The catalytic decomposition of silver coated cinnamyl alcohol during water exposure and the formation of silver nanoparticles

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ABSTRACT

Metastable Induced Electron Spectroscopy, Ultraviolet Photoelectron Spectroscopy (He I), X-ray Photoelectron Spectroscopy, and Quadrupole Mass Spectrometry are employed to study the interaction of water with Ag nanoparticles on cinnamyl alcohol films. The films have been prepared on Au(111) substrates by thermal evaporation. The water adsorption does not result in any chemical interaction with the silver nanoparticles at all, but the cinnamyl alcohol changes its chemical structure significantly. While water molecules induce a reduction of the organic groups, the film thickness seems to decrease. Thus, a decomposition of the cinnamyl alcohol films is proposed. Since no effects are observed during water interaction with pure cinnamyl alcohol films at all, a catalytic reaction appears to take place. No decomposition is found for cinnamyl alcohol adsorbed on a closed silver film, indicating that Ag nanoparticles are required for this catalytical decomposition. The MIES and UPS spectra indicate the existence of a closed metallic film directly after silver adsorption on cinnamyl alcohol, while they suggest the presence of silver nanoparticles after the exposure to water. The formation of silver nanoparticles therefore seems to happen concurrently to the catalytic decomposition of cinnamyl alcohol.

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1. Introduction

The adsorption of silver on various organic substrates is of great technological interest for diverse applications, such as corrosion protection, RF shielding, reflective coating, and many more. Over the last 20 years, especially silver nanoparticle coatings received drastically increased attention, due to their additional functions. For instance, silver nanoparticles are known to enhance the efficiency of organic light emitting devices [1], whereas silver films on TiO$_2$ nanoparticles enhance photocatalytic reaction rates [2,3]. One of the most common applications of silver particles is the functionalization of surfaces because of their antibacterial properties [4,5]. This may be useful especially on wood surfaces to preserve them from decay through attack of microorganisms by other means than lacquering or impregnation.

The presented investigation is part of a research project concerning the interaction of metals (Ag, Ti) with wood surfaces. Furthermore, the reactions with atmospheric gasses as well as typical volatile organic compounds are investigated, with perspective to future applications.

To understand the interaction behavior of Ag with wood surfaces, several molecular precursors are used to represent the organic groups of lignin and cellulose. For lignin, these precursors are sinapyl alcohol and coniferyl alcohol as two main monolignols from which lignin is synthesized in plants. Since these two are derived from cinnamyl alcohol (also known as 3-phenylprop-2-en-1-ol, the skeletal formula is included in Fig. 6), we also used this less complex molecule for our investigations [6–8]. The effect of plasma treatment of the presented molecules has been studied previously [9].

Moreover, cinnamyl alcohol is an ingredient in various cosmetic products as perfumes, deodorants or oils [10]. Unfortunately, many people experience allergic reactions through contact with this compound [11,12]. Thus, the interaction with different catalysts that may be able to reduce this allergen when added to cosmetic products is of great technological interest.

This study extends our recent investigations on the adsorption of silver on cinnamyl alcohol, which have been found to form chemically inert nanoparticles [13]. For all applications given above, the interaction of the adsorbed silver in combination with the underlying cinnamyl alcohol is of value. During these investigations, Atomic Force Microscopy (AFM) measurements were carried out ex vacuo. Hereby, the interaction of the Ag covered cinnamyl alcohol film with the components of atmospheric air, especially with water could not be avoided. Further investigation of this interaction is required.

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This paper is organized in the following way:

At first, the interaction of water vapor with a pure cinnamyl alcohol film (Cinnamyl alcohol/Au(111)) was examined (see Section 3.1). It is the intention to investigate possible interactions.

Then, the interaction of cinnamyl alcohol with water on top of a closed silver film (Cinnamyl alcohol/Ag) is presented (see Section 3.2).

Finally, the cinnamyl alcohol film was exposed to silver and to water subsequently (see Section 3.3).

2. Experimental details

An ultra high vacuum (UHV) apparatus with a base pressure of 5×10^{-11} hPa, which has been described in detail previously [14–18], is used to carry out the experiments. All measurements were performed at room temperature.

Electron spectroscopy is performed using a hemispherical analyzer (Leybold EA 10) in combination with a source for metastable helium atoms (mainly He* $^3S_1$) and ultraviolet photons (HeI line). A commercial non-monochromatic X-ray source (Fisons XR3E2-324) is utilized for XPS.

During XPS, X-ray photons hit the surface under an angle of 80° to the surface normal, illuminating a spot of several mm in diameter. For all measurements presented here, the Al K_α line with a photon energy of 1486.6 eV is used. Electrons are recorded by the hemispherical analyzer with an energy resolution of 1.1 eV for detail spectra and 2.2 eV for survey spectra, respectively, under an angle of 10° to the surface normal. All XPS spectra are displayed as a function of binding energy with respect to the Fermi level.

For quantitative XPS analysis, photoelectron peak areas are calculated via mathematical fitting with Gauss-type profiles using OriginPro 7G including the PFM fitting module, which applies Levenberg–Marquardt algorithms to achieve the best agreement between experimental data and fit. To optimize our fitting procedure, Voigt profiles have been applied to various oxidic and metallic systems but for most systems the Lorentzian contribution converges to 0. Therefore all XPS peaks are fitted with Gaussian shapes. Photoelectric cross sections as calculated by Scofield [19] with asymmetry factors after Powell and Jablonski [20], taking into account asymmetry parameters after Reilman et. al. [21] and Jablonski [22] as well as inelastic mean free paths from the NIST database [23] (using the database of Tanuma, Powell and Penn for elementary contributions and the TPP-2M equation for molecules) and the energy dependent transmission function of our hemispherical analyzer are taken into account when calculating the stoichiometries.

MIES and UPS are performed applying a cold cathode gas discharge via a two-stage pumping system. A time-of-flight technique is employed to separate electrons emitted by He* (MIES) from those caused by HeI (UPS) interaction with the surface. The combined He*/HeI beam strikes the sample surface under an angle of 45° to the surface normal and illuminates a spot of approximately 2 mm in diameter. The spectra are recorded simultaneously by the hemispherical analyzer with an energy resolution of 220 meV under normal emission within 140 s.

MIES is an extremely surface sensitive technique probing solely the outermost layer of the sample, because the He* atoms interact with the surface typically 0.3 to 0.5 nm in front of it. This may occur via a number of different mechanisms depending on surface electronic structure and work function, as is described in detail elsewhere [24–26]. Only the processes relevant for the spectra presented here shall be discussed shortly:

During Auger Deexcitation (AD), an electron from the sample fills the 1s orbital of the impinging He*. Simultaneously, the He 2s electron is emitted carrying the excess energy. The resulting spectra reflect the Surface Density of States (SDOS) directly. AD-MIES and UPS can be compared and allow a distinction between surface and bulk effects. AD takes place for all organic systems shown here.

On pure and partly oxidized metal surfaces with a work function beyond about 3.5 eV, like silver surfaces, Auger Neutralization (AN) occurs as long as the surface shows metallic behavior. As a result the impinging He* atom is ionized in the vicinity of the surface by the resonant transfer (RT) of its 2s electron into unoccupied metallic surface states. Afterwards, the remaining He$^+$ ion is neutralized by a surface electron thus emitting a second surface electron carrying the excess energy. The observed electron spectrum is rather structureless and originates from a self convolution of the surface density of states (SDOS).

All MIES and UPS spectra are displayed as a function of the electron binding energy with respect to the Fermi level, thus being able to compare MIES and UPS spectra more easily. Obviously, the binding energy scale is only valid for the AD process. Nevertheless, all spectra including structures originating in the AN process have also been displayed in this particular manner. The surface work function can be determined from the high binding energy onset of the MIES or the UPS spectra with an accuracy of ±0.1 eV.

The experiments on cinnamyl alcohol were carried out on inert Au(111) substrates. These substrates were cleaned prior to the experiments by Ar$^+$ sputtering at 4 kV for 20 min and subsequent heating up to 1000 K. The Ag reference sample was prepared by adsorption on a Si(100) substrate, which was preliminary cleaned by flashing up to 1400 K.

Silver (Sigma-Aldrich Co., 99%) was evaporated with a commercial UHV evaporator (Omicron EFM3) onto the samples. On a clean Si(100) target metallic silver films grow at a rate of 0.23 nm min^{-1} at room temperature when evaporated with an Ag$^+$ ion flux of 1 μA at the fluxmeter of the EFM3. This flux is a degree for the number of Ag atoms moving towards the sample per second. The film growth rate for Ag has been estimated from the Si 2p peak attenuation in XPS, respectively, while the growth mode has been verified to be of the Frank-van der Merwe-type via AFM measurements. During most of the experiments, silver adsorption has been carried out at dosages of 9 monolayer equivalents (MLE) as compared to the growth rate on silicon (c.f. [13]).

Cinnamyl alcohol (Sigma-Aldrich Co., >97.0%) was evaporated in a preparation chamber (base pressure <10^{-9} hPa) using a temperature controlled evaporator (Kentax TCE-BS). The preparation chamber is directly connected to the UHV chamber. During the experiments, cinnamyl alcohol has been evaporated at 40 °C for 5 min, leading to a film with a thickness of about 1.8 nm [14].

Deionized water is offered via backfilling the chamber using a bakeable leak valve. The gas line is evacuated and can be heated in order to ensure cleanness. For all gas exposures, dosages have been given in terms of Langmuir, where 1 L = 1.33×10^{-6} hPa × 1 s. A quadrupole mass spectrometer (Balzers QMG311 equipped with a Balzers QMA 140) is used to monitor the partial pressure of the reactive gasses simultaneously during all measurements. Additionally, a differentially pumped quadrupole mass spectrometer system (Balzers QMG 422) with a linear motion feed for positioning its faceplate right in front of the sample is used for detection of possible reaction products during the decomposition process. Large amounts of water have been offered in a separate HV chamber, which is directly connected to the UHV apparatus and its gas inlet system.

3. Results

3.1. Interaction of water with cinnamyl alcohol

Fig. 1 shows MIES (top left) and UPS (HeI) spectra (top right), as well as XPS spectra from the C 1s (bottom left) and the O 1s (bottom right) region of a 1.8 nm cinnamyl alcohol film on Au(111) before (black lines) and after (blue lines) the exposure to 1415 L of water. All spectra are displayed as electron count rate versus the electron binding energy. XPS spectra have the low binding energy side to the left with increasing binding energy to the right side, whereas MIES and UPS spectra have the high binding energy side to the left with decreasing binding energy to the right side.