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Silver nano structure formation in cinnamyl alcohol

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1. Introduction

Metastable Induced Electron Spectroscopy (MIES), Ultraviolet Photoelectron Spectroscopy (UPS), X-ray Photoelectron Spectroscopy (XPS), and Atomic Force Microscopy (AFM) have been employed to study the adsorption of silver and cinnamyl alcohol on Au(111) and Si(100) substrates. Initially, these investigations were carried out preceding the investigation of the adsorption behavior of silver on wood surfaces, where cinnamyl alcohol is used as model system for lignin. Even though cinnamyl alcohol has only one technical application by now, some interesting properties of nanostructure formation and catalytic decomposition have been found.

The investigations of silver adsorption on cinnamyl alcohol [1] for wood functionalisation included gas adsorption experiments regarding the technical applications. Thereby, a decomposition of the Ag loaded cinnamyl alcohol during exposure to water has been found. Thus, silver functionalised wood surfaces seem disadvantageous, while the decomposition process may be utilized for different purposes. Especially after evidences to be occuring on lignin, too, this decomposition process may be applicable e.g. for biomass valorization.

2. Experimental

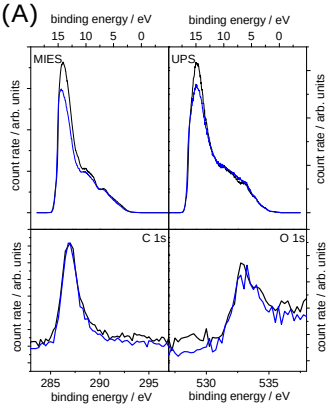
For probing the surface density of states (SDOS) we applied MIES and UPS using a hemispherical analyzer (Leybold EA 10) combined with a source for metastable helium atoms (mainly $He^*2^3S_1$) and ultraviolet photons (HeI). Additional information for chemical analysis was obtained by XPS utilizing a commercial non-monochromatic X-ray source (Fisons XR3E2-324) using Al Ka at a photon energy of 1486.6 eV. Fit curves were gained using OriginPro 7G with the Peak Fitting Module. A Veeco Dimension 3100 SPM is employed for tapping mode AFM with silicon cantilevers (NSC15 with Al backside coating from Micromasch).

H_2O (deionised) was offered via backfilling, controlled by a quadrupole mass spectrometer (Balzers QMG311 equipped with a Balzers QMA 140). Reaction products were monitored using a differentially pumped QMS system (Balzers QMG 422) with a linear motion feed for positioning before the sample.

Silver (Sigma-Aldrich, 99%) was evaporated with a commercial UHV evaporator (Omicron EFM3) with an Ag^+ ion flux of 1 µA corresponding to a growth rate of 0.23 nm min^{-1} on Si(100) at room temperature. Cinnamyl alcohol (Sigma-Aldrich, > 97.0 %) was evaporated in a preparation chamber (base pressure < 10^{-9} hPa) using a temperature controlled evaporator (Kentax TCE-BS) at 40 °C for 5 min, leading to a film with a thickness of about 1.8 nm [2].

3. Chemical inertness of the uncovered cinnamyl alcohol

(A)



Cinnamyl alcohol / Au(111) + $2{\cdot}10^{10}$ L water

Gold single crystals are known to be not affecting cinnamyl alcohol. [2]

Even though cinnamyl alcohol is known to be susceptible to humid or oxidizing environments:

No changes during water adsorption at all neither in XPS nor in MIES or UPS.

↓

The known susceptibilities to different atmospheres must be happening on much larger timescales or dosages.

↓

The decomposition of silver loaded cinnamyl alcohol films must occur via another process including some kind of interaction with the adsorbed silver.

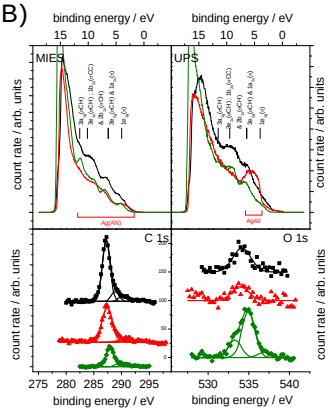
■ Cinnamyl alcohol / Au(111)
▲ Ag / Cinnamyl alcohol / Au(111)
◆ Cinnamyl alcohol / Ag / Si(100)

Cinnamyl alcohol on Au(111) is used as reference system, since it is proven to be inert against 10^{10} L H_2O.

Ag adsorption just slightly influences the cinnamyl alcohol structures in XPS, while MIES and UPS get dominated by the adsorbed silver.

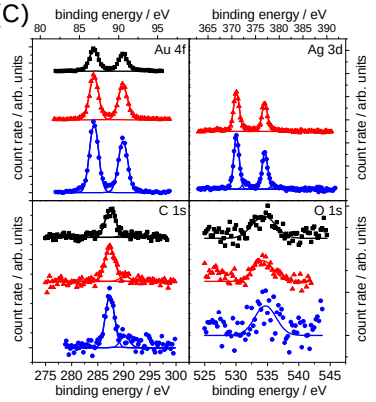
Cinnamyl alcohol adsorbed on closed silver PVD films yields:
→ Peaks at same binding energies as for adsorption on Au(111) in MIES and UPS
→ Some additional O1s species, most probably at Ag defects
→ The same C1s peak distribution as on Au(111)
→ A changed C/O ratio, maybe due to adsorption geometries
→ Similar film thicknesses on Au(111) and defective Ag.
➔ **No cinnamyl alcohol decomposition on closed Ag films,** regarding the huge amounts of water vapor during the thermal evaporation of cinnamyl alcohol.

(B)

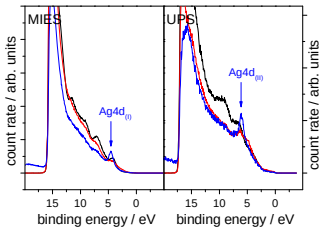


4. Catalytic decomposition of the cinnamyl alcohol and nano particle formation

(C)



■ Cinnamyl alcohol
▲ + Silver
● + 1040 L water

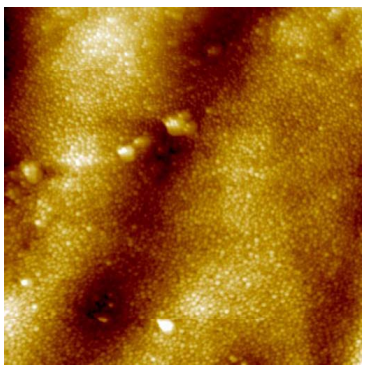


XPS Au4f:
- Decreasing film thicknesses, slightly on silver adsorption and significant on exposure to water

XPS C1s and O1s:
- Slightly increasing intensities on Ag adsorption
- Significantly decreased intensities after H_2O
→ Film degradation

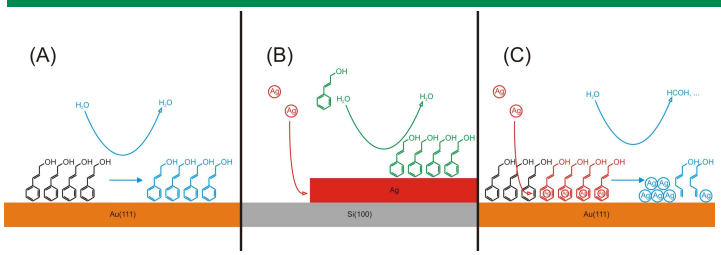
XPS Ag3d:
- Significant increased intensity after H_2O
→ Ag atoms initially insulated by cinnamyl alcohol
- Surplus species vanishing on further H_2O
→ Chemical interaction with other adsorbates

- MIES/UPS structures of cinnamyl alcohol mostly dominated by Ag(AN) and Ag4d after Ag adsorption
→ Ag adsorbed on top of the cinnamyl alcohol
- $Ag4d_{(I)}$ arising in MIES after subsequent exposure to H_2O
→ AD peak in MIES only on inhibition of resonant transfer necessary for Ag(AN)
➔ Initial formation of immersed Ag clusters (see AFM after higher dosages)
- Increased $Ag4d_{(II)}$ in UPS
→ Initially insulated Ag atoms gain contact to substrate



AFM image of a 1µm x 1µm region of a silver loaded film of cinnamyl alcohol after water dosage [1]

5. Summary



Neither cinnamyl alcohol films on Au(111) **(A)**, nor cinnamyl alcohol on closed silver PVD films **(B)** showed any degradation up to 10^{10} L of water.

Silver loaded cinnamyl alcohol films **(C)** were mainly decomposed within 1040 L water dosage.

Silver atoms were found to start clustering on exposure to water, while finally forming nano-sized particles (see AFM, diameter ~ 9 nm).

Mass spectra during water offer (not shown) yield the production of short-chained alkanes, alcohols and aldehydes.

6. Literature

[1] S. Dahle, M. Marschewski, L. Wegewitz, W. Viöl, W. Maus-Friedrichs, J. Appl. Phys. **111** (2012) 034902
[2] L. Klarhöfer, B. Roos, W. Viöl, O. Höfft, S. Dieckhoff, V. Kempter and W. Maus-Friedrichs, Holzforschung **62** (2008) 688-693

7. Acknowledgements

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Atom- und Molekülphysik an Oberflächen