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Supplementary Information

Adsorbate conformation determines catalytic chemo-selectivity: crotonaldehyde on the Pt(111) surface

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Assignment of NEXAFS transitions



Fig. 1 C K-edge step corrected NEXAFS spectra for \sim 1ML of crotonaldehyde adsorbed at 77 K as a function of photon incidence angle.

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Figure 1 shows step corrected NEXAFS spectra for ~ 1 ML coverage of crotonaldehyde as a function of photon incidence angle. The NEXAFS spectra show multiple peaks, of which two peaks, A and B, are the dominant features. The assignment of these various features is made by reference to prior work on acrolein NEXAFS spectra [1,2]. Peak A attenuates as the photon angle of incidence changes from grazing to normal incidence (eventually leading to zero), this would imply the C=C bond is parallel with the Pt (111) surface [3]. Peak B (287.1 eV) corresponds to a C=O bond π^* transition and while it does attenuate with increasing angle of incidence, it does not vanish like the C=C bond π^* transition. This implies that the C=O bond does not sit parallel to the Pt(111) surface. Peak C (287.9 eV) can be assigned to the second C=C π^* transition, while peak D (289.2 eV) can be assigned to the second C=O π^* transition. Peak E (290.2 eV) is likely to be the C σ^* transitions associated with peak D. Finally, peak F (291.0 eV) can be assigned to a C=O π^* transitions beyond this are mainly C σ^* transitions.

Crotonaldehyde uptake monitored by XPS

Figure 2 shows XP spectra as a function of crotonaldehyde exposure. It is clear that as the exposure increases the C 1s signal increases, furthermore for exposures up to ~ 1.13 L only one state is observed, with C 1s peaks at 283.6 eV and 285.9 eV. The two peak areas are in a 3:1 ratio, which are due to the CH₃CH=CH- component (283.6 eV) and to the -HC=O component (285.9 eV) in crotonaldehyde. This point defines the monolayer, *i.e.* a dose of ~ 1.13 L corresponds to a coverage of 1 ML. The data shown in figure 2 clearly demonstrate that the multilayer has C 1s peaks at ~ 285.0 eV (due to the CH₃CH=CH-component) and ~ 287.4 eV (due to the -HC=O component). Given that the NEXAFS measurements used in our paper were taken with an exposure of 1 L (*i.e. below* the monolayer point) it is clear that the observed reorientation is not due to the onset of multilayer growth.

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

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