Supporting information

Structure Determination of Adsorbed Hydrogen

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1. Sample preparation procedure and experimental details

Raney nickel was supplied as a 50 wt% slurry in water (Aldrich). The slurry was filtered at a water pump and ~50 g of the resulting cake was then transferred to a 0.5 inch stainless steel tube with a metal bellows valve at each end. This procedure was carried out in a nitrogen atmosphere as dry Raney nickel is pyrophoric. Glass wool plugs on both sides of the Raney nickel prevented the powder from moving and protected the valves. The sample was then dried under flowing hydrogen (CK Gases, 99.99%) at 120°C for six hours, weighed and then dried for a further two hours and re-weighed. If further weight loss had occurred, then drying was continued until constant weight was obtained. This procedure results in a hydrogen saturated surface as shown by INS spectroscopy, see Figure 1 of the paper. In an argon-filled glovebox, ~8 g of the dried Raney nickel was then transferred to a TiZr cell (35 × 35 × 4 mm) equipped with a metal bellows valve. The cell was sealed with gold wire. The cell was then attached to a standard ISIS gas handling centrestick and connected to a vacuum system and gas manifold. Measurements were made at room temperature of the sample under 1 bar of dihydrogen, after brief evacuation at 150°C and after prolonged evacuation at 350°C.

The INS measurements were carried out with TOSCA[3] at ISIS[4] (Chilton, UK), this provides a vibrational spectrum of the material. INS spectroscopy is particularly sensitive to hydrogen,[5] while most other elements scatter only weakly. The spectrum is similar to that obtained elsewhere[6], although more structure is evident because of the better resolution of TOSCA as compared to the instruments used previously. In agreement with previous work[6], we assign the major features at 900 and 1050 cm^{-1} to the antisymmetric and symmetric stretches respectively of hydrogen adsorbed at a threefold site.

The neutron scattering measurements were carried out on the Small Angle Neutron Diffractometer for Amorphous and Liquid Samples (SANDALS)[7] at ISIS which is optimized for the structural study of hydrogen containing systems. At the time of the experiment SANDALS was operating with 645 ZnS scintillation detectors arranged over scattering angles (2θ) from 3° to 40° with incident neutrons in the wavelength range from 0.05 to 5 Å. This instrument configuration allowed data to be collected in a *Q*-range from 0.1 to 50 $Å^{-1}$. The combination of large detector banks at low scattering angles combine to give the instrument high counting statistics while minimizing the magnitude of the signal distortions produced by inelastic scattering events arising from nuclear recoil of light atoms in the sample.

The metal catalysts, in powder form, were contained in null scattering $Ti_{0.676}Zr_{0.324}$ alloy cells of flat plate geometry. This alloy composition was specifically chosen as it has the advantage of making no coherent scattering contribution to the measured neutron scattering signal. The internal dimensions of the cell were 35×40×4 mm (width×height×thickness) and the alloy walls of the cell were 1 mm thick. This cell geometry is well matched to the neutron beam profile of the instrument that is of circular cross-section with a diameter of 30 mm at the sample position, and the forward scattering geometry of the detector array.

The data were corrected for instrument background, absorption and multiple scattering and were normalized to the incoherent scattering of a vanadium calibration sample. These corrections were performed using the Gudrun package that is based on the widely used ATLAS[8] routines. Following these data corrections the resulting interference differential scattering cross sections were then Fourier transformed to the pair distribution functions and difference functions[9] to allow the direct extraction of real space structural information.

2. *Ab initio* calculations

Unrestricted periodic DFT *ab initio* lattice dynamics calculations for a monolayer of hydrogen on Ni(111) were carried out using the Perdew Burke Ernzerhof (PBE)[10] generalized gradient approximation. A plane-wave basis set was used in conjunction with ultrasoft[11] pseudopotentials as implemented in the CASTEP code.[12,13] The geometry of a symmetric four layer slab with a 10 Å vacuum gap was optimised to obtain the equilibrium structure. An 11×11 grid of k-points in the slab plane was used for Brillouin-Zone integration and the plane-wave cut-off was 330 eV. The phonon modes were then calculated across the complete Brillouin zone using the finite displacement method[14] within a 4×4×1 supercell.

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