Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Sulphur, normally a poison, strongly promotes chemoselective catalytic hydrogenation: stereochemistry and reactivity of crotonaldehyde on clean and S-modified Cu(111)

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Calibration of crotonaldehyde dose/coverage by TPD uptake

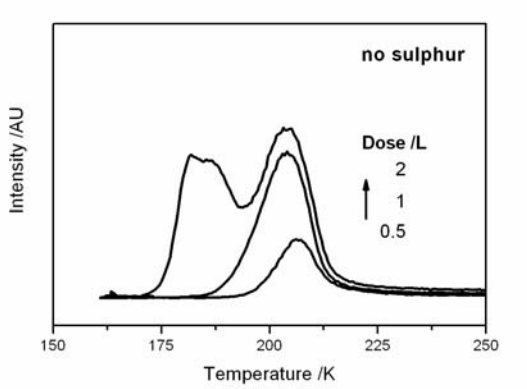

Fig. 1 TPD spectra for crotonaldehyde dosed on Cu(111)

Crotonaldehyde dose/coverage calibration was carried out in Cambridge by temperature programmed desorption (TPD) uptake as shown in Fig. 1. As the dose is increased up to 1 L (1 L = 1 Langmuir = 10^{-6} torr s) there is growth of a peak due to the contact layer (~ 210 K) this saturates at monolayer completion (~ 1 L) and is followed by growth of the second layer and multilayer peaks (~ 180 K). Equivalent measurements were made on the S-treated surface for which saturation of the first layer also occurred at ~ 1 L. Using these calibrations, accurate and reproducible dosing of crotonaldehyde was possible.

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Calibration of crotonaldehyde dose/coverage by fast XPS

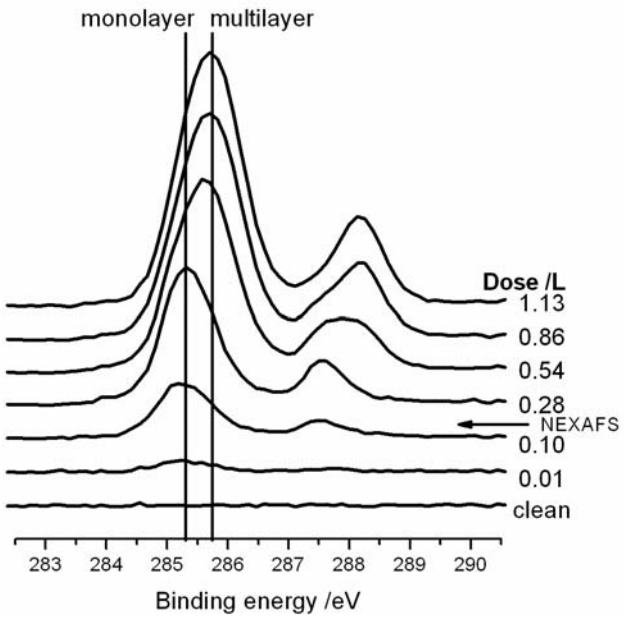

Fig. 2 C 1s region XP spectra of crotonaldehyde uptake as a function of time at 77 K

Crotonaldehyde dose/coverage was calibrated in Trieste by fast XPS uptake; the spectra are shown in Fig. 2. The binding energy scale has been corrected with respect to the Cu $3p_{3/2}$ line at 75.0 eV. The Cu(111) surface here has been pre-dosed to $\kappa_H \sim 0.7$ *ie* the same conditions used to carry out TPR, and the same conditions under which NEXAFS was taken. Note that the spectra were recorded at 77 K. This is well below the hydrogenation reaction temperature as determined by TPR, so we may be sure that the XPS uptake is not complicated by the presence of product species on the surface.

The C 1s signal increases as dose is increased, and up to 0.28 L, only one state is observed. The ratio of the peak areas is 3:1, exactly as is expected for crotonaldehyde where the lower binding energy peak (285.30 eV) corresponds to the $CH_3CH=CH-$ moiety, and the higher binding energy peak (285.73 eV) corresponds to the -HC=O moiety. Between 0.28 and 0.54 L, there is a shift toward higher binding energy and this marks the beginning of multilayer growth. The 3:1 area ratio is maintained throughout showing that the molecule is intact on the surface. NEXAFS was taken at a dose of 0.16 L, well below the monolayer point.

Note that crotonaldehyde was dosed by back-filling the chamber in Cambridge, and by means of a capillary doser in Trieste. This difference in dosing methods accounts for the apparent differences in dose required to achieve a monolayer.