since doped silicatene may be considered as a 2D version of zeolite-like materials [8,9]. So far most studies were devoted to characterization of the geometrical structure of this material [5,10]. In addition, due to the low reactivity of silica toward adsorption of small molecules many projects concern metal cluster growth (“functionalization”) on silicatene rather than bare 2D SiO₂ surfaces. Gas-surface interactions on silicatene have not been studied in much detail. An exception are projects devoted to CO adsorption [11,12] and water/hydroxyl adsorption on silicatene [13–15]. Benzene adsorbing with its plane parallel to the surface as well as tilted adsorption was seen on some surfaces [16]. In a single

paper, benzene interaction with bare silicatene was studied by vibrational spectroscopy [17]; here parallel adsorption was concluded. Benzene physisorbs via interaction with surface oxygen on silicatene [17]. Benzene adsorption on Mo(1 1 2) and on the oxygen precursor, Mo(1 1 2)-p(1 × 3)-O, used to nanofabricate silicatene was not studied before. These Mo surface on their own have, however, some applications as catalysts (liquefaction of coal, hydrodesulphurization, selective oxidation of hydrocarbons and alcohols, NO_x reduction, etc.) and are used e.g. as a supports for thin oxide film formation [18].

2. Experimental procedures

2.1. Experimental setup

The experiments were conducted in an ultra-high vacuum (UHV) chamber equipped with a mass spectrometer for temperature programmed desorption (TPD), a CMA (cylindrical mirror analyzer) based Auger system (AES), as well as the common surface science tools; for details, see Ref. [19]. The lowest adsorption temperature reached with liquid N₂ cooling and He gas bubbled through the Dewar amounts to ~85 K. The reading of the thermocouple has been calibrated (±5 K) in situ by TPD measurements of condensed alkanes (see Table S1 for these data). Binding energies, E_d, were determined from the TPD peak positions (with uncertainty

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of ± 0.5 kJ/mol) using a Redhead analysis and a pre-exponential of 1×10^{13} /s. The heating rate amounts to 1.6 K/s. The gases were dosed by backfilling the vacuum chamber with exposures, χ , given in Langmuir ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr} \times 1 \text{ s}$).

2.2. Sample fabrication and characterization

The Mo(1 1 2) surface was cleaned by sputtering and UHV flashing up to 1600 K. The nanofabrication of 2D silica films in UHV is rather tricky and cumbersome. Preparation procedures were described for the first time by Freund and Goodman (see e.g. Refs. [3–5]). In our study, for the silica film preparation, first the Mo(1 1 2)-p(1 \times 3)-O surface was made (7×10^{-8} mbar O_2 at 950–1000 K for ~ 5 min). Afterwards, in most cases, a one step process for forming the thin film by depositing Si in oxygen ambient (900 K, 7.0×10^{-8} mbar O_2) on that oxygen structure was applied.

A good film shows a hexagonal LEED (low energy electron diffraction) pattern [3,4] (Fig. 1B) whereas the Mo substrate has a rectangular unit cell [20] (Fig. 1A). The hydrophobicity of the film depends distinctly on the film quality [14]. Therefore, water TPD can be used as an analytical technique (see Ref. [14] for details). Defected films are hydrophilic whereas good 2D silica films are hydrophobic [14]. Fig. 1C depicts water TPD results typical of our samples. Starting well below saturation exposures, the leading edges of the water TPD curves line up, which is indicative of zeroth-order desorption over the entire concentration range and a hydrophobic surface. Thus, our films have a low macroscopic defect density. In addition, AES was used to characterize the surfaces. Fig. 1D shows AES of the clean oxygen precursor surface as well as the silica film.

Note that according to structural models [21] the Si film is an atomically thin honeycomb-like 2D network of (distorted) corner-sharing SiO_4 tetrahedra [21]. Thus, silicatene is a 2D crystal and one of the inorganic analogs to graphene. A detailed literature list can be found e.g. in the supplemental to Ref. [14]. In the literature [22,23], the Mo(1 1 2)-p(1 \times 3)-O surface is described as a missing-row type reconstruction induced by oxygen, i.e., basically an 'oxide'-like surface. Mo(1 1 2) has a so-called ridge-and-trough structure with Mo surface atoms forming an array of rows.

3. Presentation of the results and discussion

3.1. Adsorption kinetics of benzene on 2D silica (silicatene)

3.1.1. Experimental results

Fig. 2 shows a set of benzene TPD curves for silicatene, as a function of benzene exposure, χ . The TPD data are somewhat unusual. At low exposures (see inset), the benzene TPD peak (α peak) shifts to lower temperature with increasing exposure. This would be consistent with repulsive lateral interactions (or different adsorption configurations), which is related to polarization effects of the substrate and/or repulsive hydrogen-hydrogen interactions [17]. Benzene by itself is non-polar. More importantly, while the α peak saturates (at $\sim 15 \text{ L}$), a second structure (c-peak) appears at 15–18 L exposure which continued to grow in intensity with exposure. In addition, the low temperature flanks of this c-peak approximately line up. Therefore, we assign this structure to the condensation of benzene (c-peak) and multilayer formation. Unusual is that the condensation peak temperature is somewhat larger (by 10 K) than the (final) monolayer α TPD peak temperature. Therefore, the binding strength of benzene in condensed films is larger than the binding to the silicatene surface. (The general shape of the TPD data was well reproducible, see Fig. S1 for a 2nd data set). Note that only TPD peaks characteristic of the fragmentation pattern of gaseous benzene were observed and no carbon residuals

were detected in AES after TPD runs (Fig. S2). Thus, the adsorption is molecular.

3.1.2. Discussion

Structurally similar TPD data have been seen in prior studies (see e.g. Refs. [16,24] and references therein). An example is, CD_3I (methyl iodine) adsorption on $\text{TiO}_2(1 1 0)$ [24]. Also in that case, a TPD peak that appears at larger exposures desorbs at a greater temperature than TPD structures which are evident at lower exposures. Thus, multilayer desorption temperatures are greater than monolayer desorption temperatures, as it also is the case in our study. Therefore, such unusual kinetics is indeed feasible. But, differences in details of the TPD data are apparent. Whereas, in our study only two TPD peaks are evident, for methyl iodine in total five TPD structures were reported. These methyl halide desorption structures were assigned to different adsorption sites and different molecular orientations of CD_3I on $\text{TiO}_2(1 1 0)$. Although the TPD data in these two studies show similarities, the mechanistic explanation is unlikely the same. For example, the surfaces and probe molecules have very different structures.

What causes this unusual kinetics? What is the origin of our TPD peaks? It is known from several studies that clean, well-ordered, and crystalline silica thin films are hydrophobic (for water adsorption) [14]. Thus, in the sub-monolayer adsorption regime water forms clusters due to non-wetting (hydrophobic) interactions with the surface. It appears plausible that other adsorbates also form clusters rather than a perfect 2D layer. Therefore, the benzene substrate interaction will be a rather weak physisorption (weak adsorbate-surface interaction). We assign desorption from this not perfectly uniform sub-monolayer to our α TPD peak (low exposure, low temperature TPD peak). Extending the benzene exposure further results in forming a multilayer which is assigned to the c TPD peak (large exposure, larger temperature TPD peak). Multilayers of benzene will be dominated by induced dipole-dipole interactions (adsorbate-adsorbate interactions). The adsorbate-adsorbate interactions (c TPD peak) are stronger than adsorbate-substrate (α TDS peak) interactions, which is a plausible result for non-wetting surfaces. Note, however, that the difference in desorption temperatures of the α and c peaks amounts to only 10 K (~ 1 kJ/mol). Due to the probably non-wetting adsorption of benzene ("hydrophobic" interaction) a porous benzene layer would form. Note that surface defects and functional groups on silica can result in hydrophilic surfaces [14]. For example, benzene adsorption on polycrystalline silica wafer follows standard kinetics of molecular adsorption (see Fig. S7 in Ref. [25], here the c-peak is at lower temperature than the α peak). These results also would suggest that the hydrophobicity of the surface not only affects the mono-layer adsorption structure, but also the molecular structure (growth mode) of the multilayer. In an earlier HREELS study [17], perfect layer by layer growth of benzene on silicatene was assumed. Also in this π - π stacking model strong benzene-benzene interactions are predicted, but a more disordered growth we proposed also would result in similar π - π attractive electrostatic interactions. A perfect layer-by-layer growth [17] would not explain the differences seen for polycrystalline and crystalline silica surfaces. Unfortunately, a direct observation of benzene's growth mode on silicatene is currently not available.

Also for other surfaces an unusual sequence of TPD peaks was seen for benzene (see e.g. Ref. [16] for $\text{MgO}(1 0 0)/\text{Mo}(1 0 0)$ and references therein). One interpretation is a coverage dependent geometric arrangement of benzene at the surface. At some concentration benzene adsorbs tilted with respect to the surface plane which would certainly affect binding energies and TPD peak positions. This mixed tilted and flat adsorption of benzene would result in a disordered multilayer, as also suggested here.

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