EELS Study of Phenol on TiO_2 (110)

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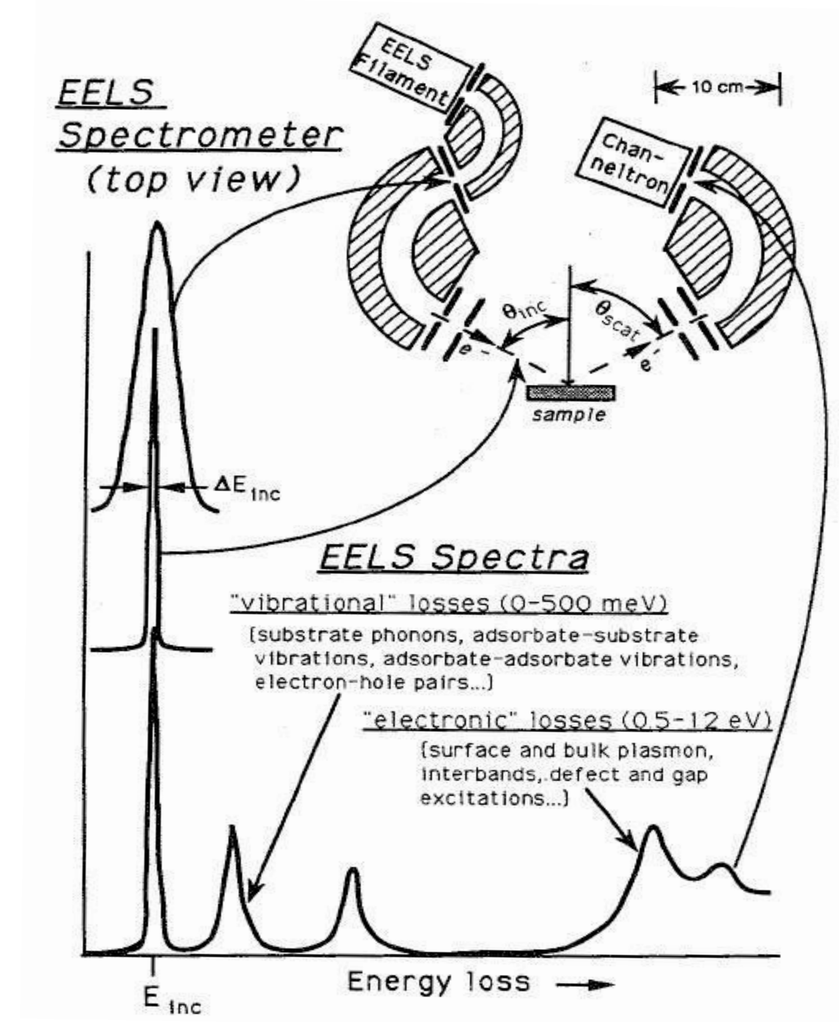
Abstract

Environmentally Persistent Free Radicals (EPFR), present in particles that are within the nano-scale, have been found to be a problem to long term health and is unknown how initial formation occurs. This study seeks to understand the basic interaction of simple precursor EPFR molecules on well-characterized single crystal metal oxide surfaces. Specifically, here we employ energy electron-loss spectroscopy to probe the vibrational and electronic properties of phenol on a TiO_2 (110) crystal. It was found that there is little difference between the vibrational modes of phenol at both 90 and 300 K; however, there are some differences in the electronic excitations. EELS does reveal that upon annealing to 300K only monolayer adsorption of phenol occurs.

Environmentally Persistent Free Radical (EPFR)

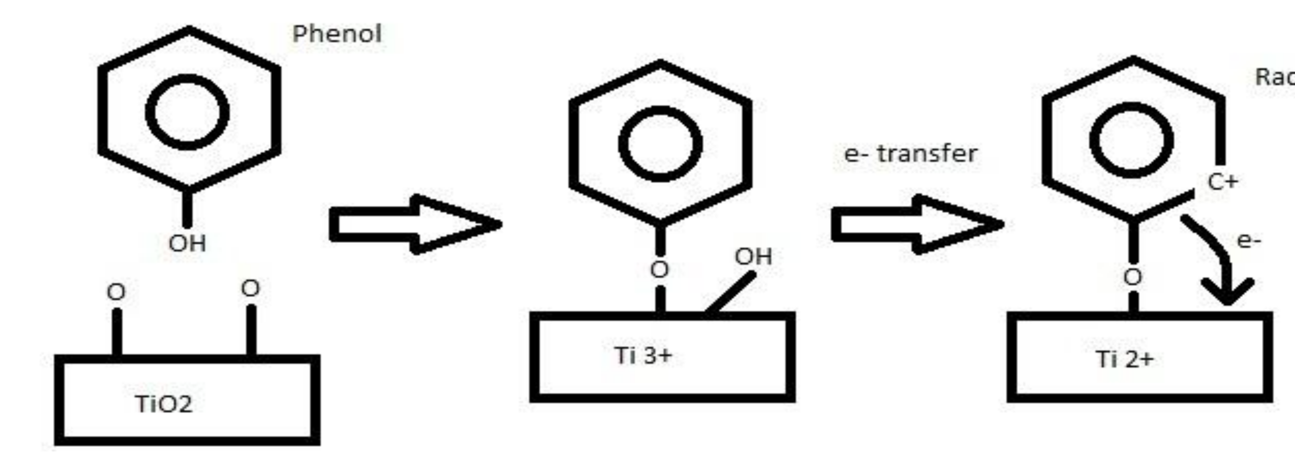
- Radicals are particles that typically have lifetimes of a fraction of a second
- EPFR are longer lived particles that can last up to hours or days
- Are found within natural settings such as combustion reactions and ground soil
- EPRF's are hazardous to health if inhaled and it is unknown on how they form

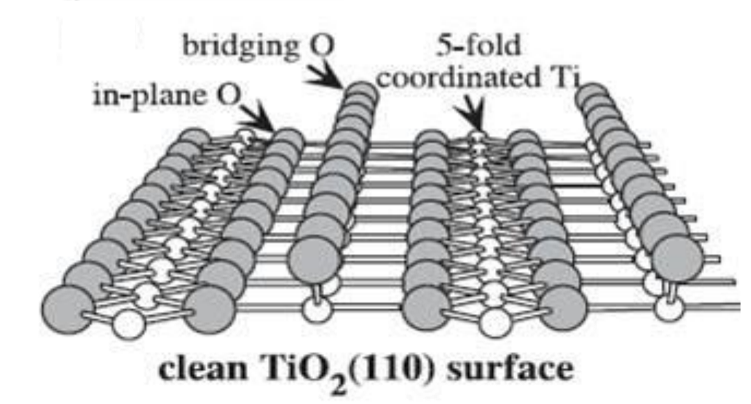
Electron Energy Loss Spectroscopy



EELS:
- A very surface sensitive probe
- Vibrational modes similar to what IR spectroscopy yields
- Allows us to probe phenol vibrations and excitations

Method: phenol on TiO_2(110)

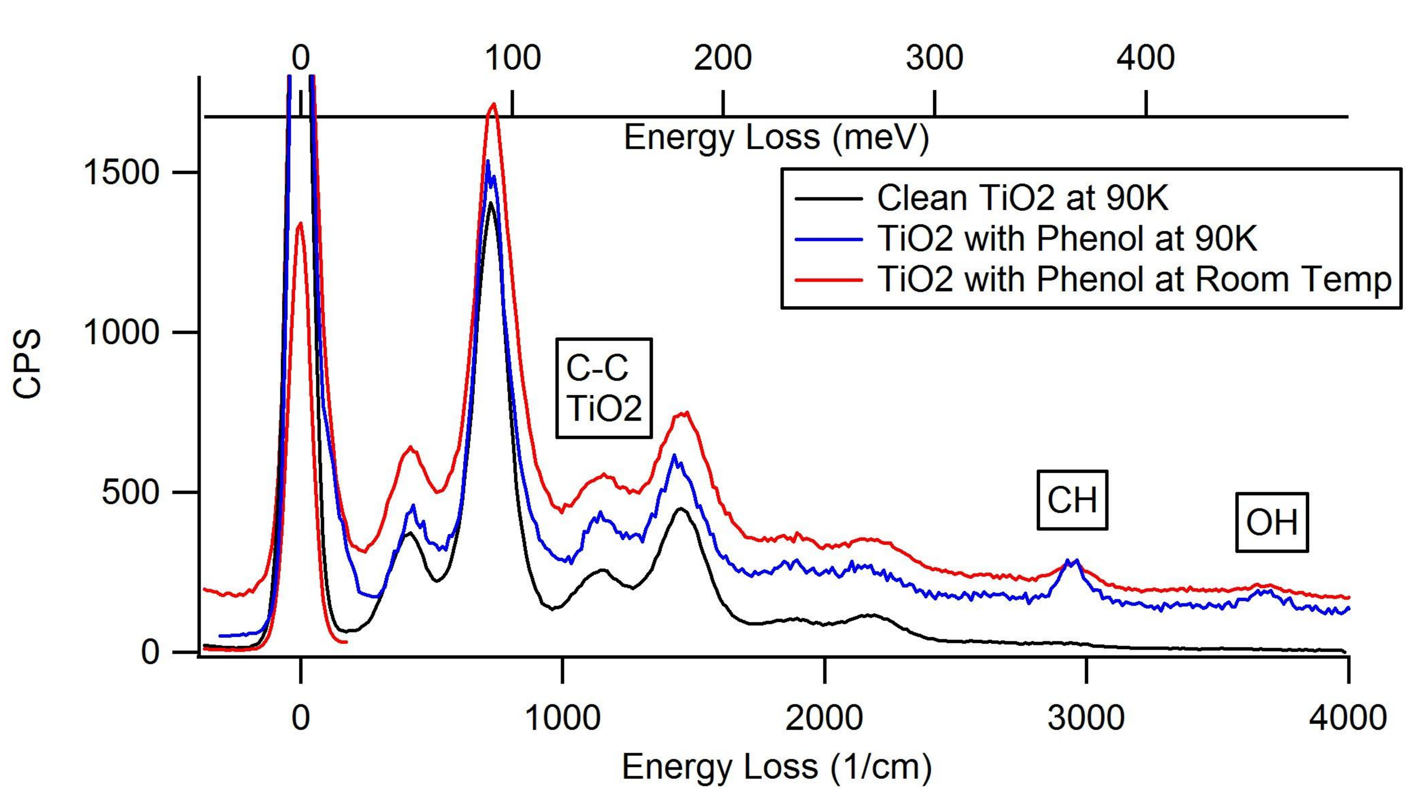




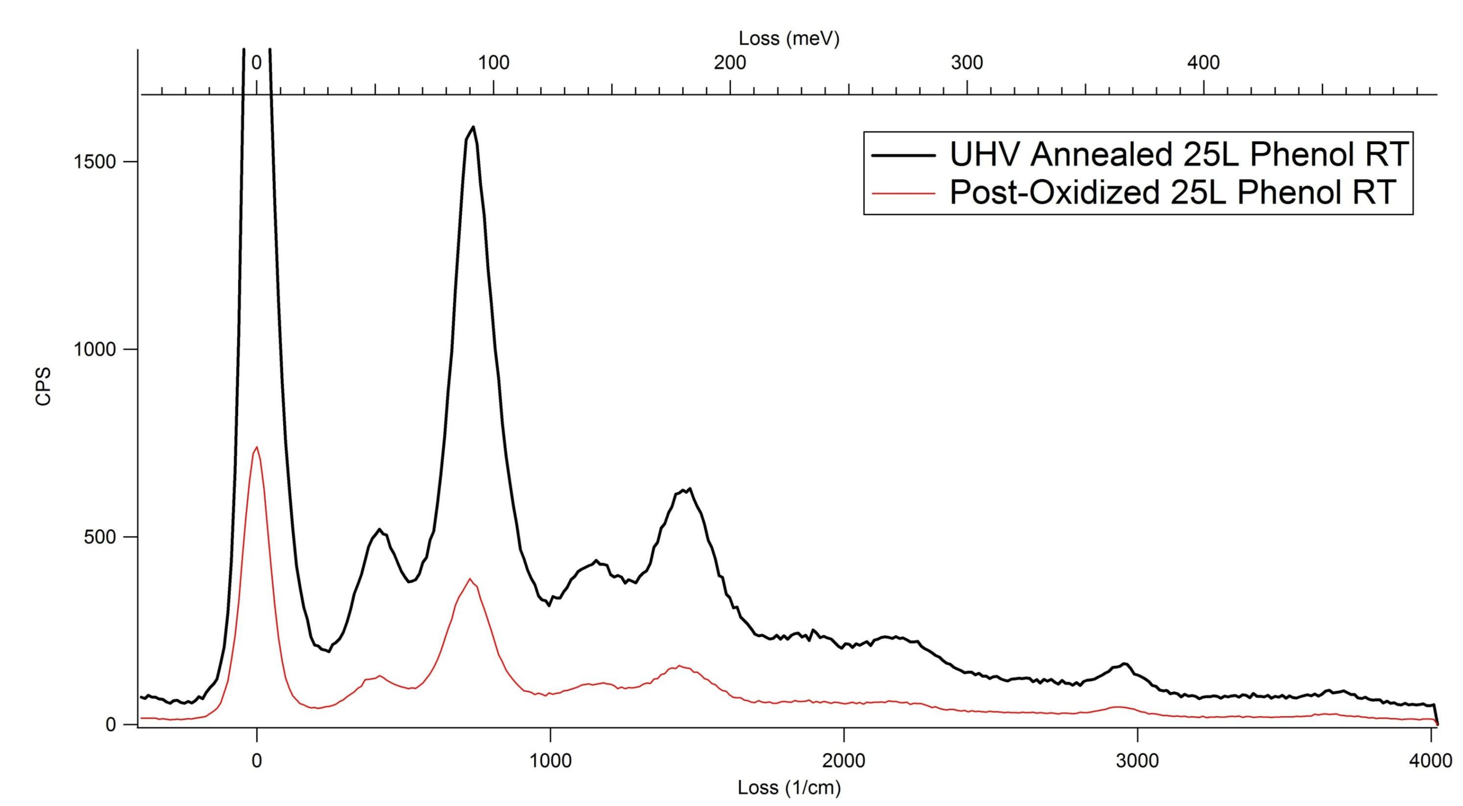
Our approach is to probe the chemical interaction between phenol, a pre-EPFR molecule, and a model transition metal oxide substrate [TiO_2(110)]

The general process used throughout the study followed these steps:
- Use a Ultra High Vacuum (UHV) system to isolate the sample
- Sputter with neon using an ion gun
- Anneal to smooth the surface and restore order to the bonds
  - ❖ Reduced surface versus an oxidized surface (stoichiometric)
- Leak valves are used to let in specific amounts of gas particles or vapor
- Auger spectroscopy checks to see if surface is free of any contaminants
- EELS scans surface for vibrational and electronic losses

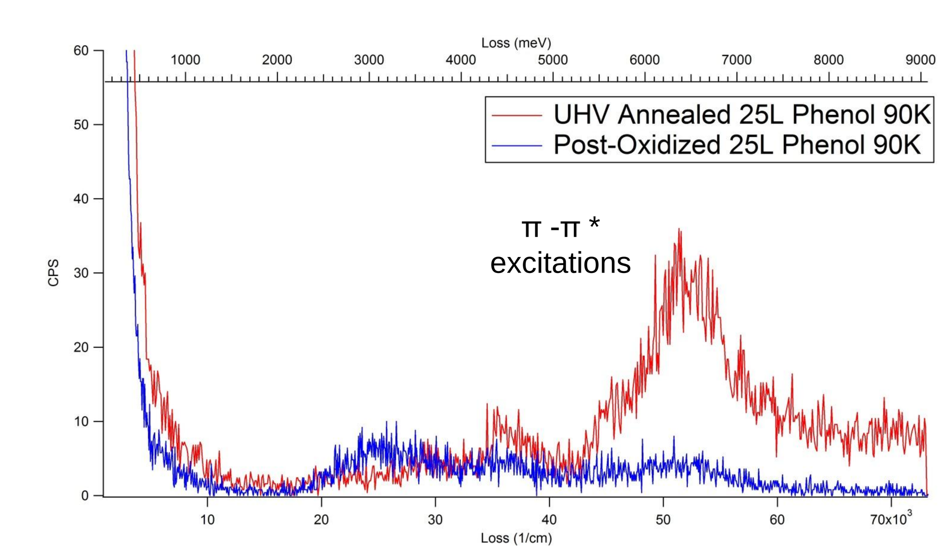
Data

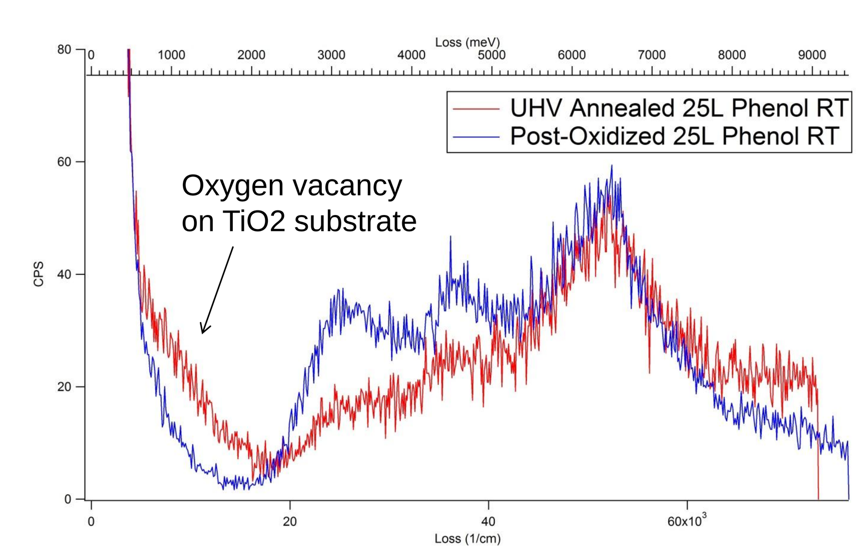


Key features:
- EELS shows vibrational signature of adsorbed phenol
- phenol is not lost as the temperature is raised from 90K to room temp
- OH bond at all temperatures → not radical formation (~physisorbed)
- CH and OH present → molecule is NOT planar to surface



Key features:
- EELS reveals little difference between phenol adsorption between stoichiometric (oxidized) and reduced TiO2 surface→ oxygen vacancies do not alter chemisorption behavior





Key points:
- At low temperature, EELS reveals differences in electronic losses of physisorbed phenol between oxidized and reduced TiO2 surface → this is not understood???
- At room temperature, excitation spectra are similar → this is in agreement with vibrational spectra
- At room temperature, emergence of oxygen defects (~0.8 eV) indicates no multilayer adsorption

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Future Work

In the future, work will be done to create these same conditions at higher pressures and higher temperatures. It is currently unsure if the chemisorption process is correlated with pressure. New parts have been ordered that will allow the group to expand part of the chamber and add necessary equipment to further the research. This will also allow the group to compare the collected data with data from other groups.

Further work is also planned at the Center for Advanced Microstructures and Devices (CAMD). The Ultraviolet Photoemission Spectroscopy (UPS) will be used to further understand the bonds.

Acknowledgements

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