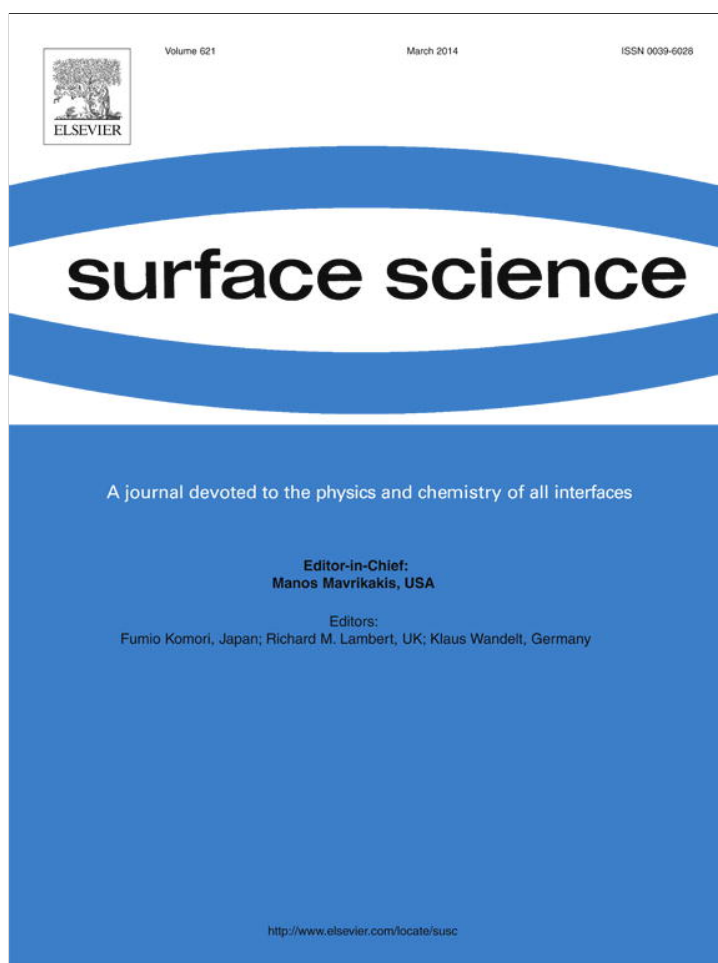


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

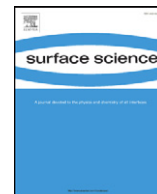
In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/authorsrights>



Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

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

S. Dahle^{a,c}, O. Höfft^b, W. Viöl^{c,d}, W. Maus-Friedrichs^{a,e,*}^a Institut für Energieforschung und Physikalische Technologien, Technische Universität Clausthal, Leibnizstrasse 4, 38678 Clausthal-Zellerfeld, Germany^b Institut für Elektrochemie, Technische Universität Clausthal, Arnold-Sommerfeld-Str. 6, 38678 Clausthal-Zellerfeld, Germany^c Hochschule für Angewandte Wissenschaft und Kunst, Fakultät für Naturwissenschaften und Technik, Von-Ossietzky-Straße 99, 37085 Göttingen, Germany^d Anwendungszentrum für Plasma und Photonik, Fraunhofer IST, Von-Ossietzky-Str. 99, 37085 Göttingen, Germany^e Clausthaler Zentrum für Materialtechnik, Technische Universität Clausthal, Leibnizstrasse 4, 38678 Clausthal-Zellerfeld, Germany

ARTICLE INFO

Article history:

Received 29 November 2012

Accepted 11 November 2013

Available online 22 November 2013

Keywords:

Catalytic decomposition

Cinnamyl alcohol

Silver nanoparticle

Metastable Induced Electron Spectroscopy

Ultraviolet Photoelectron Spectroscopy

X-Ray Photoelectron Spectroscopy

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.

© 2013 Elsevier B.V. All rights reserved.

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 TiO₂ 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.

* Corresponding author at: Institut für Energieforschung und Physikalische Technologien, Technische Universität Clausthal, Leibnizstrasse 4, 38678 Clausthal-Zellerfeld, Germany.

E-mail address: w.maus-friedrichs@pe.tu-clausthal.de (W. Maus-Friedrichs).

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 $\text{He}^* \text{ } ^3\text{S}_1$) and ultraviolet photons (Hel 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 Hel (UPS) interaction with the surface. The combined He^*/Hel 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 $1 \mu\text{A}$ 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 $1 \text{ L} = 1.33 \times 10^{-6} \text{ hPa} \times 1 \text{ s}$. 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 (Hel) 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.

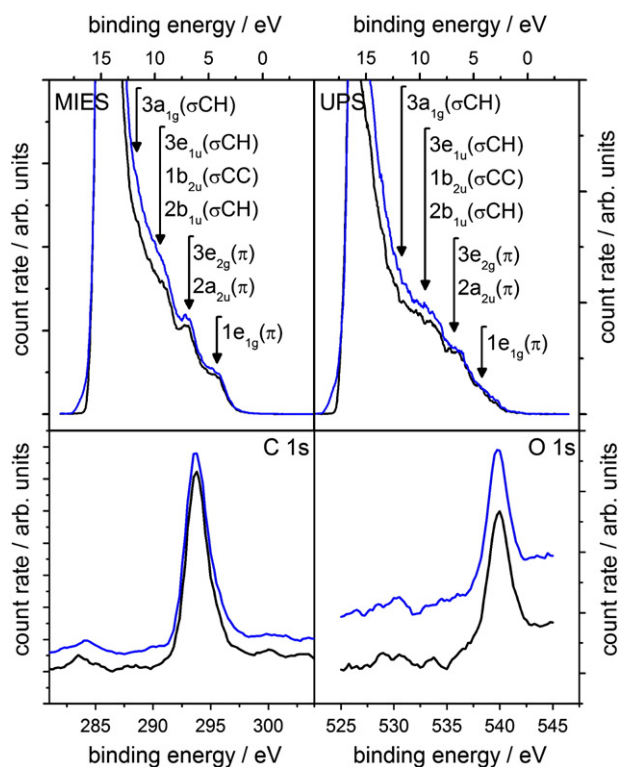


Fig. 1. MIES (top left), UPS (top right), XPS (Al K_{α}) C 1s (bottom left) and O 1s (bottom right) spectra of a 1.8 nm cinnamyl alcohol film on Au(111) before (black lines) and after (blue lines) in-situ exposure to 1415 L of water.

The MIES and UPS spectra yield a small increase of the secondary electron peak while the valence structures of the cinnamyl alcohol film remain unchanged. These structures include the $1e_{1g}(\pi)$ orbital around 4.4 eV (a), the $3e_{2g}(\sigma\text{CH})$ and $1a_{2u}(\pi)$ orbitals at 7.0 eV (b), the $3e_{1u}(\sigma\text{CH})$, $1b_{2u}(\sigma\text{CC})$ and $2b_{1u}(\sigma\text{CH})$ orbitals between 8.5 and 10.5 eV (c), and the $3a_{1g}(\sigma\text{CH})$ orbital at 11.7 eV (d) [9], while the C 2s peaks at 13.7 eV and 17.3 eV vanish within or beyond the secondary electron peak [8]. In XPS the increasing contribution of secondary electrons gives rise to a growing background, while the C 1s and O 1s peaks remain unchanged. Since no water induced features, like for example OH groups appear in MIES, their coverage must be negligible.

The exposure of a cinnamyl alcohol film to about 15 hPa of water for 30 min (corresponding to $2 \cdot 10^{10}$ L) has been carried out furthermore, but will not be shown here. As for the small water exposure, the spectra do neither show any change in shape nor in the intensity of the electronic structure of the cinnamyl alcohol nor any change of the work function. All XPS fit results were similar to those obtained in our previous work [13] and are therefore not shown here.

3.2. Interaction of water and cinnamyl alcohol with a closed silver film

During the interaction of cinnamyl alcohol with water no evidence for any decomposition was found even for dosages up to $2 \cdot 10^{10}$ L. Therefore in this second step, the interaction of cinnamyl alcohol with silver was investigated, again in the presence of water vapor. Thus, we evaporated cinnamyl alcohol onto a closed layer of silver and exposed this system to water. For the interpretation, these results are opposed to reference spectra of the closed silver film as prepared as well as a cinnamyl alcohol film on Au(111), which is known to show no chemical interaction.

Fig. 2 depicts MIES (top left), UPS (top right), XPS C 1s (bottom left) and XPS O 1s (bottom right) results for a 14 nm silver film grown on a

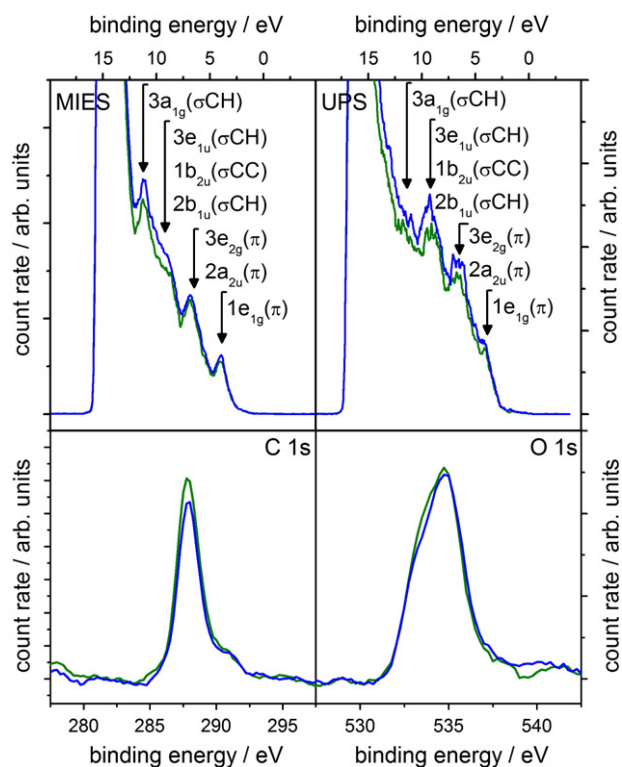


Fig. 2. MIES (top left), UPS (top right), XPS (Al K_{α}) C 1s (bottom left) and O 1s (bottom right) spectra of a 14 nm silver film on Si(100) after the adsorption of 1.8 nm of cinnamyl alcohol (green lines) and after subsequent exposure to 350 L of water (blue lines).

Si(100) wafer after the adsorption of 1.8 nm of cinnamyl alcohol (green lines) as well as after the subsequent exposure to 350 L of water. The MIES (top left) and UPS spectra (top right) of the cinnamyl alcohol film on silver show the same structures as discussed before in Section 3.1. The slightly different shape of the features may be due to a changed adsorption geometry on the roughly structured Ag film compared to the Au(111) crystal face. The intensity of the σCC and σCH peaks is slightly increased, indicating an adsorption with the propanol chain sticking out of the surface in contrast to a most probably flat adsorption on the Au(111). Furthermore, the cinnamyl alcohol molecules should be rather mobile, since the experiment temperatures were close to the melting point. However, the polycrystalline silver film on silicon should exhibit a rather large amount of defects, which can act as traps for the adsorbed molecules. Thus, the defects decrease the effective mobility of the cinnamyl alcohol molecules on the surface, leading to much sharper structures in MIES and UPS. After the exposure to water, the background increases and a small shoulder around 11 eV indicates some water remaining on the surface. Nevertheless, the cinnamyl alcohol structures remain unchanged after the exposure to water. This means, that no interaction between the cinnamyl alcohol adsorbed on a closed silver film and water takes place at all. The XPS results show the same structures as in Section 3.1. The O 1s intensity slightly increases in comparison to the C 1s intensity, indicating some water remaining within the film. However, the C 1s structure corresponding to cinnamyl alcohol does not change, which means that again no reactions between cinnamyl alcohol and water take place.

3.3. Interaction of water with Ag coated cinnamyl alcohol

The experiments on the interaction of water with cinnamyl alcohol (Section 3.1) and the interaction of cinnamyl alcohol with the closed silver film in the presence of water vapor (Section 3.2) do not show

any decomposition effects. In the following, we exposed silver to the cinnamyl alcohol film to study its interaction with water.

Fig. 3 shows MIES (left) and UPS spectra (right) of a 1.8 nm film of cinnamyl alcohol adsorbed on a cleaned Au(111) substrate (black lines), 9 MLE silver adsorbed onto the cinnamyl alcohol (red lines) and the latter after subsequent in-situ exposure to 1040 L of water (blue lines), as well as a silver reference film from [13] (green lines). The spectra of the cinnamyl alcohol film reveals exactly the characteristic peaks already described in Section 3.1. After silver adsorption the MIES spectrum consists of the Ag 4d AN structures with one broad feature between 2 eV and 6 eV due to the AN process involving two electrons from the 5s orbital, and another feature between 5 eV and 11 eV caused by the AN process including electrons arising from Ag 4d and 5s [27]. The presence of strong AN features is clearly visible from the shoulder of the AN 5s_{5s} orbital around 3 eV, where no structure of the cinnamyl alcohol could be found. The UPS spectrum consists of one main Ag 4d doublet feature. Nevertheless, there is still some intensity from the cinnamyl alcohol peaks remaining besides the silver features in both spectra, UPS as well as MIES. Therefore, most of the silver is present at the surface of the cinnamyl alcohol layer, but the silver coating does not form a completely closed layer. Also, a diffusion of some part of the silver into the cinnamyl alcohol film cannot be excluded. After the subsequent exposure to 1040 L of water, the background as well as the AN structures in the MIES spectrum decrease, giving rise to a surplus peak at 4.6 eV denoted as Ag*₍₁₎ which matches quite well with the lower binding energy Ag 4d peak in the UPS spectra. This surplus peak supports the assumption of a structural change on the surface for its indication of the quite unusual silver AD MIES process. At the beginning, the closed silver layer allows for the metastable helium atom to resonantly lose its 2s electron and become neutralized by the AN process afterwards. Obviously, this preliminary resonant transfer process is inhibited when the agglomerating silver atoms form isolated nanoparticles on top of the insulating cinnamyl alcohol film. Thus, the AD process becomes more likely. There again, the low binding energy Ag 4d peak in UPS decreases together with the background signal, while the high binding energy Ag 4d peak at 6.0 eV appears to be more dominant (marked as Ag*₍₂₎). According to the literature, this is a typical indication for nanoparticles [28–30].

Fig. 4 depicts the XPS Au 4f (top left), C 1s (bottom left), O 1s (bottom right) and Ag 3d (top right) spectra of the 1.8 nm cinnamyl alcohol film on Au(111) as prepared (black lines and squares), after the adsorption of 9 MLE silver (red lines and triangles) and after subsequent in-situ exposure to 1040 L of water (blue lines and circles) corresponding to Fig. 3. The increasing intensity of the Au 4f doublet clearly indicates a

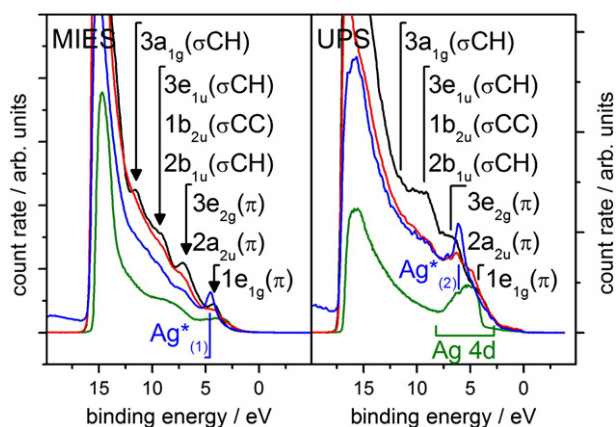


Fig. 3. MIES (left) and UPS (right) spectra of a 1.8 nm film of cinnamyl alcohol adsorbed on a cleaned Au(111) substrate (black lines), 9 MLE silver adsorbed onto the cinnamyl alcohol (red lines) and the latter after subsequent in-situ exposure to 1040 L of water (blue lines), as well as a silver reference film from [13] (green lines).

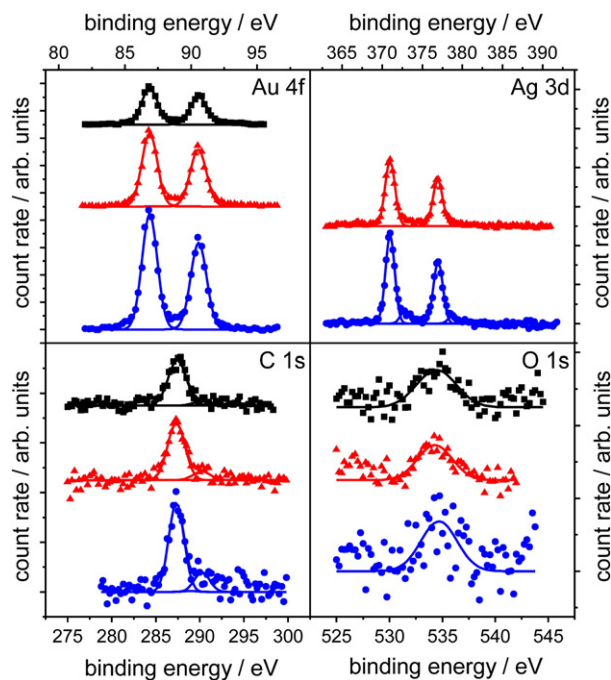


Fig. 4. XPS (AlK_α) Au 4f (top left), C 1s (bottom left), O 1s (bottom right) and Ag 3d (top right) spectra of a 1.8 nm film of cinnamyl alcohol on Au(111) as prepared (black lines and squares), after the adsorption of 9 MLE silver (red lines and triangles) and the latter after subsequent in-situ exposure to 1040 L of water (blue lines and circles).

decreasing overall film thickness on Ag adsorption and even more on the exposure to water. The Ag 3d structure after Ag adsorption resembles very well the results for a pure silver film, in both cases the under-ground correction was slightly insufficient between the two peaks. In contrast to that, the Ag 3d doublet clearly shows a second chemical state after water dosage at the high binding energy side of each peak. The intensities of the C 1s and O 1s structures increase during the Ag adsorption as well as during the water dosage. This is maybe due to an improved electrical conductance through the cinnamyl alcohol layer and thus a better charge compensation in the layer. On the one hand, a significantly charged sample would defocus the emitted photoelectrons during their travel towards the analyzer and thus lead to a decreasing overall intensity. On the other hand, some examples can be found within the literature, where metal–organic films exhibited anomalously large photoelectron mean free paths, which would also significantly influence the photoelectron peaks' intensities [31]. The Au substrate should not be influenced by these additional adsorbed layer, thus these findings indicate an increased C 1s intensity even on decreasing film thicknesses. The area fraction of the C 1s peak corresponding to oxidized carbon atoms, i.e. representing C=O and O–C–O bonds, increases during Ag adsorption and even more with the water exposure (see Table 1). This indicates some kind of ongoing oxidation mechanism, which could not be recognized during the measurements concerning cinnamyl alcohol on Au(111) as well as cinnamyl alcohol on a closed silver film.

Fig. 5 shows mass spectra from the differentially pumped QMS system measured during the water adsorption on 9 MLE silver coated 1.8 nm cinnamyl alcohol film (see Fig. 4). All possible reaction products were monitored during the exposure, but only those developing related to the reaction are shown. The top left diagram shows the spectra of the fragments of water, the bottom left diagram contains the spectra of ethanol and its fragments. Formaldehyde and its deprotonated fragments are displayed in the bottom right diagram, while the spectra of molecular oxygen, the methyl cation and small carbon-oxides are

Table 1
Summarized XPS results for 1040 L water on silver coated cinnamyl alcohol.

System	Figure	Peak	Correlation	Binding energy/eV	FWHM/eV	Relative intensity
Cinnamyl alcohol/Au(111)	4	C 1s	C–C, C–H	287.4	2.42	0.90
			C–O	289.0	2.42	0.01
			C=O, O–C–O	290.3	2.42	0.09
Ag/Cinn. alc. /Au(111)	4	O 1s	C–O–H	534.4	4.41	1.00
		C 1s	C–C, C–H	287.3	2.32	0.87
			C–O	288.9	2.32	0.00
1000 L H ₂ O/Ag/Cinn. alc./Au	4	O 1s	C–O–H	534.3	3.86	1.00
			C–O–H	534.7	4.00	1.00
		C 1s	C–C, C–H	287.3	2.06	0.81
			C–O	288.9	2.06	0.01
			C=O, O–C–O	290.2	2.06	0.18
			C–O–H	534.7	4.00	1.00

shown in the top right graph. The exposure to water at about 3.5×10^{-7} hPa was started about 120 s after the beginning of the QMS measurement and was controlled for its purity using the second QMS.

Even though the partial pressure of the water itself exceeded the chosen sensitivity range, the fragments OH, H₂, H and O resemble its partial pressure inside the differentially pumped system quite well. The exponential converging behavior may be caused by the small slit of about 2 mm between the spectrometers faceplate and the sample. Another factor may also be the uptake rate due to the surface processes. The slight decrease towards the end reflects the development of the partial pressure of water.

The spectra of the fragments of ethanol yield a maximum at about 1000 s, corresponding to 260 L and a significant decrease afterwards, indicating a possible induction period or a change of the conversion process. There against, the partial pressure of formaldehyde reaches its maximum at about 1500 s, corresponding to 390 L and stays approximately constant until the end of the gas dosage at 1040 L. In between these two, the partial pressure of ethanol has its maximum, even though a saddle point is visible around 1000 s, thus corresponding to the peak of its dehydrogenated species.

4. Discussion

The adsorption of water onto a cinnamyl alcohol film as presented in Section 3.1 shows no evidence for any interaction at all. Even an

exposure to $2 \cdot 10^{10}$ L (not shown) does not lead to any interaction. Thus, the degradation of cinnamyl alcohol being stored in water containing atmospheres, which is reported in literature [32], obviously happens on much larger timescales. Additionally, this excludes any decomposition of the cinnamyl alcohol due to the Au(111) substrate in the presence of water.

The timescale for this established degradation of cinnamyl alcohol is especially different from the dosages necessary for the interaction for the silver coated cinnamyl alcohol shown in Section 3.3. The decomposition observed during this experiment therefore must involve processes including the adsorbed silver. Ex-situ AFM measurements showed the formation of nanoparticles [13], which might behave differently compared to a closed silver film. These possible influences of the structure of the nanoparticles have to be excluded first to understand how the decomposition process works. Therefore, the results presented in Section 3.2 deal with cinnamyl alcohol adsorbed on a closed silver film. No significant differences were found between the spectra of cinnamyl alcohol on the Ag film before and after exposure to 350 L of water, which would have been sufficient for a significant decomposition as was shown in Section 3.3.

The investigations on the interaction of water vapor with silver coated cinnamyl alcohol films presented in Section 3.3 differed very significantly from those two discussed before. The overall film thickness of the cinnamyl alcohol and silver composite layer seems to increase considerably upon water dosage. The determination of this film thickness is

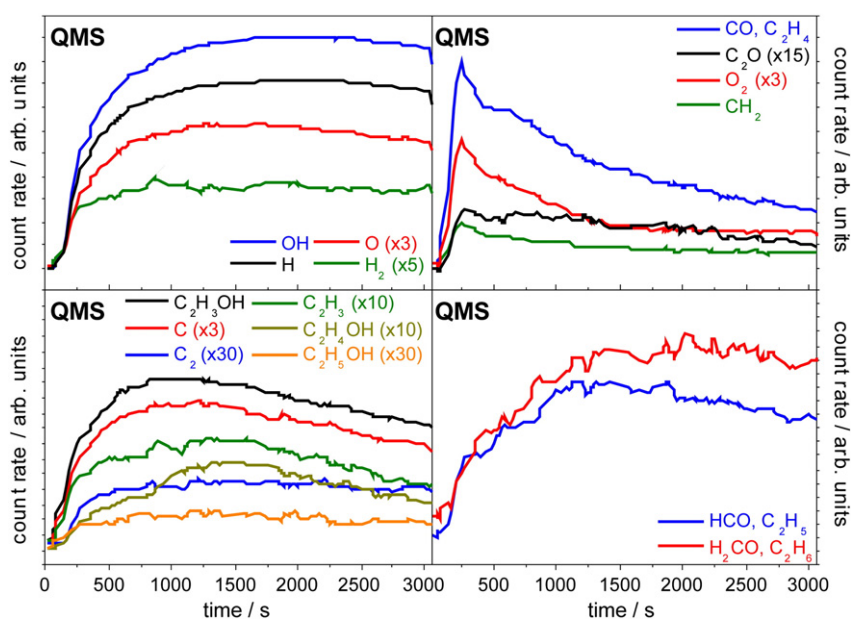


Fig. 5. QMS spectra of desorption species from 9 MLE silver adsorbed onto a 1.8 nm film of cinnamyl alcohol on Au(111) during in-situ exposure to 1040 L of water.

uncertain to some extent, since the evaluation was deduced for a substrate that is fully covered by a homogeneous film. In the presented case, the heterogeneous double layer system did not fulfill this condition and there might also be some diffusion of silver into the cinnamyl alcohol layer, which cannot be determined by the applied methods. Furthermore, it seems that the silver coated cinnamyl alcohol even went through a structural change upon water dosage. Thus, the film thickness calculation typically used for the interpretation of XPS spectra during adsorption experiments can only be used as a hint rather than an exact matter of fact.

The apparent decrease of the thickness of the cinnamyl alcohol film supports the results of the differentially pumped mass spectrometer, which showed a distinct amount of small hydrocarbon molecules being desorbed from the sample right from the beginning of the water dosage. The development of the partial pressures of the molecules seems to show two phases. During the first 1000 s of the exposure, mostly CO, C₂H₃OH and the like are desorbed. There again, the production rate for formaldehyde is maximal starting at 1500 s. The partial pressure of ethanol reached its maximum slightly before the partial pressure of formaldehyde, but a saddle point is found for ethanol corresponding to its dehydrogenated species. This development suggests a decomposition process with two distinct reaction pathways at different reaction rates.

The XPS results yield an oxidation of the carbon species in the silver coated cinnamyl alcohol film during the exposure to water. The Ag 3d structure clearly shows the appearance of a second peak at 1.9 eV higher binding energy compared to the metallic silver peak (see Fig. 5, Section 3.3), which vanishes during the exposure to $2 \cdot 10^{10}$ L of water. Thus, it is very likely that the surplus Ag 3d peak corresponds to some intermediate species being involved in the catalytic decomposition.

The MIES spectrum of the silver coated cinnamyl alcohol film after exposure to 1040 L of water shows a distinct feature which most certainly corresponds to Ag 4d via the AD process. This is most unlikely for silver surfaces due to its high work function of more than 3.5 eV, which causes a resonant transfer of the electron occupying the He 2s state during the atoms approach towards the sample's surface. Afterwards, the resulting He⁻ ion relaxes through the AN process as described in Section 2. The appearance of an AD peak representing silver states clearly shows that the resonant transfer must be hindered somehow.

It has been shown earlier by Stracke for Mg clusters on top of a MgO crystal surface that this kind of surface configuration leads to AD peaks in MIES, even though AN structures were expected for Mg [33]. When

the metastable helium atom approaches the surface under an angle of 45° to its normal, the MgO surface does not provide surface states which would allow for the resonant transfer of the He 2s electrons being the first step of the AN process. Therefore, the helium atoms reach the Mg clusters as metastable neutral atoms instead of being ionized before. Thus, these metallic clusters lead to an AD peak in MIES, whereas for a closed film the spectrum would only show AN structures.

The same reason might induce the AD peak for the adsorbed silver during water exposure. As found during AFM measurements earlier [13], silver nanoparticles are present when exposing the silver coated cinnamyl alcohol film to air. The formation of these nanoparticles during water dosage would be indicated by the observed AD peak, since the agglomerating silver would form clusters surrounded by insulating organic molecules. The MIES results therefore might suggest the formation of the nanoparticles during the exposure of the silver coated cinnamyl alcohol to water. Therefore, the process leading to this agglomeration of the silver atoms upon water dosage has to be discussed.

All XPS results of this section are summarized in Table 1. The description of an actual reaction pathway leading to a decomposition of the cinnamyl alcohol and the concurrent agglomeration of the silver atoms would be guesswork rather than reasonable deduction basing on the hitherto existing results. Therefore, it will not be discussed in further detail at this point. A future investigation on the determination of the exact reaction pathway will be carried out, employing Fourier-Transform Infrared Spectroscopy in an ultra high vacuum environment for direct observation of the reaction intermediates as well as some in-vacuo imaging techniques.

A schematic representation for each of the three described model systems is depicted in Fig. 6 to clarify the investigated interfaces and interactions.

5. Summary

The interaction of water with silver coated cinnamyl alcohol films was found to lead to a catalytic decomposition of the cinnamyl alcohol film. The silver nanoparticles found afterwards by means of AFM investigations [13] were proven to be essential for this process by excluding all other possible decomposition pathways. Neither on pure cinnamyl alcohol films nor on films adsorbed on a closed silver layer, any interaction could be observed. Furthermore, the spectroscopic results during the exposure of the silver coated cinnamyl alcohol film suggested the formation of silver nanoparticles concurrent to the water dosage.

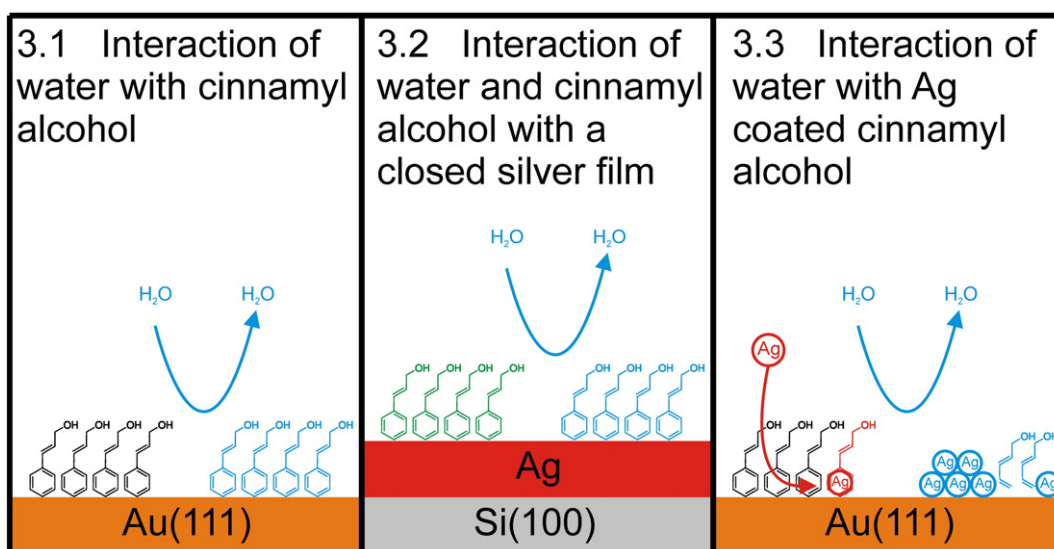


Fig. 6. Schematic representations of the investigated model systems.

The effective pathway of the catalytic decomposition process could not be proven experimentally until now. Further studies on this decomposition process including in situ FTIR investigations are in preparation to clear out the exact process pathway leading to the formation of ethanol and formaldehyde from cinnamyl alcohol.

Acknowledgments

We thankfully acknowledge Marcel Marschewski for his technical assistance and the Deutsche Forschungsgemeinschaft (DFG) for the financial support under project numbers MA 1893/18-1 and VI 359/9-1.

References

- [1] K.Y. Yang, K.C. Choi, C.W. Ahn, *Opt. Express* 17 (2009) 11495.
- [2] S. Kato, Y. Hirano, M. Iwata, T. Sano, K. Takeuchi, S. Matsuzawa, *Appl. Catal. B Environ.* 57 (2005) 109.
- [3] H.-Y. Chuang, D.-H. Chen, *Nanotechnology* 20 (2009) 105704.
- [4] C.-N. Lok, C.-M. Ho, R. Chen, Q.-Y. He, W.-Y. Yu, H. Sun, P.K.-H. Tam, J.-F. Chiu, C.-M. Che, *J. Proteome Res.* 5 (2006) 916.
- [5] V. Ilic, Z. Saponjic, V. Vodnic, S. Lazovic, S. Dimitrijevic, P. Jovancic, J.M. Nedeljkovic, M. Radetic, *Ind. Eng. Chem. Res.* 49 (2010) 7287.
- [6] L. Klarhöfer, F. Voigts, D. Schwendt, B. Roos, W. Viöl, O. Höfft, W. Maus-Friedrichs, *Holzforschung* 61 (2007) 523.
- [7] L. Klarhöfer, B. Roos, W. Viöl, O. Höfft, S. Dieckhoff, V. Kempter, W. Maus-Friedrichs, *Holzforschung* 62 (2008) 688.
- [8] L. Klarhöfer, W. Viöl, W. Maus-Friedrichs, *Holzforschung* 64 (2010) 331.
- [9] L. Klarhöfer, PhD thesis at the Clausthal Technical University (2009), ISBN 978-3-940394-74-3.
- [10] J. Daphi-Weber, H. Raddatz, R. Müller, *HighChem hautnah – Aktuelles aus der Lebensmittelchemie*, 5, Gesellschaft Deutscher Chemiker, 2010, ISBN 978-3-936028-64-5. 94.
- [11] Die Diagnostik der Kontakallergie, 3. Aufl., Firma Hermal, 1997.
- [12] S. Kayser, *Chemikalien und Kontakallergie – eine bewertende Zusammenfassung*, Medizin & Wissen, 2001.
- [13] S. Dahle, M. Marschewski, L. Wegewitz, W. Viöl, W. Maus-Friedrichs, *J. Appl. Phys.* 111 (2012) 034902.
- [14] T. Ikari, A. Keppler, M. Reinmüller, W.J.D. Beenken, S. Krischok, M. Marschewski, W. Maus-Friedrichs, O. Höfft, e.-J. Frank Endres, *Surf. Sci. Nanotech.* 8 (2010) 241.
- [15] W. Maus-Friedrichs, M. Wehrhahn, S. Dieckhoff, V. Kempter, *Surf. Sci.* 249 (1991) 149.
- [16] D. Ochs, W. Maus-Friedrichs, M. Brause, J. Günster, V. Kempter, V. Puchin, A. Shluger, L. Kantorovich, *Surf. Sci.* 365 (1996) 557.
- [17] D. Ochs, M. Brause, B. Braun, W. Maus-Friedrichs, V. Kempter, *Surf. Sci.* 397 (1998) 101.
- [18] S. Krischok, O. Höfft, J. Günster, J. Stultz, D.W. Goodman, V. Kempter, *Surf. Sci.* 495 (2001) 8.
- [19] J.H. Scofield, *J. Electron Spectrosc. Relat. Phenom.* 8 (1976) 129.
- [20] C. Powell, A. Jablonski, *J. Electron Spectrosc. Relat. Phenom.* 178 (2010) 331.
- [21] R.F. Reilman, A. Msezane, S.T. Manson, *J. Electron Spectrosc. Relat. Phenom.* 8 (1976) 389.
- [22] A. Jablonski, *Surf. Interface Anal.* 23 (1995) 29.
- [23] C.J. Powell, A. Jablonski, NIST Electron Inelastic-Mean-Free-Path Database – Version 1.2, National Institute of Standards and Technology, Gaithersburg, MD, 2010. (<http://www.nist.gov/srd/nist71.cfm>).
- [24] Y. Harada, S. Masuda, H. Ozaki, *Chem. Rev.* 97 (1997) 1897.
- [25] H. Morgner, *Adv. At. Mol. Opt. Phys.* 42 (2000) 387.
- [26] G. Ertl, J. Kuppers, *Low Energy Electrons and Surface Chemistry*, VCH Verlag, Weinheim, 1985.
- [27] P. Stracke, S. Krischok, V. Kempter, *Surf. Sci.* 473 (2001) 86.
- [28] Z. Pásti, G. Pető, Z.E. Horváth, A. Karacs, L. Guzzi, *Solid State Commun.* 107 (1998) 329.
- [29] G.K. Wertheim, S.B. DiCenzo, D.N.E. Buchanan, *Phys. Rev. B* 33 (1986) 5384.
- [30] G. Faraci, E. Costanzo, A.R. Pennisi, Y. Hwu, G. Margaritondo, *Z. Phys. D: At. Mol. Clusters* 23 (1992) 263.
- [31] H.C. Yang, K. Aoki, H.G. Hong, D.D. Sackett, M.F. Arendt, S. Lin Yau, C.M. Bell, T.E. Mallouk, *J. Am. Chem. Soc.* 115 (1993) 11855.
- [32] Merck chemical data sheet, <http://assets.chemportals.merck.de/documents/sds/emd/deu/de/8025/802504.pdf> (accessed at 13th Feb. 2010).
- [33] P. Stracke, PhD thesis at the Clausthal Technical University (2000), ISBN 3-89825-292-2.