



Full Length Article

Thermal desorption and stability of cobalt phthalocyanine on Ag(100)



Agata Sabik*, Franciszek Gołek, Grażyna Antczak

Institute of Experimental Physics, Faculty of Physics and Astronomy, University of Wrocław, 50-204, Poland

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ABSTRACT

By performing work function change (ΔWF) measurements, we characterized thermal stability and desorption of cobalt phthalocyanine (CoPc) molecules on the Ag(100) surface from sub-monolayer to multilayer coverages. Based on the temperature dependence of the ΔWF we were able to determine the desorption temperature from multilayer. Obtained dependences of ΔWF and a low-energy electron reflectivity (R) for sub- and monolayer reveal that layers with contact with Ag(100) have higher thermal stability and their desorption is accompanied by decomposition of CoPc molecule. Exploring the time evolutions of the ΔWF at various temperatures allowed us to establish effective activation energies and effective frequency prefactors for processes occurring at various temperatures. The effective activation energies remain almost the same, from sub-monolayer to multilayer (2.97 eV – 2.62 eV), whereas the frequency prefactors vary from 10^{13} s^{-1} (monolayer) to 10^{24} s^{-1} (multilayer). For multilayer only desorption occurs, whereas for layers in contact with reactive Ag(100) surface (monolayer) the decomposition occurs at the same temperature range as desorption. Low-energy electron diffraction was used to describe CoPc molecular arrangements. To the best of our knowledge, we are the first who have observed $(5 \times 5)R \pm 37^\circ$ structure for CoPc on Ag(100).

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1. Introduction

Among the variety of organic molecules, metal phthalocyanines (MPcs), i.e. macrocyclic coordinative compounds, exhibit a remarkable chemical and thermal stability simultaneously with the interesting (opto-)electronic properties that could be tuned e.g. by changing the central metal atom [1]. For these reasons, MPcs are, on the one hand, the promising candidates for molecular electronic devices, on the other hand, model systems for both experimental and theoretical investigations. In the case of cobalt phthalocyanine (CoPc), application studies were performed with respect to spintronics [2,3] or gas sensors [4]. Interestingly, MPcs form ordered layers on various metal surfaces e.g. aluminium, gold or silver. Recently, a lot of efforts have been made to understand their adsorption and thin film growth on the monocrystalline substrates [5,6]. The electronic and structural properties of CoPc-Ag interface have been investigated by various surface science techniques, such as photoelectron spectroscopy [7–11], scanning tunnelling microscopy (STM) [11–13] or low-energy electron diffraction (LEED) [9,10,13]. The CoPc adsorption on Ag(100) or Ag(111) results in non-trivial charge transfer. The charge donation

to the molecule is localized and involves mainly molecular orbitals associated with the central cobalt atom [7–12]. An additional feature that occurs is charge back-donation which is associated with the rehybridization of π electrons delocalized over the molecular ligand with silver substrate [11].

Thermal desorption is a central process in understanding thermal stability of functional materials on the surfaces. Most studies and procedures concerning thermal desorption concentrated on the desorption of small species. The complex nature of molecules frequently complicates the description of the process, e.g. by the activation of various degrees of freedom during annealing. The thermal desorption of the molecular layer often competes with the dissociation of the molecules [14]. Despite the technological importance of macrocyclic organic molecules, their thermal desorption was rarely examined. Detailed temperature-programmed desorption (TPD) studies combined with comprehensive molecular dynamics analyses were carried out for 1.0 ML of linear hydrocarbons on various surfaces [15–24]. The authors found that the activation energies and frequency prefactors increase with chain length. Similar correlation between activation energy and chain length was reported for polyethers on graphite [25]. Additionally it was shown that the presence of terminal double bonds in hydrocarbons increases the desorption activation energy [18]. The correlation of the multilayer desorption activation energies and frequency prefactors with number of carbon atoms in the

* Corresponding author.

E-mail address: agata.sabik@uwr.edu.pl (A. Sabik).

Table 1
Parameters of thermal desorption for polyaromatic hydrocarbons [33]. E- activation energy, ν - frequency prefactor.

System	Experimental Technique	1 ML	
		E, eV(T, K)	ν , s ⁻¹
Benzene/HOPG	TPD(0.7 K/s)	0.50 ± 0.08(151)	1 × 10 ^{16±3}
Naphthalene/HOPG	TPD(1.0 K/s)	0.8 ± 0.1(235)	5 × 10 ^{16±2}
Coronene/HOPG	TPD(2.0 K/s)	1.3 ± 0.2(390)	2 × 10 ^{16±2}
Ovalene/HOPG	TPD(2.0 K/s)	2.2 ± 0.2(490)	5 × 10 ^{21±3}

organic molecule was observed also for cyclic molecules (e.g. para-quaterphenyl, para-sexiphenyl etc.) [14,26,27]. The monolayer desorption of cyclic organic molecules is frequently accompanied by dehydrogenation/cyclodimerization of the molecules [14]. For multilayer desorption of hexaazatriphenylene-hexacarbonitrile (HATCN) from gold [28] and silver [29] (111) surfaces authors do not detect dependence of desorption parameters on the type of the surface. For desorption of monolayer of rubicene, indigo and quinacridone molecules from SiO₂ and carbon covered SiO₂ surfaces [14,30–32] authors found that molecules decompose during the desorption from those reactive surfaces [14]. From those studies there are clear that both desorption activation energies and frequency prefactors depend on the number of carbon atoms in organic molecule and their contact with reactive surface frequently cause decomposition of the molecules. Dependence of monolayer desorption parameters on the size of the polyaromatic hydrocarbons adsorbed on unreactive HOPG is presented in Table 1 [33]. The dependence of the desorption activation energy (from 0.5 eV for benzene to 2.2 eV for ovalene) with number of carbon atoms in the molecule is clear from Table 1. The frequency prefactor also increase from 10¹⁴ s⁻¹ for benzene to 10²¹ s⁻¹ for ovalene [33]. The CoPc molecule, investigated in this paper, is composed of 32 carbon, (similar as ovalene), one cobalt, eight nitrogen and 16 hydrogen atoms. For such size of molecule, based on study reported in Ref [33] we expect prefactor, at least, in the range of 10²¹ s⁻¹ and activation energy in the range of 2–3 eV. Additionally, CoPc in our studies is adsorbed on more reactive Ag(100) surface then HOPG, what makes the decomposition of the molecule very likely to happen.

In Table 2 we present desorption parameters available for large organic molecules, such as 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) [34], MPcs [35–41] or oligopyridine (2,4'-BTP) [42]. For multilayer desorption the values of activation energy are around 2.3 eV. There is no clear dependence of activation energy on the type of surface from which molecules are desorbed. In most available studies the frequency prefactor was assumed to be in the range of 10¹⁸ s⁻¹. Such assumed frequency prefactor slightly influences determined value of an activation energy. The multilayer desorption proceeds at temperature range 480–600 K. Determined temperature depends on the heating rate used. The first layer, owing to the interaction with the substrate, is bonded more strongly than further overlayers of the material. For desorption of monolayer the type of surface is an important factor, since frequently, large molecules in contact with reactive surfaces undergo decomposition in the same temperature range as desorption [35,36,38]. After desorption of CuPc molecules from monolayer adsorbed on Cu(100), the surface does not come back to clean state, and some adsorbed fragments of CuPc remain on the surface [35]. Snezhkova et al. [36] reported a partial desorption of 1.0 ML of FePc from Cu(111) above 593 K and provided evidence for the fragmentation of FePc molecules during the desorption [36]. Annealing leads to partial dehydrogenation, polymerization of the benzene groups, and creation of dendrite-like chains from FePc on Cu(111) [36] and CuPc on Ag(111) [37]. Manandbar et al. [37] observed dendrite-like chains from CuPc after partial desorption of monolayer at 780 K from Ag(111). Thussing and Jakob

[38] reported partial dissociation of CuPc molecules during the desorption of 1.0 ML from Ag(111) surface with Cu atoms staying on the surface and the rest of molecule desorbed in segments of ¼ Pc [38]. The temperature-programmed X-ray photoemission spectroscopy (TP-XPS) was applied to investigate the influence of the central metal atom in MPc (M = Co, Cu, Fe) upon the molecular adsorption and thermal stability on Ir(111) covered with graphene (graphene/Ir(111)). In the case of FePc, the study was extended to highly oriented pyrolytic graphite (HOPG) and Au(110) substrates [39,40]. The authors showed that, on the surface of graphene/Ir(111), all MPcs exhibit layer-by-layer growth of flat lying molecules. For CuPc desorbed from graphene/Ir(111) their data are consistent with desorption of intact molecules, whereas for CoPc and FePc they observe thermal desorption above 820 K, and decomposition of the molecule above 900 K. Clearly Au(110), HOPG and graphene/Ir(111) are less reactive surfaces than Cu(100), Cu(111) or Ag(111), which is visible in tendency of decomposition of Pc molecules during desorption. The desorption activation energies of Pc monolayer from non-reactive surfaces vary from 2.6 eV for CuPc desorbed from graphene/Ir(111) [39] to >3.2 eV for Co- and FePc desorbed from Au(110) [41]. Desorption activation energies clearly depend on the type of central atom of Pc molecule. For reactive surfaces competition between different types of decomposition (dehydrogenation, dissociation, etc.) and thermal desorption is observed.

So far we explored the influence of size of the molecule and possibility of decomposition on the desorption characteristics. Another factors which can influence desorption parameters are the molecule-molecule interactions and the initial molecular state (e.g. mobile/immobile, flat-laying/upright standing) [42]. Roos et al. studied the thermal desorption of 2,4'-BTP from HOPG by TPD and STM [42]. The molecules lie flat on the surface and are rotationally/translationally mobile in the sub-monolayer, but remain immobile and upright standing in the multilayer [42]. The activation energy for the desorption varies from 2.69 eV to 2.48 eV, from sub-monolayer to multilayer, respectively. The frequency prefactors varies from 10¹⁵ s⁻¹ for sub-monolayers to 10²⁴ s⁻¹ for multilayers. According to authors, such prefactors result from different initial molecular states for desorption [42].

Recently, we have shown that work function change (ΔWF) measurements by means of the retarding field diode method, known also as Anderson method, are suitable for studying MPc-metal interfaces and provide insight into the low-energy electron reflectivity (R) of the sample [43,44]. In this work, we have concentrated on the study of thermal stability and the desorption of CoPcs on the Ag(100) surface from the sub-monolayer to the multilayer regime. LEED investigations were carried out to probe structural properties of CoPc layer before and after the thermal treatment of the sample.

2. Experiment

The experiments were carried out in an ultra-high vacuum system with a base pressure in the range 1 × 10⁻¹⁰ mbar. We probed the ΔWF and R , with accuracy ±0.01 eV and ±1%, respectively, implementing the retarding field diode method with the e-gun setting described in [43]. In the e-gun all electrodes have been at positive potentials with respect to the ground. The electrons can escape from the e-gun only when the Ag(100) sample is in front of e-gun (around 2 cm) at high enough positive potential. The beam diameter used is around 1.5 mm. The total current needed to determine reflectivity is measured with voltage of +180 V applied to the sample. For such voltage it was assumed that all electrons from the e-gun reach the sample. Further increase of voltage does not change the current detected from the sample. For ΔWF and R the shift

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