Adsorption and Dehydrogenation of Tetrahydroxybenzene on Cu(111) and Ni(111)

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Motivation

Surface functionalization in the form of two-dimensional networks is a method of growing interest for the development of functional, periodic nanometer-scale structures with. great potential in catalysis, for example. A common problem in generation of such structures is that more stable covalent assemblies are prone to structural defects limiting the achievable degree of order, while highly ordered hydrogen-bonded structures often lack the necessary stability. Metal Organic Networks are intermediate between those two types of structures. They posses quite interesting 3D-analgoues, Metal Organic Frameworks.

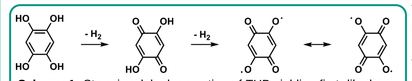
Tetrahydroxybenzene (THB) was recently found to dehydrogenate on Cu(111) [1] and form a regular network consisting of a completely dehydrogenated THB species and Cu-adatoms [2]. Interestingly, STM and XPS investigations showed that the nodes of this network consist of Cu-trimers, where each Cu-atom is bonded to two dehydrogenated THB-molecules via their oxygen atoms. With such a complex node, this network is a very realistic truly two-dimensional MOF analogue that allows to exploit the surface-science toolkit to investigate MOF-like structures. Furthermore, the generation of monodispersed and very small metal (oxide) clusters is of great interest in the area of catalysis.

References

[1] F. Bebensee, K. Svane, C. Bombis, F. Masini, S. Klyatskaya, F. Besenbacher, M. Ruben, B. Hammer, T. Linderoth, Adsorption and Dehydrogenation of Tetrahydroxybenezene on Cu(111), *Chem. Commun.* 2013, **49**, 9308-9310.

[2] F. Bebensee, K. Svane, C. Bombis, F, Masini, S. Klyatskaya, F. Besenbacher, M. Ruben, B. Hammer, T. Linderoth, A Surface Coordination Network Based on Copper Adatom Trimers, *Angew. Chem. Int. Ed.* 2014, **53**, 12955-12959.

Introduction and Aims



Scheme 1: Stepwise dehydrogenation of THB yielding first dihydroxy-benzoquinone (DHBQ) and then a 2,5-dioxy-p-benzosemiquinone diradical on the Cu(111) surface.

The network formed by the dehydrogenated THB on Cu(111) is interesting for its unusual threefold-coordination motif: the monodisperse Cu-trimers may be interesting in catalysis and the structure effectively mimics a truly 2-D MOF. For these reasons, a more detailed characterization of the Cu-nodes is obviously highly desirable, yet experimentally challenging due to the signal arising from surface Cu-atoms.

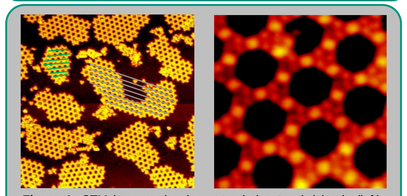


Figure 1: STM images showing extended network islands (left) and the Cu-trimer nodes in high resolution (right).

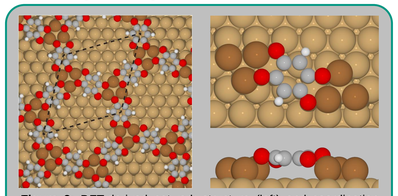


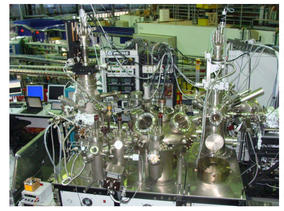
Figure 2: DFT-derived network structure (left) and coordination geometry of individual molecular building block (right).

Aims:

1. Details of the electronic structure of the network on Cu(111)

2. Explore other surfaces for network formation, particularly Ni(111)

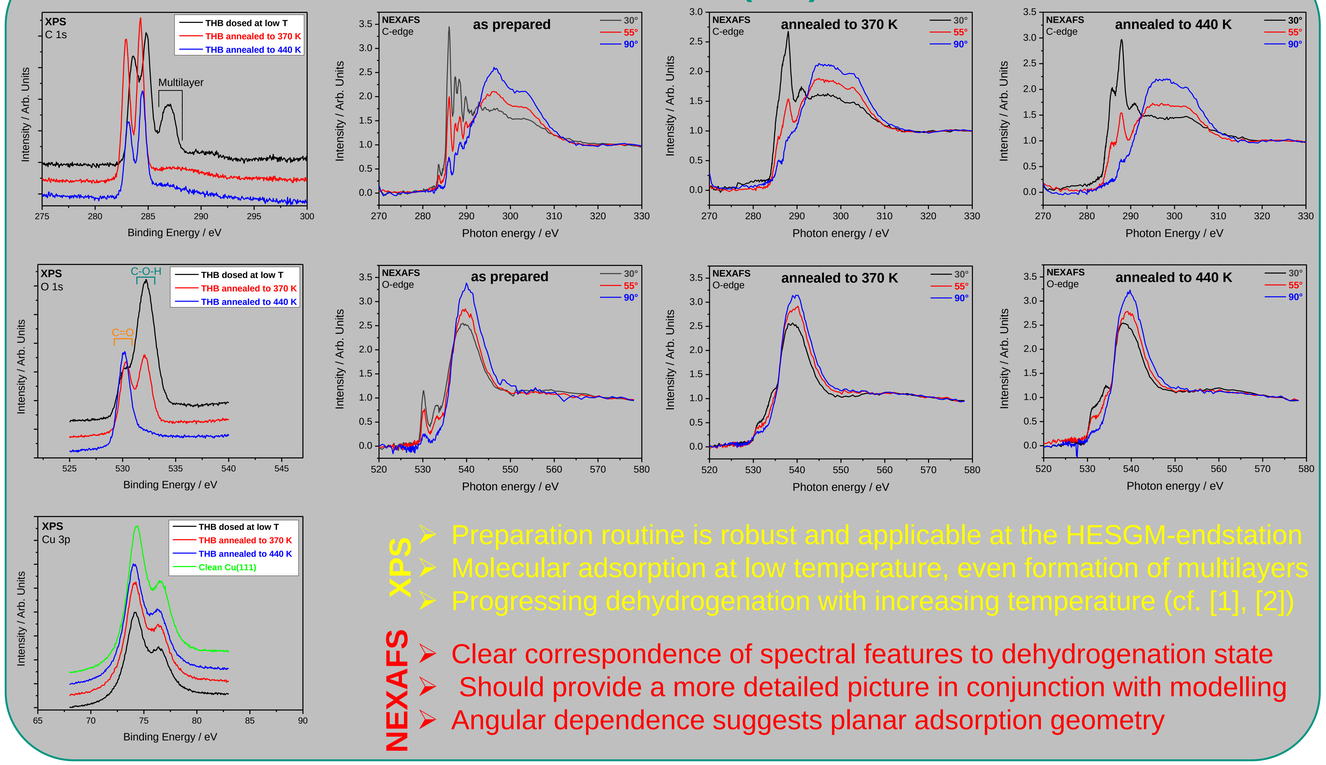
Experimental



All experiments reported were carried out at the HESGM-endstation shown in the picture to the left.
The endstation provides a preparation chamber for sputtering and annealing. It is furthermore equipped with a LEED optics to check the surface structure.
The attached analysis chamber allows for NEXAFS and XPS experiments using a home-build detector and a hemispherical analyzer, respectively.

- The Ni(111) and Cu(111) substrates were prepared via sputter-anneal cycles until XPS showed no carbon contamination and a clear LEED pattern was observed
- THB molecules (provided by Dr. M Tsotsalas) were sublimated onto clean Ni(111) and Cu(111) substrates held at 110 K from a home-built Knudsen cell at 330 K.
- The sample transfer to the analysis chamber after preparation lead to only a moderate increase of the sample temperature (below 15 K).
- After characterization of the as prepared samples, the respective samples were annealed for 20 minutes at the stated temperatures in order to achieve the desired dehydrogenation. The subsequent measurements were performed after re-cooling the sample to 110 K.

THB on Cu(111)



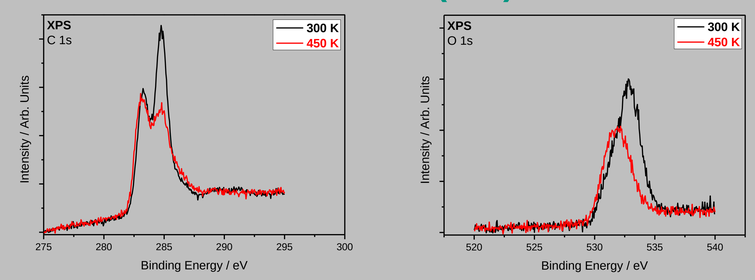
XPS

- Preparation routine is robust and applicable at the HESGM-endstation
- Molecular adsorption at low temperature, even formation of multilayers
- Progressing dehydrogenation with increasing temperature (cf. [1], [2])

NEXAFS

- Clear correspondence of spectral features to dehydrogenation state
- Should provide a more detailed picture in conjunction with modelling
- Angular dependence suggests planar adsorption geometry

THB on Ni(111)



- **XPS** indicates drastically different dehydrogenation product!
- Quality of **NEXAFS**-data clearly not satisfactory (not shown)

Conclusions and Outlook

- **Different dehydrogenation states can be studied using NEXAFS**
  - Complete with simulations and experiments on high density phase on Cu(111)
- **Ni(111) is not a suitable substrate for network formation!**
  - Investigate other promising candidates, e.g. Pt(111)
  - Acquire missing NEXAFS data to rationalize failure of network formation