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Article

Supplemental Material

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Supporting Information

A Combined Experimental and Theoretical Study of Methyl Acetoacetate Adsorption on Ni{100}

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This document contains:

- NEXAFS fitting and determination of tilt angle with respect to the surface plane
- XPS data of the NEXAFS layers (**Figure S1**)
- Initial configurations of MAA on Ni{100} (**Figure S2, Table S1**)
- Core-level shift calculations of C 1s for the most stable *bidentate deprotonated* configuration (**Table S2**) and comparison with experimental data (**Figure S3**)

NEXAFS

Data Analysis

The NEXAFS were fitted using an equation which consist of a linear background, a step function and several Gaussian functions depending on the number of resonances (eq. 1):

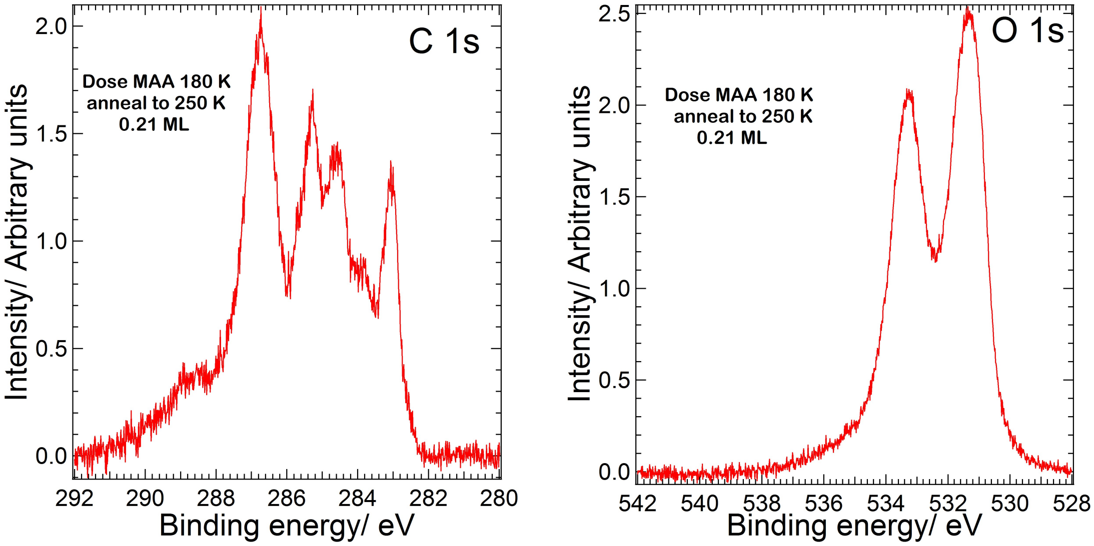
$$I(E) = B_0 + B_S(E - S_P) + S_H\left[\frac{1}{\pi}\arctan\left(\frac{E - S_P}{0.2 * S_W}\right) + \frac{1}{2}\right] + \sum_i G_{i,H}\exp\left[-4\ln 2\frac{(E - G_{i,P})^2}{G_{i,W}^2}\right] \tag{1}$$

Where B_0 is the offset at the point of the adsorption step, B_S is the slope of the linear background, S_P is the step position, S_H is the step height, S_W is the width of the step, and $G_{i,H}$, $G_{i,P}$ and $G_{i,W}$ are the height, position and full width at half maximum of the ith resonance.

The tilt angles with respect to the surface plane, α, corresponding to each resonance were obtained by fitting the intensity of the peak as function of the angle of incidence θ using the following equation [1] for surfaces with 4-fold symmetry:

$$I(\gamma) = \frac{I_\alpha}{3}\left[1 + \frac{1}{2}(3\cos^2(90^\circ - \theta) - 1)(3\cos^2\alpha - 1)\right] \tag{2}$$

XPS data for layer studied by NEXAFS



(a) (b)

Figure S1: XPS data of the MAA layer used for the NEXAFS study. (a) C 1s region ($h\nu = 400$ eV) and in the (b) O 1s region ($h\nu = 650$ eV)

DFT Modelling

Figure S2 shows the start geometries for all configurations tested by DFT modelling. Table S1 lists the adsorption energies of the optimised configurations. After relaxation, *flat-enol top I* (*top II*) converged to *4-hollow I* (*4-hollow II*). Regarding the *bidentate deprotonated enolate* candidates, the molecular plane in *O-bridge 1 row* remained perpendicular with respect to the surface whereas it tilted in the case of *O-bridge 2 rows*. Configurations with diketo MAA are far less stable than those discussed in the main section.

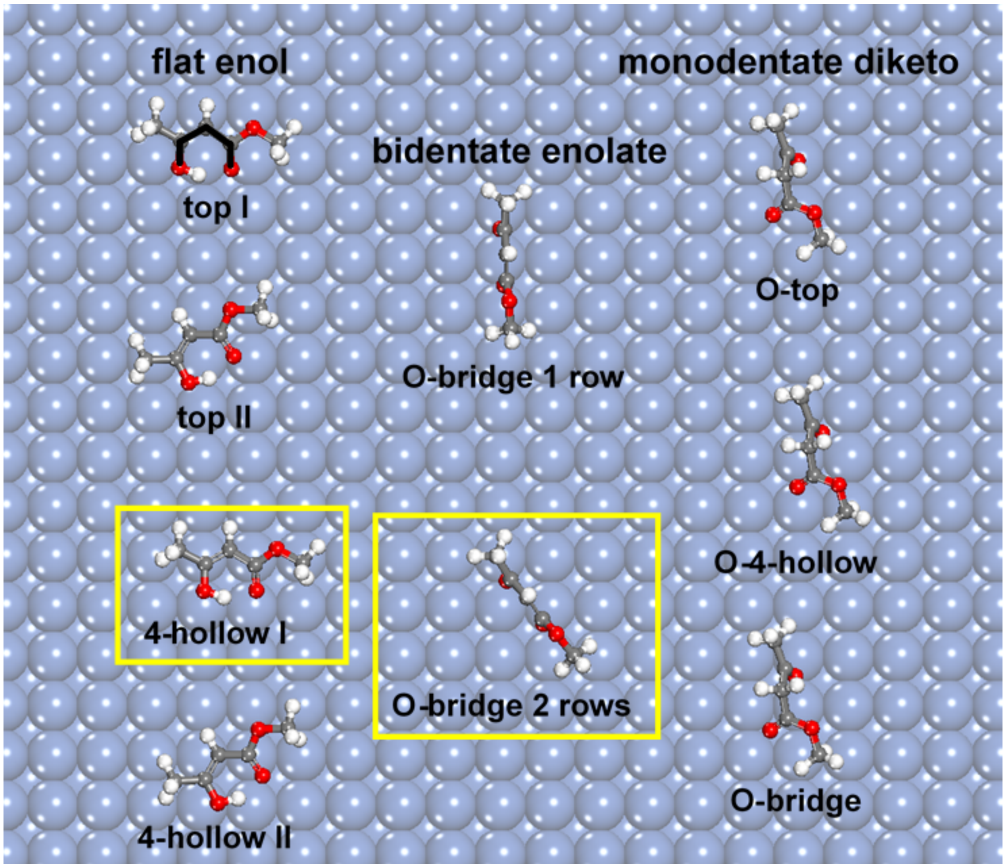


Figure S2: Initial configurations of MAA on the Ni{100} surface considered in the present study. To facilitate visualization, the O-CCC-O chain is highlighted and the dissociated H removed. The candidates discussed in the main section are indicated by yellow rectangles.

Table S1: Adsorption energies of the optimised configurations shown in Figure S2.

Start Configuration	E_{ads}
flat-enol	
top I (converged to 4-hollow I)	-1.91 eV
top II (converged to 4-hollow II)	-1.69 eV
4-hollow I	-1.91 eV
4-hollow II	-1.69 eV
bidentate deprotonated enolate	
O-bridge 1 row	-1.78 eV
O-bridge 2 rows	-1.82 eV
monodentate diketo	> -0.95 eV

XPS: C 1s core level shifts

Table S2: Core-level shift values for the C 1s photoemission of the *bidentate deprotonated* configuration according to DFT. For numbering, refer to Figure 1 in the main section.

Atom numbering	ΔBE **(eV)**
C1	0.00
C2	3.00
C3	1.56
C4	2.29
C5	0.83

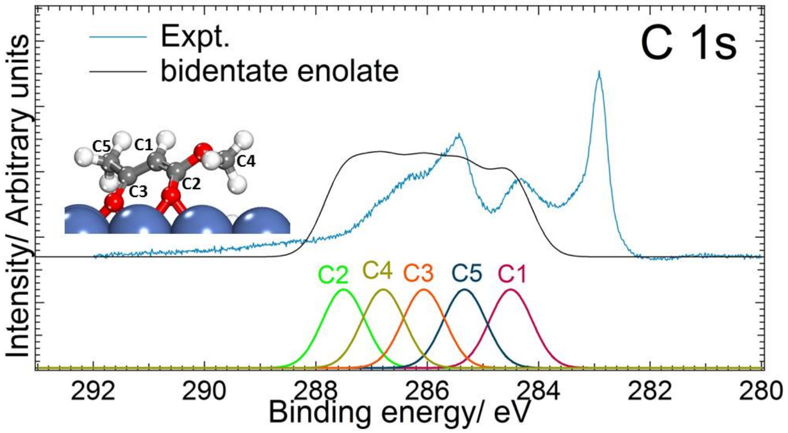


Figure S3: Top panel: Comparison of experimental C 1s XPS spectrum obtained upon annealed the MAA layer to 340 K (0.16 ML) with modelled XPS spectrum of the *bidentate deprotonated*. Bottom panel: individual Gaussian peaks of FWHM 0.9 eV placed at the core-level shift positions of Tab. S2.

References

(1) Stöhr, J.; Outka, D. A. Determination of molecular orientations on surfaces from the angular dependence of near-edge X-ray-absorption fine-structure spectra. *Phys. Rev. B* **1987**, *36*, 7891–7905