



**Experiment title:** Quantifying the structure of chiral modifiers adsorbed on clean and pre-covered Ni surfaces using NIXSW -towards atomistic models of enantioselective catalysts

**Experiment number:**  
SI-1524

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|--------------------------|---|--|
| <b>Beamline:</b><br>ID32 | <b>Date of experiment:</b><br>from: 12 <sup>th</sup> June 2007 to: 19 <sup>th</sup> June 2007 | <b>Date of report:</b><br>10/03/08<br><br><i>Received at ESRF:</i> |
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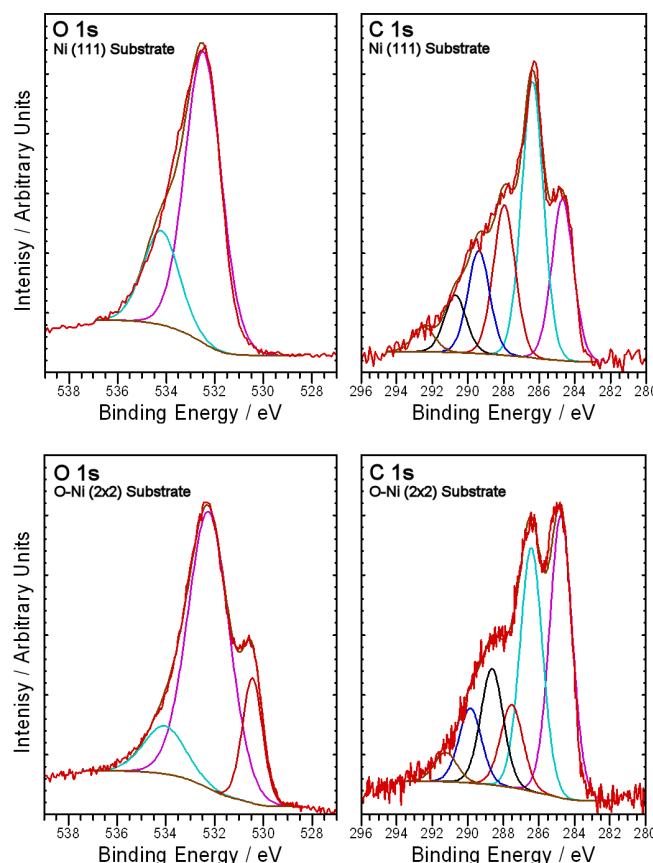
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## Report:

During the course of this beamtime we used Normal Incidence X-ray Standing Waves (NIXSW) technique to study saturation coverages of a chiral modifier, tartaric acid, on Ni(111) surfaces. This technique provides direct quantitative information of the adsorption geometry of adsorbates on surfaces and allows the stereoselectivity of the system to be understood. Chiral modifiers on metal substrates play an important role in chirally selective heterogeneous catalysis.

The beamtime was successful with multiple data collected for saturated (~0.2ML) coverages of L-(R, R)-tartaric acid on clean Ni(111) and O-p(2×2) Nickel surfaces for two Bragg reflections; [111] and  $\bar{1}\bar{1}1$ . Information regarding the adsorbate height and possible adsorption structures has been derived.

Figure 1 displays typical NIXSW data collected for saturated L-(R, R) tartaric acid on Ni (111). For the O 1s and C 1s regions individual components must be fitted and assigned to the chemical species present in the system. The signal to noise ratio is inherently low for submonolayer coverages of organic compounds on metal substrates so the 51 scans taken for photon energies 3042-3052 eV in 0.2 eV steps were summed and components



*Figure 1. Synchrotron XPS and fitted lineshapes of L-(R, R) tartaric acid on Ni(111) (top) and on the O-Ni (2×2) surface (bottom).*

fitted to the resultant spectra. This allowed the position and FWHM parameters of the individual components to be defined and propagated through the individual scans to retrieve the intensity of each chemically core-level shifted line. The NIXSW response for the individual O 1s and C 1s components are then determined exclusively through intensity variations and cannot shift in position or alter in width to compensate for noise. For the O 1s response, 2 components are fitted at 532.4 and 534.0 eV which correspond to the carboxyl and hydroxyl components respectively. When adsorbed on the O-Ni (2×2) reconstructed surface an extra state corresponding to NiO appears at 530.5 eV. The C 1s response is more complicated to fit due to a broad background response which extends from approximately 288-294 eV. This feature is not seen when performing XPS with an Al-K $\alpha$  source and so must be related to the higher intensity and energy of the synchrotron x-rays. From the XPS measurements two peaks are present in the 284 – 286 eV range with a peak separation of 1.6 eV and are assigned to the COHH group (lower B.E.) and the COOH group (higher B.E.) in the molecule, the others are background signals.

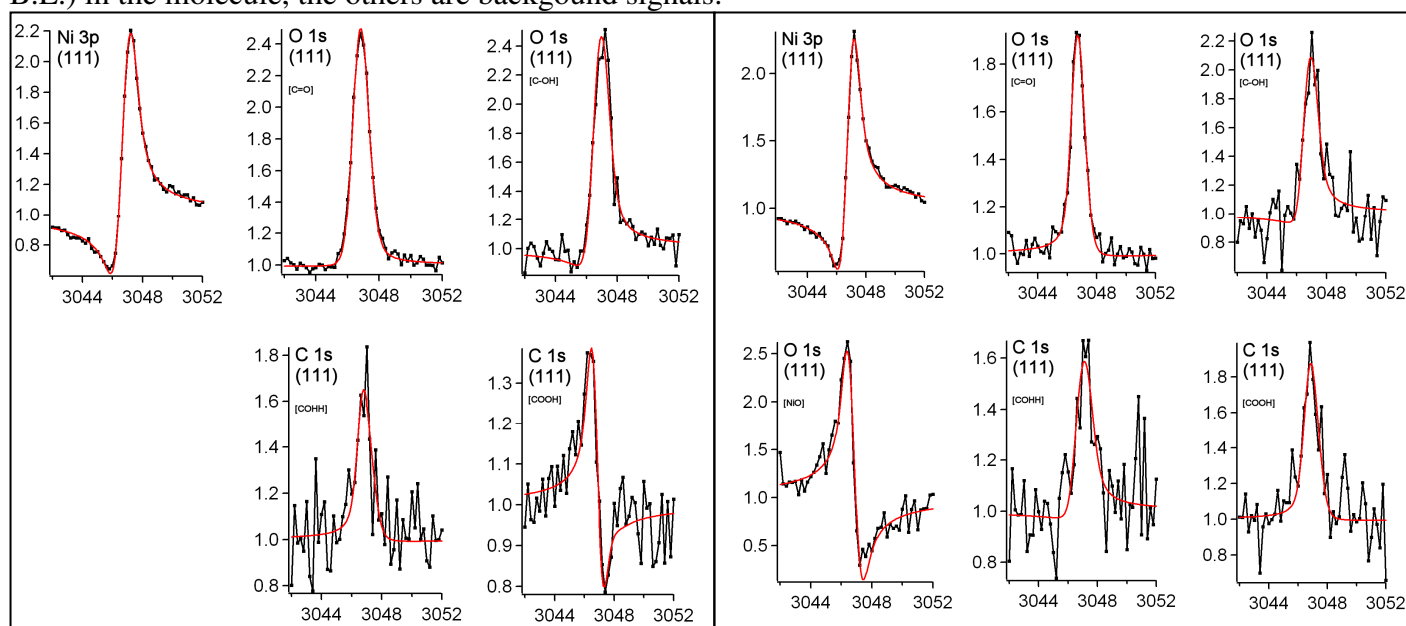


Figure 2. Fitted (red) NIXSW spectra (black) for the (111) reflection. Left panel: Ni (111) substrate. Right panel: O-Ni (2×2) reconstructed surface.

Figure 2 contains a selection of characteristic NIXSW spectra for the [111] reflection. All spectra have been fitted based upon the non-structural parameters taken from Ni 3p data. Analysis of this data is currently being undertaken with the use of a NIXSW solver program that has been written in house<sup>1</sup>. For the chiral molecules this had to be re-written to force rotational symmetries only rather than the mirror symmetries available to racemic systems. Initial results are encouraging and the solver program has shown that the structure for the oxygen (2×1) reconstructed substrate agrees very well with previous LEED-IV studies<sup>2</sup>. Our preliminary results for the molecular adsorption indicate the molecule is bound with carboxylate groups closest to the surface. Work is ongoing to check the uncertainty in positions, uniqueness of the result and most importantly to form a model adsorption structure from the co-ordinates obtained so far. It is planned that this analysis will be completed shortly and a paper will be submitted for publication in either Surface Science or The Journal of Chemical Physics.

<sup>1</sup> M. Basham and R. A. Bennett, Computer Physics Communications **177**, 459-466 (2007).

<sup>2</sup> W. Braun and G. Held, Surface Science **594**, 203-211 (2005).